

Emerging Solutions for Biofuel-Induced Corrosion for ASTs & USTs



Real world problems caused by the use of Ethanol, Bio-diesel, and Ultra-Low Sulfur Diesel, and a look at possible solutions

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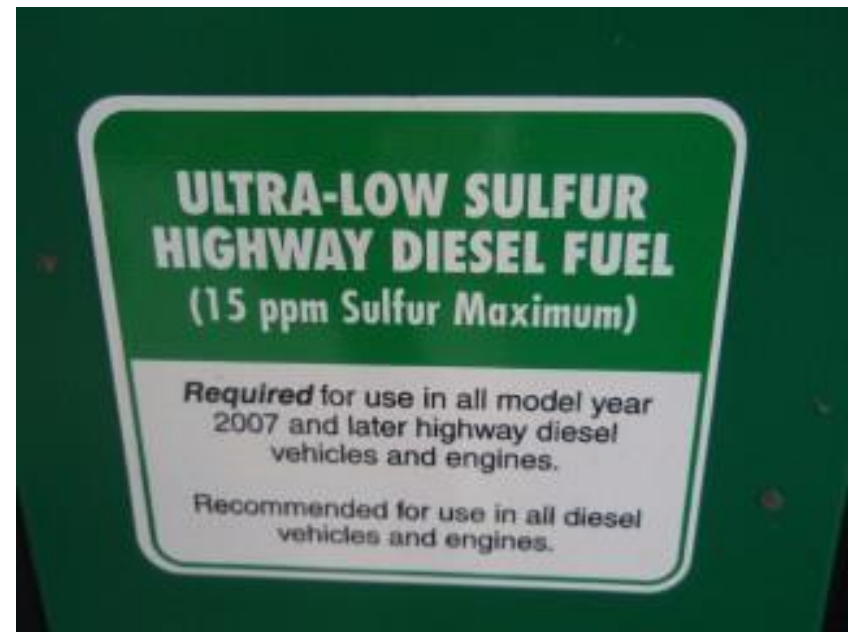
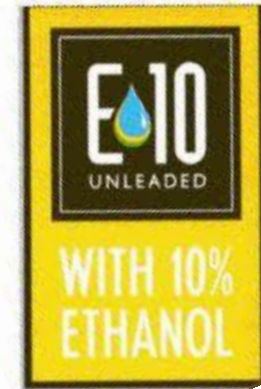
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Alternative Fuels



- E-10 Ethanol
- E-15 Ethanol
- E-85 Ethanol
- B-20 Bio-diesel
- ULSD – Ultra-Low Sulfur Diesel





ETHANOL TK 17

Why are we using Ethanol? (from government sources)

- Air pollution – as an oxygenate to make fuel burn cleaner and reduce air pollution
- Augment the nations fuel supply and reduce reliance on foreign fuels
- Stimulate the economy
- It's a “Green” Fuel



Problems with Ethanol...

1. Ethanol does not burn that much cleaner than regular gasoline
2. Using Ethanol leads to an energy drop-off
3. Using Ethanol competes with food crops and increases food costs
4. Chemically-speaking, Ethanol wants to become water
5. Phase Separation
6. Some older fiberglass systems are not compatible
7. Ethanol loves to eat soft metals, rubber, and plastics
8. More frequent dispenser filter changes
9. Ethanol has a scouring effect on tank systems
10. Ethanol is destroying our petroleum pumping infrastructure

Alternative fuels (ULSD, Ethanol and Bio-diesel)



- Have only been in widespread use nationally for about five to six years
- Growing number of problems with the integrity of storage tank system equipment

Evidence of problems discovered from facility monthly visual inspections and State UST regulatory and fuel quality inspections



Black "Gunk" in tank

A photograph showing a dark, thick, black, gummy substance (gunk) inside a tank. The gunk is covering a large area of the tank's interior. A metal flange with several bolt holes is visible on the right side of the frame. A brown, curved object, possibly a pipe or fitting, is visible in the lower right corner.



Corrosion

A photograph showing a long, horizontal metal pipe that has been severely corroded. The pipe is covered in a thick, reddish-brown, flaky layer of rust. The pipe is lying on a concrete floor. In the background, the lower legs and feet of a person wearing blue jeans and brown work boots are visible. A metal grate is also visible in the upper right corner.

Ethanol – E-10 & E-85



Problems



Diesel sump, same facility, Georgetown, South Carolina, November 2011



Regular Unleaded gasoline sump, same facility, Georgetown, South Carolina, November 2011



Mississippi (e10)

Photo 12-09



South Carolina (e85)



Kentucky (e10)



Ohio



Idaho



Delaware (e85)

Installed 3-07 – Photo 3-08



Minnesota (e85)



Washington



California



Iowa



Florida (e10)



Florida (e10)



Florida (e10)

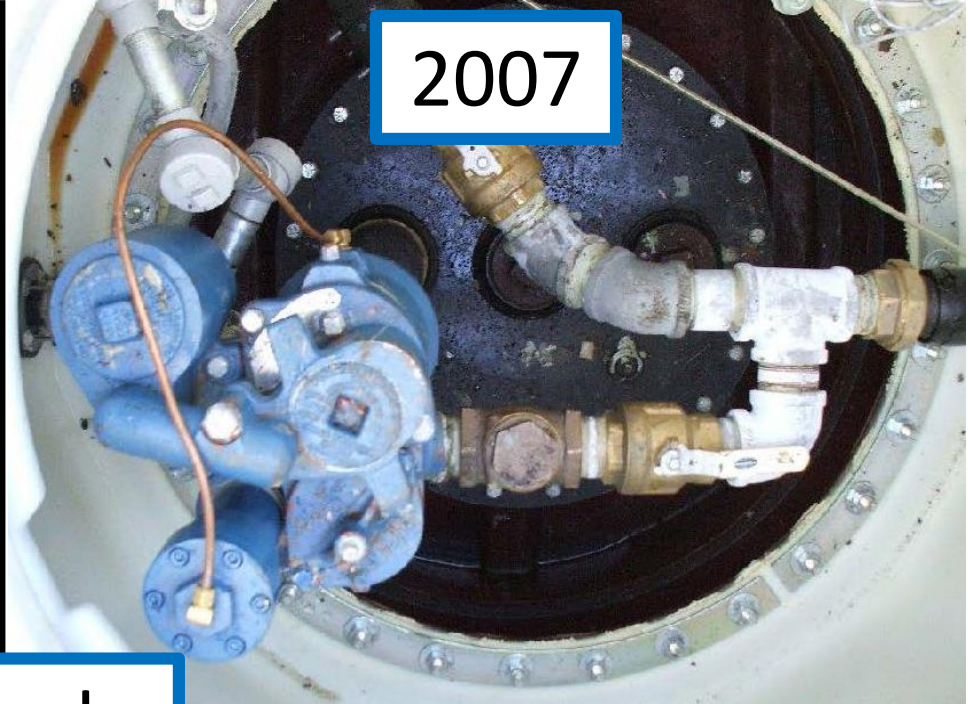
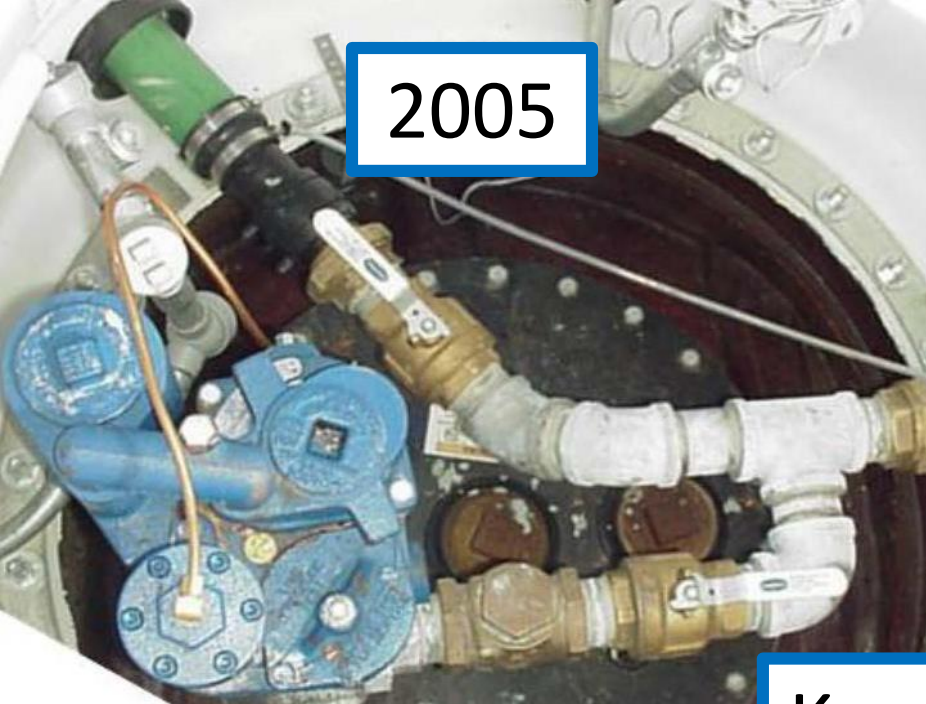
How Long Does It Take For This Severe Corrosion To Occur?



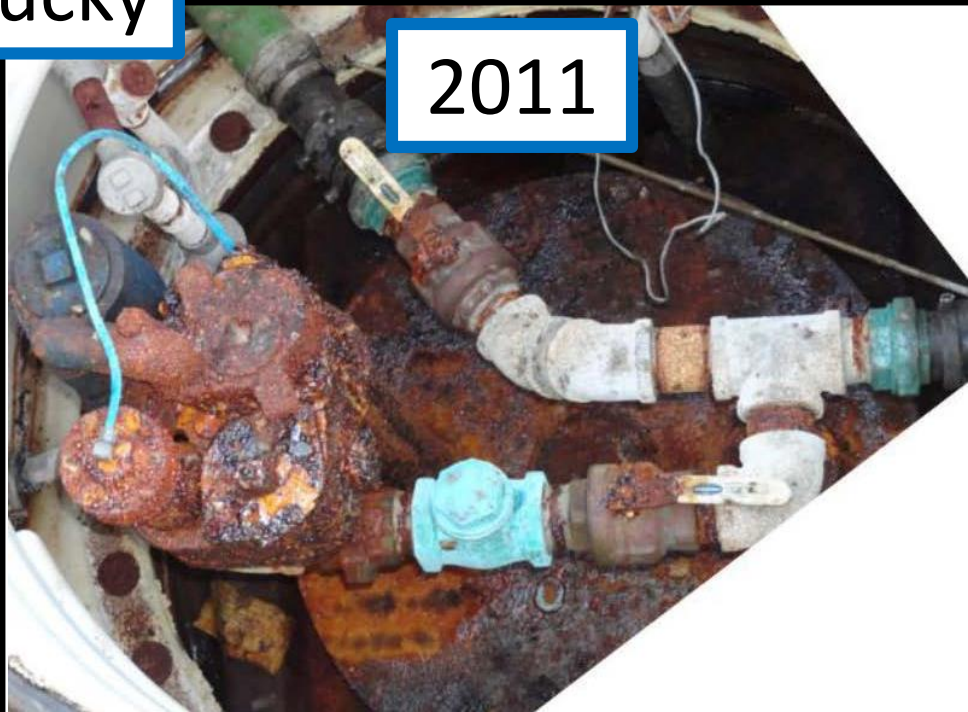
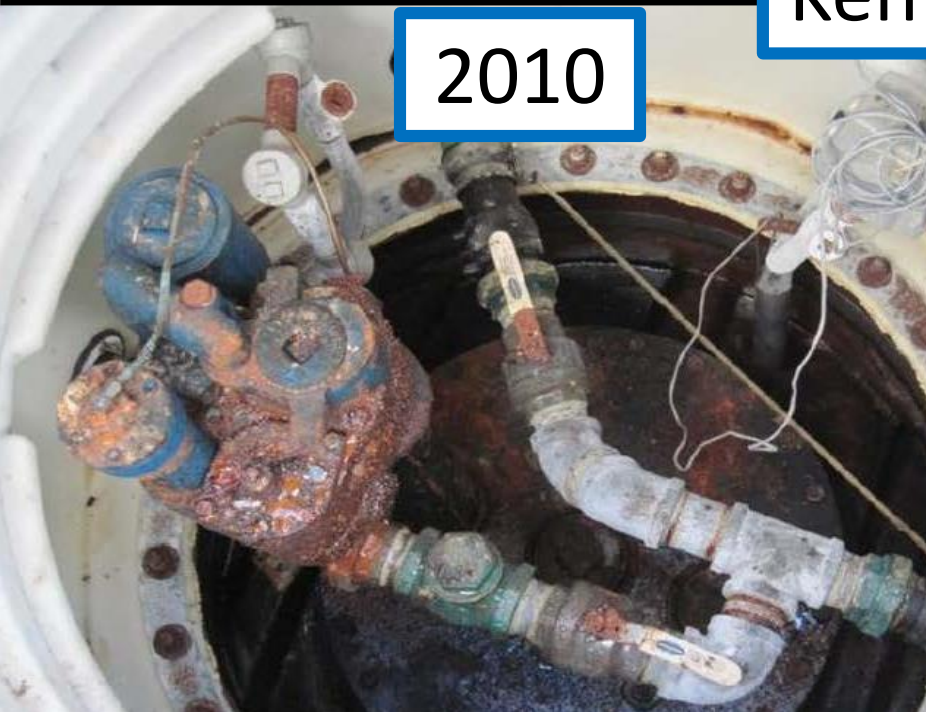
Tennessee - March 2010



Tennessee - August 2010

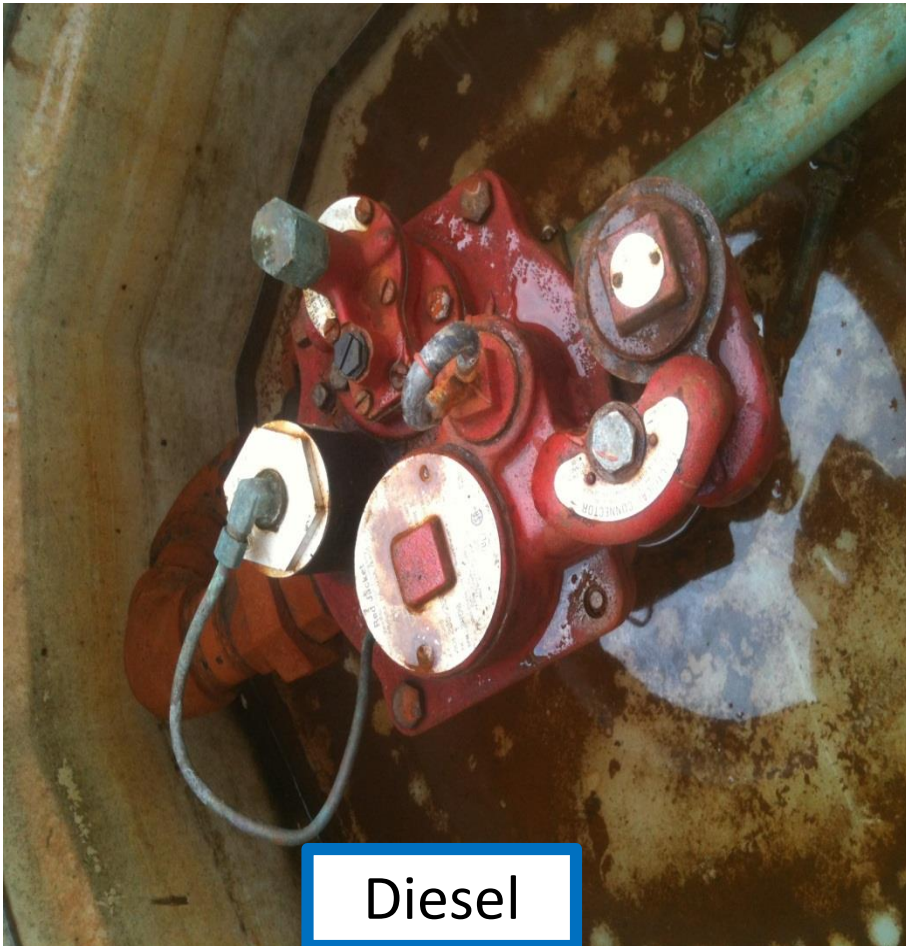


Kentucky

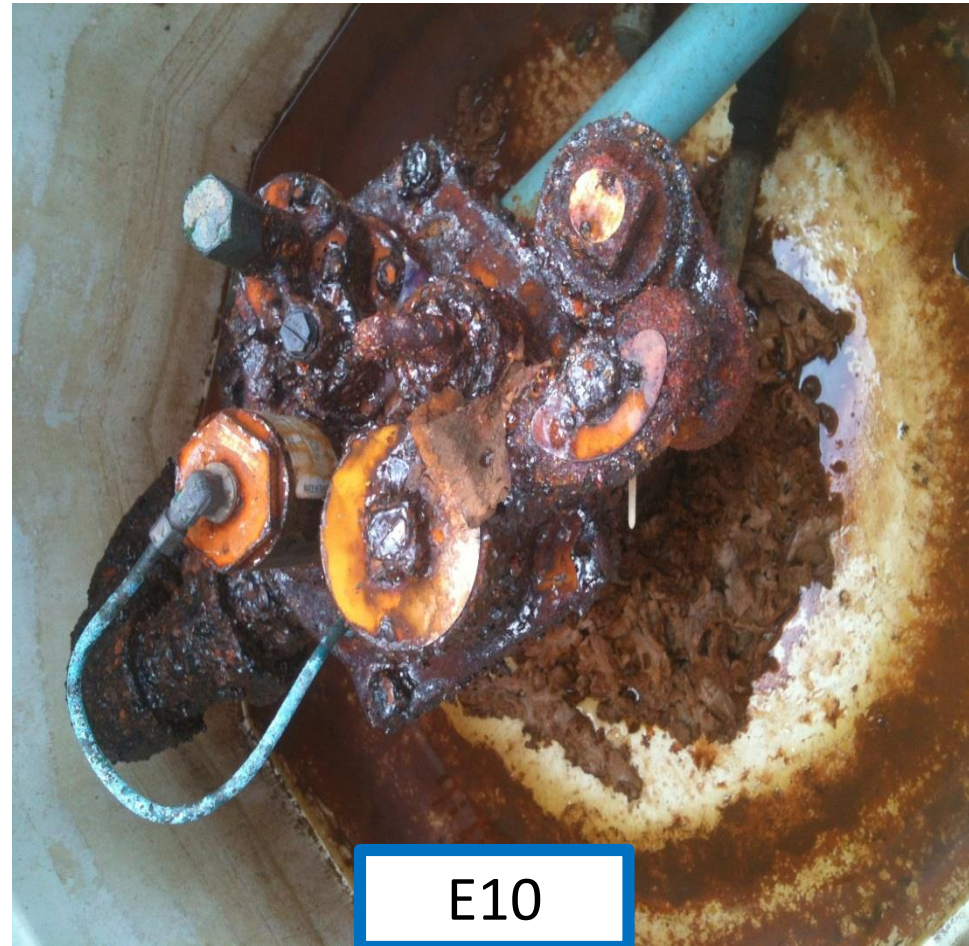


Diesel vs. Gasoline

Mississippi



Diesel



E10

Installed 8-07 - Photos 3-12

Same Facility - Same Equipment – Same Day- Different Sumps

What's this "whirlybird" doing here with the tank vents?



Kentucky

What's this open pipe doing here?



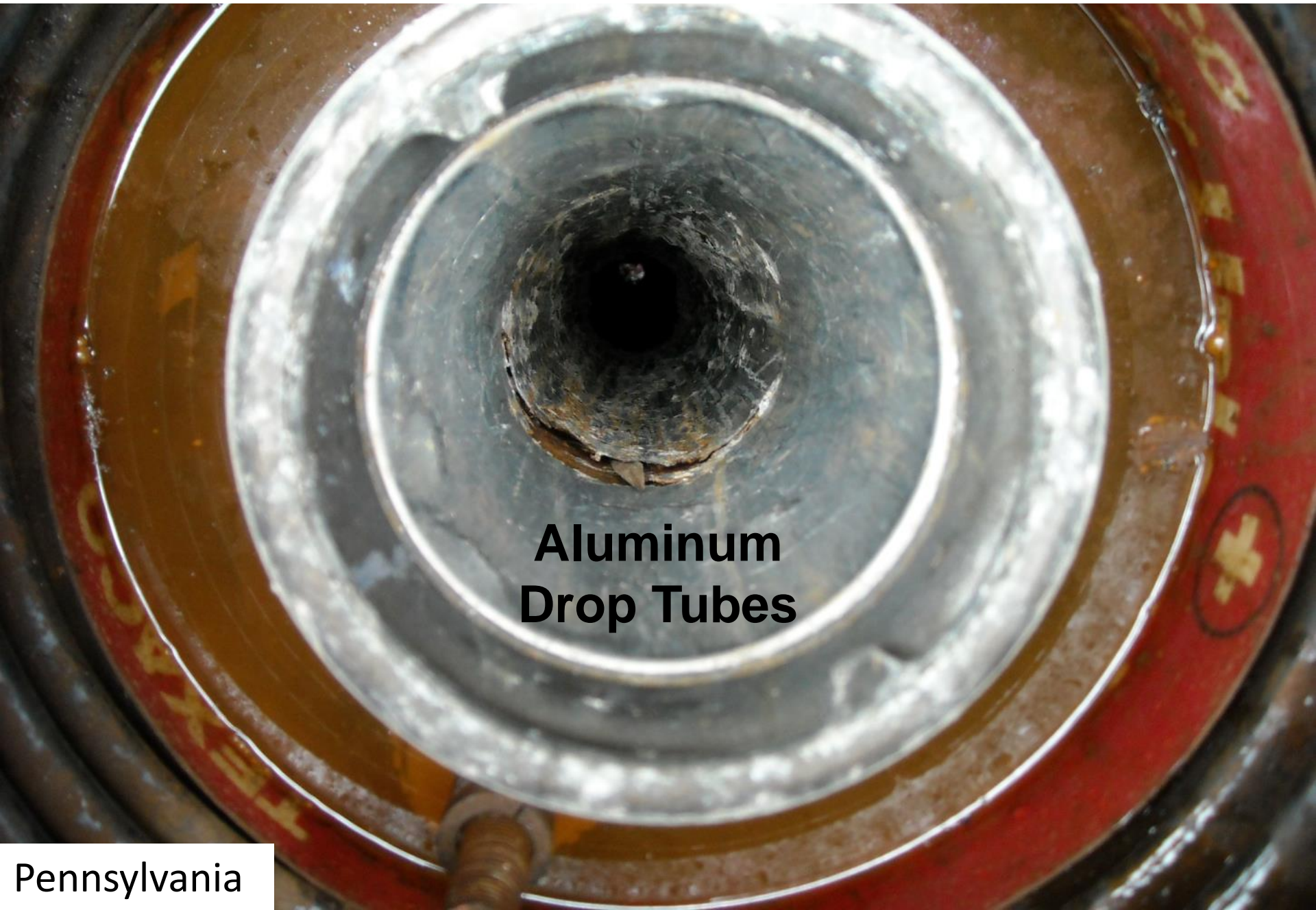
Kentucky

Other Problem Areas – ATG Equipment



Evidence of vapor leaks

What other components could be affected by corrosion?



**Aluminum
Drop Tubes**

Corrosion on Aluminum Drop Tubes



Minnesota

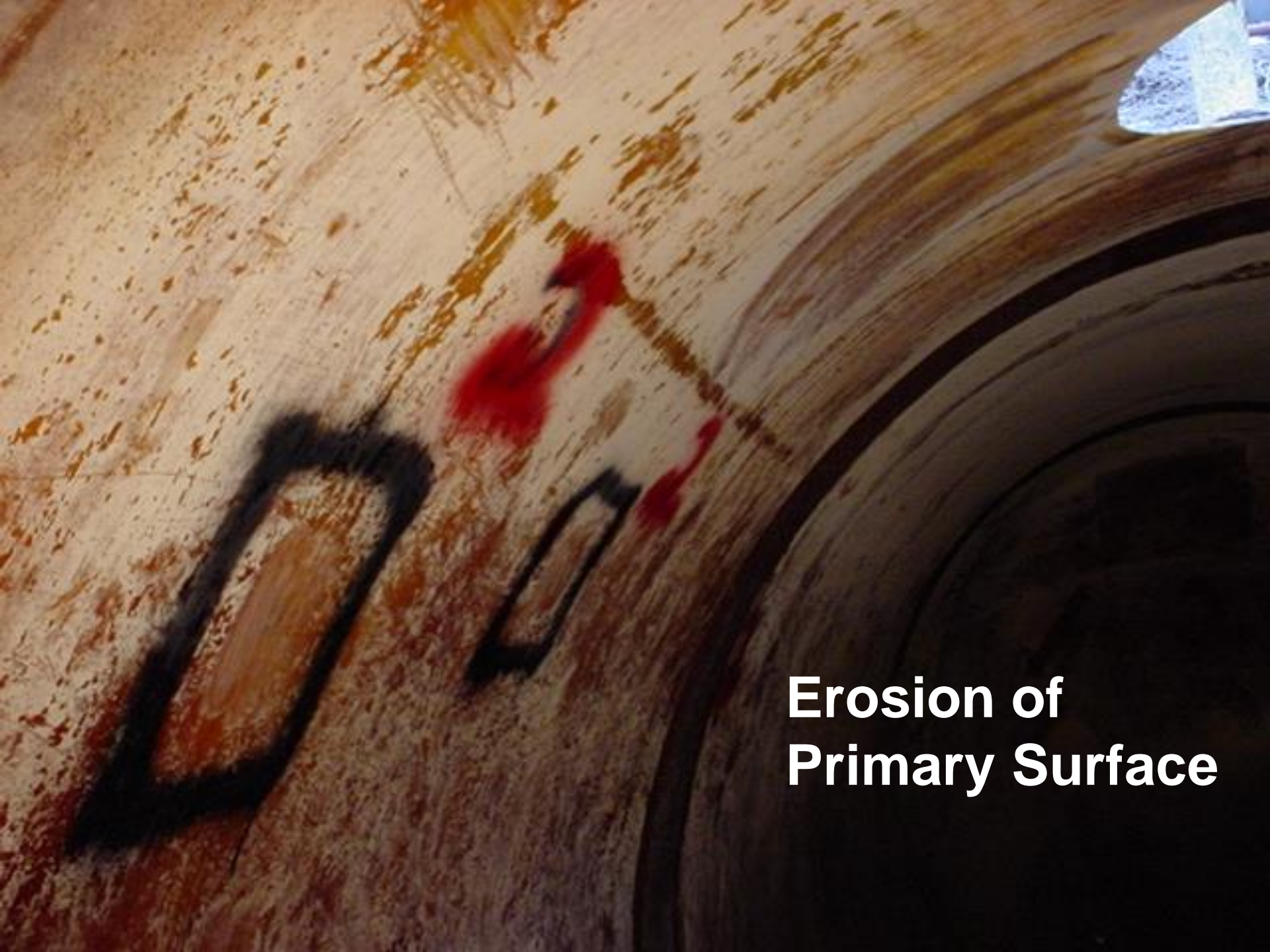


Corrosion on Ball Float Valve Overfill Protection Equipment





**Observations with Older Single-wall
Fiberglass Tanks in E-10 Service for
less than Two Years**



**Erosion of
Primary Surface**

Cracking





Internal erosion, wicking and delamination

2006 7 25



Delamination of gel coat

2006 7 25

BLISTERS
↓ T-3

Blisters on sidewall

Ethanol-Free Gasoline Has Become a Marketing Tool



Advertising Ethanol-Free Fuels



CONTAINS
NO ETHANOL

Reg-90 Octane Marine Fuel

PUSH TO
SPEAK
WITH
ATTENDANT

WARNING
Improper use may cause a
hazardous condition:
• Avoid static hazard
• Return of nozzle
• In case of fire do not
remove nozzle
• No smoking or flames
at nozzle or nozzle
• Use nozzle only
• Do not tip off
Nozzle to prevent
overweight
Handy

Shell
Marine Fuel

\$ Per Gallon (including tax)

4759

Shell
Marine Fuel

REGULATED OCEANO RACING
THROTTLE MOTOR
90
PUSH HERE

3559N MACH
BY IPDGO
3559N MACH
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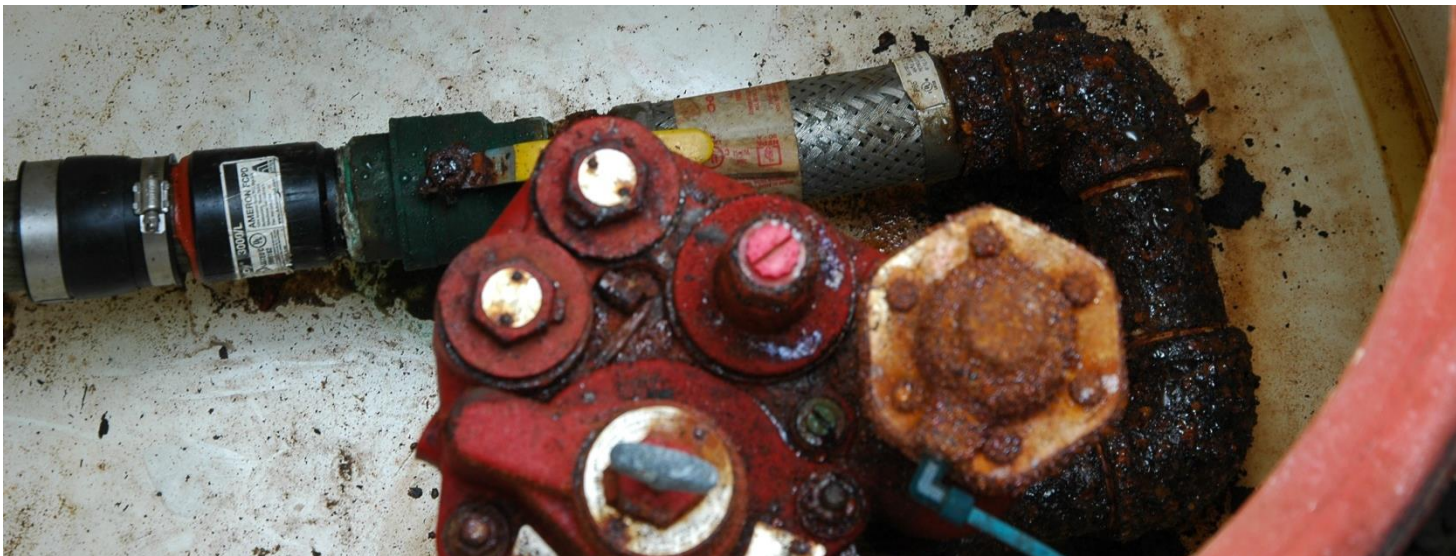
Recent National EPA/State Regulator Field Study with Ethanol Corrosion

- EPA provided sampling kits
- Passive diffusion samplers were placed in piping sumps to measure the concentrations of ethanol and acetic acid
- Data came from Florida (35), Tennessee (13), Illinois (6), Wisconsin (4), California (2), and Iowa (1)
- 27 RUL, 2 MUL, 26 PUL, 5 E-85, and One Diesel



Findings

- Many sumps had high concentrations of Ethanol or Acetic Acid
- No significant difference between RUL & PUL
- Corrosion worse in sumps with high concentrations
- Corrosion worse in sumps with water
- For Ethanol to cause corrosion in a sump, there must be ethanol, bacteria, and water
- Eliminating one of these could prevent corrosion?



Other Problems

- Warranties for UST and AST Fuel System Components
- Vehicle Warranties
- Concerns with traditional problems from ethanol fuel use such phase separation, degradation of soft metals, increased filter replacement, and the scouring effect on fuel tanks
- UST & AST owner acceptance
- Consumer confidence



Vapor Corrosion Inhibitor Testing and Ethanol Corrosion Prevention Efforts...

- More Field Trials
- Invite Participation
- Future considerations:
 1. VCI media and levels
 2. Tightness of sumps
 3. Tightness of piping connectons
 4. Existing rust, manual removal of corrosion
 5. Surface penetrants and coatings
 6. Venting of vapors
 7. Combinations of the above

Recent Field Studies for Remedies



Zerust Vapor Corrosion Inhibitors

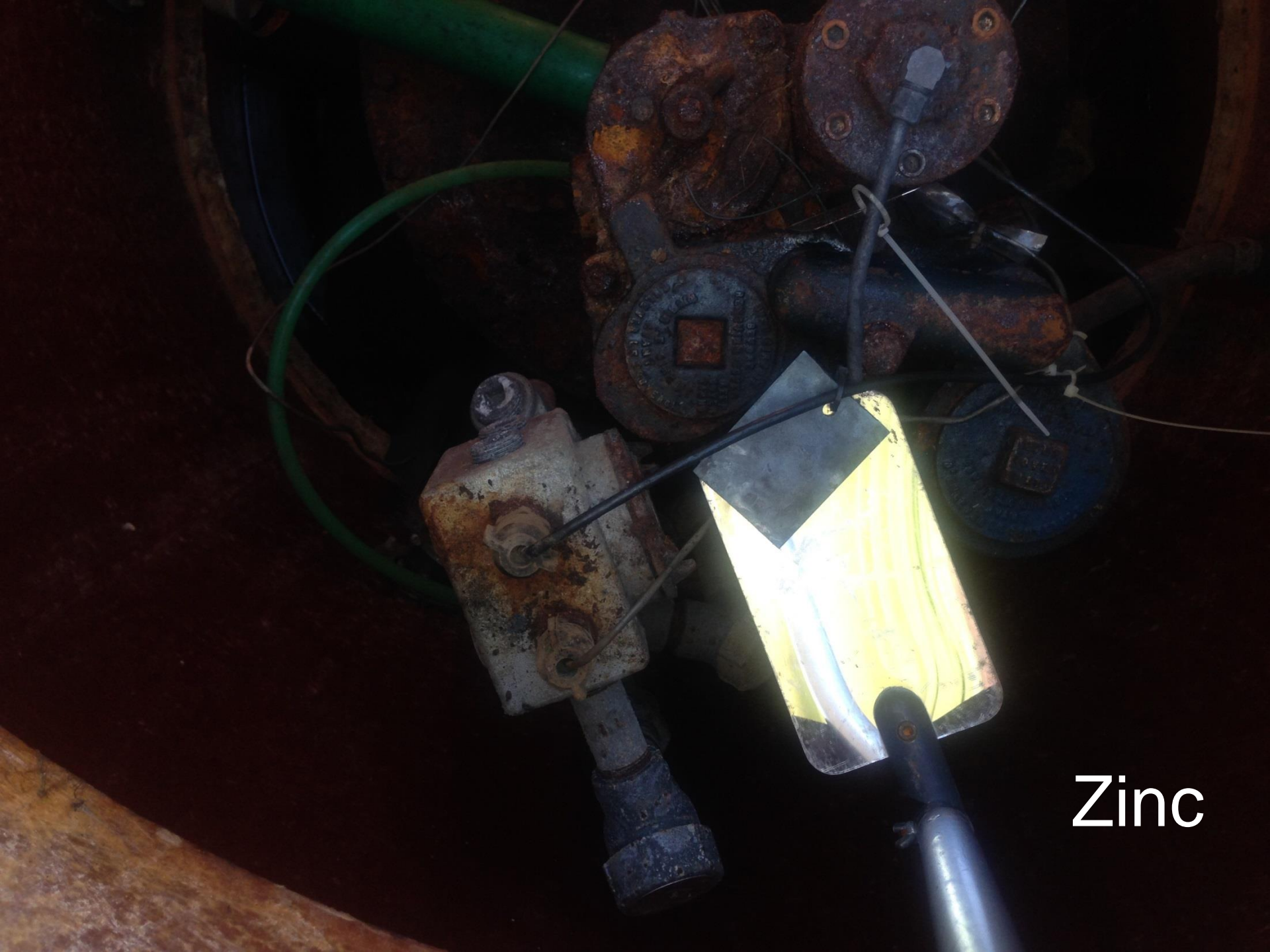




Copper

Brass & Copper





Zinc

Ethanol Vapor Saturation...





Spray

Before



Iron Ox

After



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Ultra-Low Sulfur Diesel

**ULTRA-LOW SULFUR
HIGHWAY DIESEL FUEL
(15 ppm Sulfur Maximum)**

Required for use in all model year
2007 and later highway diesel
vehicles and engines.

Recommended for use in all diesel
vehicles and engines.

Ultra Low Sulfur Diesel



Submersible Pump & Riser
(Left hand side is aluminum;
Right hand side is steel)



Submersible Pump Head
(in vapor space -- never
contacts fuel)

STP column pipe inside FRP tank



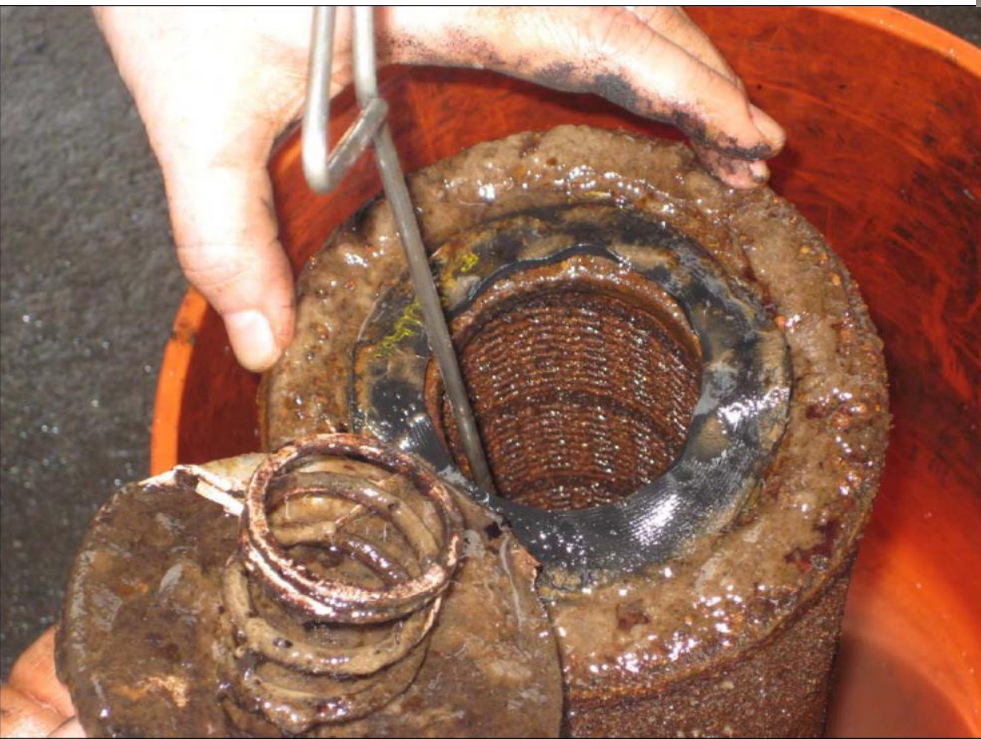
Pump connection corroded thru





In service less than one year
STP Column Pipe

Problems with Ultra Low Sulfur Diesel and Steel Components



FE Petro Equipment



Old vs New
Corrosion, Pitting

Leak detection equipment not functioning





**Filter
threads**

Strainer



“Coffee Grounds”



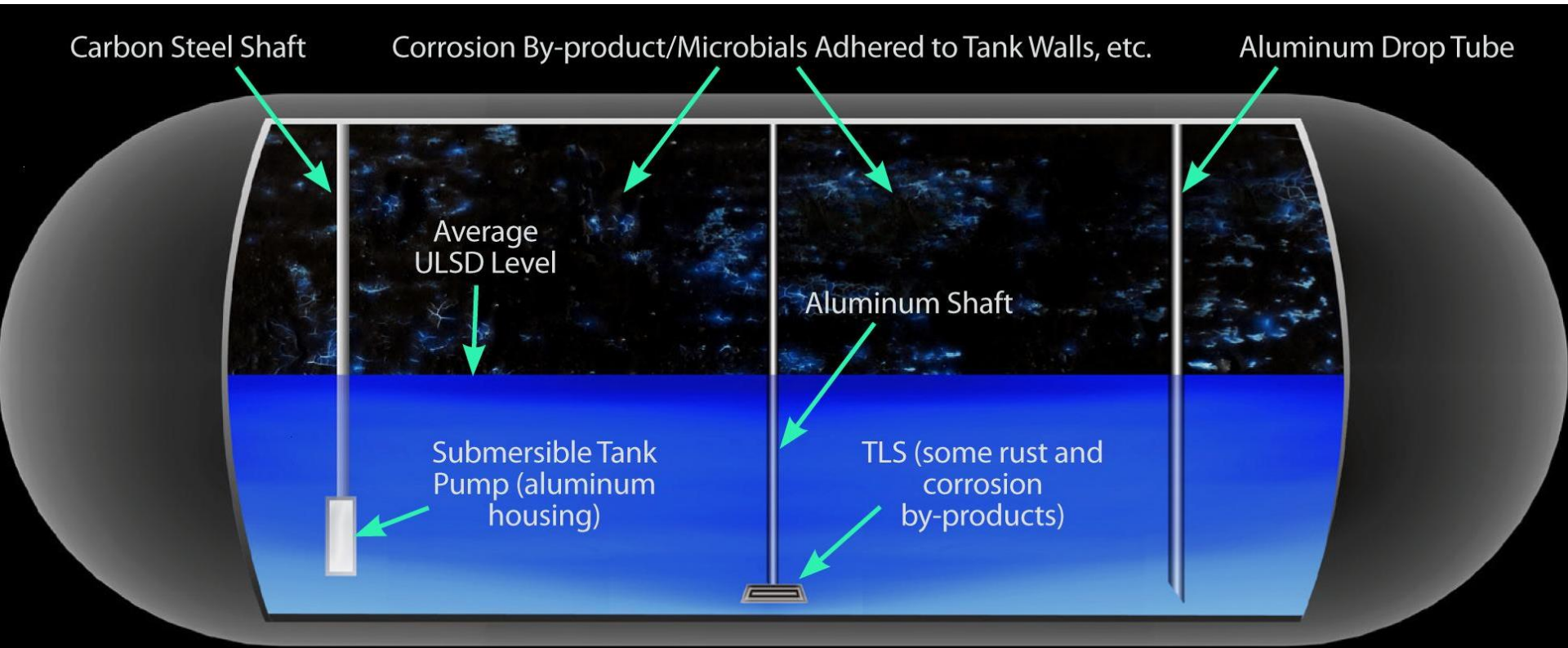
**Problems reported from all regions of the country-
No problems reported at refineries, pipelines, not
associated with individual supplier**



Problems Observed

- **Filters clogging/requiring more frequent replacement**
- **Seal/Gasket/O-ring deterioration**
- **STP replacement/Column pipe wear/Motor problems**
- **Tanks rusting/leaking (includes tanks of vehicles)**
- **Meter Failure**
- **Line leak detectors damaged or broken**
- **Automatic nozzle shutoff failure/shorter lifespan**
- **Tank probes malfunctioning**
- **Check valves not seating**
- **Shear valves not sealing/failing tests**
- **Swivels failing/shorter lifespan**
- **Dispenser leaks/failures/ premature replacement**
- **Solenoid valves clogged/failing**
- **Corrosion on the riser pipe**
- **Pipe failure**

ULSD Corrosion – UST Detail



UST showing corrosion and possible microbial corrosion spots.

Likely Causes

- No one cause, but rather a mixture.....
- Microbial influence getting a lot of attention:
- Salt and other contaminants also a contributing factor?
- Corrosion inhibitor depletion (aka “soap”) theory – acidic additives form soaps if contacted with excessive tank water cations from salts or caustic:
- Poor housekeeping, no biological monitoring, improper application of biocides exacerbates problem

The Clean Diesel Fuel Alliance

- Created in early 2006
- Participants include:
 1. Government
 2. Engine Manufacturers
 3. Marketers
 4. Refiners
 5. Marketers
 6. Equipment Producers

The screenshot shows the homepage of the Clean Diesel Fuel Alliance Information Center. The header features the text "Government - Industry - Consumers" above the main title "Clean Diesel Fuel Alliance" and "INFORMATION CENTER". Below the header is a navigation bar with links: "> Skip Navigation", "> About ULSD", "> EPA Standards", "> EIA", "> ULSD Compliance", "> Media Room", and "> Contact Us". A green sidebar on the left contains a menu with the following items: "> Highway ULSD Fuel", "> Non-Road ULSD Fuel", "> Vehicle Performance", "> Environment & Health", "> Frequently Asked Questions", and "> Quicklinks to Member Web Sites". The main content area has a light blue background with a cloud pattern. It features a large heading: "Ultra Low Sulfur Diesel (ULSD) fuel and new engines and vehicles with advanced emissions control systems offer significant air quality improvement." Below this heading are four columns of text, each with a small image and a link. The first column is titled "Highway ULSD Fuel" and mentions a major reduction in sulfur content, with a link to "Highway Diesel". The second column is titled "Non-Road ULSD Fuel" and mentions EPA standards for locomotive, marine, and non-road engines, with a link to "Non-Road Diesel". The third column is titled "New Diesel Technology" and describes Ultra Low Sulfur Diesel (ULSD) as a cleaner-burning fuel with a maximum of 15 ppm sulfur, with a link to "Vehicle Performance". The fourth column is titled "Environmental Benefits" and describes how ULSD fuel and new engine technologies improve air quality and provide health benefits, with a link to "Environment and Health". At the bottom of the main content area, there are two more links: "Para leer en español el folleto sobre diesel ultra bajo en azufre" and "Energy Tomorrow Radio Podcast on ULSD". A small graphic of a fuel pump nozzle is also visible, with text: "ULTRA-LOW SULFUR HIGHWAY DIESEL FUEL (15 ppm Sulfur Maximum)" and "Remember to use only all diesel vehicles and engines."

Website: www.clean-diesel.org

Members of the Clean Diesel Fuel Alliance

- AAA
- Alliance of Automobile Manufacturers
- American Petroleum Institute
- American Trucking Associations
- Association of American Railroads
- Association of International Automobile Manufacturers
- Association of Oil Pipe Lines
- Diesel Technology Forum
- Engine Manufacturers Association
- Independent Liquid Terminals Association
- Manufacturers of Emission Controls Association
- National Automobile Dealers Association
- National Association of Convenience Stores
- National Association of Fleet Admins.
- NATSO, Inc., representing Truck Stops & Travel Plazas
- National Petrochemical & Refiners Association
- National Tank Truck Carriers, Inc.
- Petroleum Equipment Institute
- Petroleum Marketers Association of America
- Society of Independent Gasoline Marketers of America
- Steel Tank Institute
- Truck Renting and Leasing Association
- U.S. Environmental Protection Agency
- U.S. Department of Energy
- U.S. Energy Information Administration
- Western States Petroleum Association

Clean Diesel Alliance Study

The Battelle/Tanknology proposal was chosen and funded by API, PEI, STI, NACS, PMAA, NATSO, AAR, and Ford

Theories Investigated

- **Aerobic and anaerobic microbes** are producing byproducts that are establishing a corrosive environment in ULSD systems
- **Aggressive chemical species (e.g., acetic acid)** present in ULSD systems are facilitating aggressive corrosion; and
- **Additives** in the fuel are contributing to the corrosive environment in ULSD systems

Test Sites

- **Chose 6 sites with similar throughput and history of issue:**
 - 1 site that does not show symptoms of corrosion
 - 5 sites with history of severe, rapidly induced corrosive symptoms
- **Sites in three states**
 - 2 in California
 - 3 in NY (including no symptoms site)
 - 1 in NC



Site Inspections

- Feb 8-23: Inspected 6 sites
- Report Completed Late Summer 2012



Inspection Process Disassembled System



Inspection Process Fuel Sampling



**Inspection
Process
Water Bottom
Sampling**



**Inspection
Process
Video Inside Tank
and Vapor
Sampling**



Biological Analysis to Extract DNA



ULSD Corrosion – Assessment



New steel
corrosion coupon



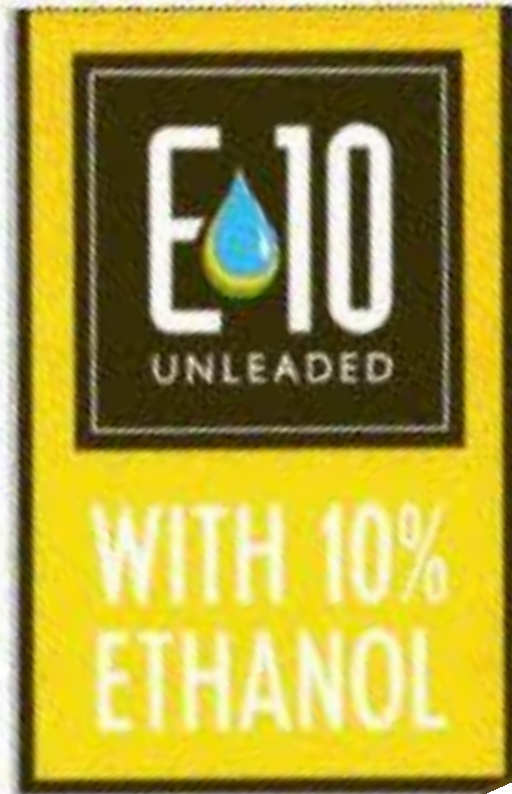
After 3 months

So what did the Study Conclude?

- More studies are needed, but one of the causes of corrosion with ULSD systems is...



Conclusion- The Source of the Problem...Ethanol!



STI conducted own study

- Study included both fiberglass and steel tanks
- USTs from five regions of the countries tested
- One fiberglass and one steel tank in each region
- Tanks were chosen randomly with no previous investigation of any corrosion issues
- Both fuel and water bottom sample obtained

Testing

- Testing was based on Battelle study
- Analysis based on what appeared to be causing corrosion in tanks
 - Ethanol
 - Acetate
 - Other acids
 - pH level of fuel

STI conducted own study

- Acetic acid and ethanol found in 5 regions
- Highest levels of acetic acid found in fiberglass tanks
- However data inconclusive to answer big questions
 - Is same type of corrosion happening in steel tanks?
 - Is acetic acid/ethanol responsible for corrosion?

Results

- Ethanol found in all but one region of the country
 - How is ethanol getting in diesel fuel
 - Transporting trucks is one possibility
 - Also possible for ethanol to be formed inside the tank
- Acetic acid found in all but one region of the country

Equipment from Southeast Region in fiberglass tank



FRP tank riser NW area

Acetate 462 ppm



Steel Tank riser, NW area

Acetate 108 ppm



FRP riser,
MA area
Acetate
25,600
ppm



Mixed Results

- Hypothesis that high acetate would indicate high corrosion
- Photos of risers don't indicate this
- Next step cameras inspected inside tanks at 3 locations

STI Research

- Las Vegas service stations tanks under same owner
- FRP tank vapor control fitting – top right photo
- Steel tank vapor control fitting – bottom right photo



Solutions, and What's Next?

- Clean Diesel Alliance may be funding another study
- ASTM and other industry professionals constantly in search of solutions
- Work with reputable fuel quality companies to provide biocides and other fuel treatment services and remedies to maintain fuel quality

Bio-Diesel

- Many Bio-diesel plants shut down when the price dropped
- Problems with feedstocks and maintaining quality
- Problems with cold-flow and scouring effects on tanks
- Problems with “shelf-life”
- Expensive to refine
- Prone to microbial growth



photo: propelbiofuels.com

Questions?

