UAN Corrosion Management

By Dr. Craig Myers, Senior Research Scientist and Phil Bureman, Industry Technical Consultant
Agenda

• Who Is Nalco?
• WIIFM
• UAN Corrosion Mechanisms
• UAN Corrosion Prevention
  – Key Factors
  – Illustrations
Who Is Nalco?

• Global leader in Specialty Chemicals
  – Water Treatment
  – Petroleum Production and Refining
  – Paper Manufacturing & Finishing

• 11,000 employees worldwide

• $4.0 Billion Sales in 2008
  – UAN Corrosion Management Leader since 1994
    • Primarily with UAN producers
If a UAN tank located on your property leaks, you may be liable for contamination in ground and surface water.
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

Your business reputation may be put at risk

The EPA and OHSA might become your new business partners
UAN Corrosion Can Be Quite Serious!
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
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

Let’s now venture into our UAN tank...
Typical Vertical Surface Appearance

• Vertical weld zones typically show no damage at all
• Note that sludge is unable to accumulate here
Horizontal Surface Appearance

Excellent floor welds

Moderate Corrosion

Plate thickness ranges from 1/4” to 1/2” with 3/8” the most common, so 100 mil pits are very significant.

Moderate/Severe Corrosion

Damage always on lower edge of lap weld
What Kinds of Corrosion Occur in UAN Tanks?

- Surface Corrosion
- Sludge Formation
- Under Deposit Corrosion
Surface Corrosion & Sludge Formation in UAN

- A corrosion coupon was put in a jar with a small amount of UAN 32.
- The jar was sealed for 7 days in bright sunlight (the coupon had the existing corrosion spot)
- No sign of new corrosion while sealed
- The jar was then opened ~ 3 hours and then re-sealed for 24 hours

Note the severe corrosion that developed on the coupon after the release of the ammonia

However, this severe corrosion was easily wiped off with a paper towel and the original corrosion spot remains

Key Take-Away: A little bit of “surface corrosion” creates a lot of sludge!
**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.
How You Can Control Corrosion

- Control sludge deposition!
  - Tank design, maintenance, operations
- Control chemistry of your UAN
  - Quality product, proper ratios, excess NH$_3$, and inhibitor
- Good tank construction and repair practice
# Deposition Factors

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<td>Monitor railcar unloading and tank transfers.</td>
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Lack of Sludge Removal: Consequences

One operator did not open a tank for 17 years. By that time it had been leaking for over a year. The sludge from the tank filled two 30,000 gallon rail cars when it was cleaned out. It took over a year of wrestling with the state environmental board to be able to finally land apply the sludge to dispose of it. Even after extensive and expensive repairs, the tank floor had to be completely replaced 3 years later.

Sample 210 mil pit from corrosion underneath the deposits
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Limited Sludge Egress

6” of Sludge Accumulated Behind Separator Ring in a NH3 Tank Converted to UAN Service

Resulting Corrosion Underneath the Deposits: 150 To 175 mil pits.
UAN inlet pipe line header and outlet vortex breaker for UAN tank storage tanks, for prevention of sludge settling and inadvertent removal of tank tramp oil.
Outlet Vortex Breaker: Prevents sucking out tank tramp oil.

Inlet Pipe and header with spouts that create tank circulation and helps prevent sludge settling.
Optimum Tank Design

UAN circumferential inlet pipe line header with sloped tank bottom tank and center sump design to prevent sludge settling and keep it moving out of the tank.
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UAN Puddles Cause Surface Corrosion

Surface Corrosion in Railcar Heel

Followed by Pitting Under the Deposits

Pitting in Tank Bottom Left for Several Months with UAN Puddles
Passivating Treatments for Out of Service Tanks and Vessels

Organic-based “Temporary Corrosion Inhibitors”

UAN heel in UAN rail car: surface NOT pre-treated

UAN heel in UAN rail car: pre-treated surface
Passivating Treatments for Out of Service Tanks and Vessels

**Inorganic Corrosion Inhibitor Treatment**

Tank with a dusting of surface corrosion due to several months of inactivity was mopped with inorganic corrosion inhibitor before being put back into service. Doing so at start of idle would have been better.
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Check Incoming Cargos for Clarity and Solids

Beware of Tramp Oil

Beware of Solids & Sludge

Heavy sludge in UAN rail car
In 2002, Tank 2 had a severe pH upset (down to pH of 3), resulting in massive surface corrosion. Iron levels spiked to 400 ppm. The UAN was filtered and sent to Tank 3…
Results of the pH Upset

When Tank 2 was opened, as expected, the damage was massive and the floor was replaced. Leak near chine weld shown below.

But when Tank 3 was opened, it was found to have extensive sludge deposits and some damage as well. The iron that remained soluble (Fe$^{+2}$) during the transfer had eventually oxidized and deposited.
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Effect of pH on Corrosion Near Weld vs. Metal Plate in Uninhibited UAN 32

• Put a welded A36 coupon in a flask at 50 C and constant pH and gradually lower the pH by air stripping out the NH3

• A clear “transition pH” is reached where corrosion visibly takes off

• This “transition pH” is much higher (i.e. reached sooner) in the weld zone (pH= 6.6) than the bulk metal (pH=5.75)

Q: So, if pH is a key parameter for corrosion, what affects the pH?
A: Excess NH3 and Temperature
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!
Effect of Temperature on Corrosion Susceptibility in Uninhibited UAN 32

\[ \text{NH}_4^+ \rightleftharpoons \text{NH}_3 \text{ (gas)} + \text{H}^+ \text{ (acid)} \]
Reaction shifts to right (acidic) as temperature increases

Paint tanks white to reduce heating in summer.
Effect of Excess Ammonia (Initial pH) on Corrosion Susceptibility in Uninhibited UAN 32

- Low pH 6.7
- Med pH 7
- Hi pH 7.5

A36 Welds in UAN 32 corrode severely
A36 Plate in UAN 32 corrodes severely
Control Your Excess NH3, pH, & Temp....
Don’t Let This Happen To Your UAN Tanks!

8 Days In UAN32 With % Excess NH3 @ 0.003
And Tank Temperature @ 150 Deg. F.
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UAN Salt Out Contributes to Sludge

UAN salt deposit in a rail car

Close-up of salt deposit showing corrosion flake
The Ratio of AN to Urea in UAN Determines the Salt Out Temperature

The ideal ratio range is 1.1 to 1.4
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UAN Inhibitors

- Essential part of corrosion management
- Not all inhibitors are created equal
- Use a trusted source of UAN
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What is the "Heat Affected Zone"

- Plate area within an inch or so of the weld that is highly heated during welding.
- Makes metal more vulnerable to corrosion by:
  - Adding residual stresses from heating/cooling
  - Aggregating inclusions
  - Changing the metal grain structure

Grooving-type corrosion along a weld is typical of the influence of the HAZ.

Proper welding techniques can help to minimize the residual stresses.
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This poor looking, uneven weld repair at a major UAN producer eventually allowed the two plates to separate when the tank was filled to capacity causing a major leak. Tank had to be emptied and re-repaired.
Faulty Repair Plate Installation

Five years after this repair plate was poorly installed on the tank bottom, a crack has appeared in the chine weld where the repair plate meets the tank wall.
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Comparison of Support Plates

Unusual Roof Support Plate
The roof weight is focused on a single small floor plate, lower than the main floor. Welds around this square plate were the only place significant corrosion took place.

Typical Roof Support Plate
The roof weight is spread across several plates and underlying strata. No unusual focus of corrosion observed.
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Corrosion at Compromised Metallurgical Site

Through Wall Pitting
Lifting lugs were removed from this plate by knocking them off with a sledgehammer. Perforation of the tank bottom occurred in 6 locations.

Close Up of Through Wall Pitting
Note how the corrosion practically drilled through the affected metallurgy.
Consider Adding Your Own Corrosion Inhibitor

- Inhibitors are relatively inexpensive and most are easy to handle and safe to work with.
- Depending on your source of UAN and inhibitor package, treat costs will vary from $0.20 to $0.60 per ton of UAN treated.
- Do not add petroleum oil to any UAN tank, car, truck, or pipe
  - Some top treats for prevention of “notch or ring” corrosion may be effective
- Consider a pre-treatment program for cleaned tanks or any idle equipment
Key Take Aways…

• UAN corrosion creates risk for your business
• UAN can be very corrosive
• But **YOU** can manage this risk:
  – Minimize sludge deposits
  – Good control over UAN chemistry
  – Proper tank design and maintenance practices

Questions?
Thank You For Your Time!

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