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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



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



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 <u>new</u> 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



Key Take-Away: A little bit of "surface corrosion" creates a lot of sludge!



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

Key UAN Corrosion Mechanisms

Surface Corrosion in UAN

 $NH_4NO_3 \rightarrow NH4^+ + NO_3^-$

 $NH_4^+ \leftarrow \rightarrow NH_3 + H^+$

 $H^+ + NO_3^- \rightarrow HNO_3$

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

NH₃ NH₃ NH₃ UAN "Thin Film" VUAN "Thin Film" Bulk UAN @ Vertical Wall Pitting Corrosion in UAN Crevice or Under-Deposit Corrosion

Fe⁺² → Fe⁺³

 $Fe^{+3} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$

Solution

 $NH_4NO_3 \rightarrow NH4^+ + NO3^-$

 $NO_3^- + H^+ \rightarrow HNO_3$

The H⁺ can't diffuse out of the crevice fast enough. To remain electrically neutral, 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 NH₃, and inhibitor
- Good tank construction and repair practice

Deposition Factors

FACTOR	Prevention
Lack of Sludge Removal	Timely cleaning and inspections, at least every 3 to 5 years
Limited Sludge Egress	Design to accommodate sludge movement and removal
Heels or Puddles Left in Tank	Clean and passivate tanks that are not in use.
Sludge Transfer	Monitor railcar unloading and tank transfers.

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.

Design Improvements

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



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: pre- treated surface

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



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



Do Not Create Your Own Sludge Problems



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.

UAN Chemistry Factors

FACTOR	Prevention
Excess Ammonia (pH)	pH > 7, excess NH3>0.008%
UAN ratio	Avoid salt out conditions. AN:Urea desirable ratio 1.1 to 1.4
Inhibitor	Trusted UAN source with proper inhibitor content
UAN 28 vs. 32	Try to avoid storing UAN 28 for long periods of time

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



Effect of Temperature on Corrosion Susceptibility in Uninhibited UAN 32



Effect of Excess Ammonia (Initial pH) on Corrosion Susceptibility in Uninhibited UAN 32



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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Metallurgical Factors

FACTOR	Prevention
Heat-affected Zone Along Welds	Good welding practice, control of UAN chemistry factors
Weld Quality	Careful inspection, particularly of any repairs
Mechanical Stress	Good design practice in high stress areas, e.g. support footings
Damaged Metallurgy	Good Housekeeping, don't start up a tank in a damaged state

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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Faulty Floor Repair Weld

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



Thank You For Your Time!



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