

Confined Space Hazards from a Marine Chemist/ Certified Industrial Hygienist Perspective

John Edgar
MS, MSPH, CIH, CMC

Let me introduce myself.

- BS/MS Jacksonville State University
- USCG 1980-2000
 - MSO Tampa (Marine Inspector)
 - MIO Houston (Marine Inspector)
 - Post Graduate School UAB (MSPH)
 - USCG Headquarters (MTH-1)
 - SESAC
 - CTAC
 - MSO New Orleans
 - ISC Seattle

Introduction Continued

- Marine Chemists of Louisiana
- Rimkus Consulting Group, Inc
- Relle IAQ Solutions, Inc.
- Southern Marine Chemists
 - Co-chair of JASRA Health and Safety Committee

Today's Discussion Areas

- Modern (Green) Degreasers & Hydrogen Sulfide
- Marine Diesel Fuel LEL Testing Issues
- LEL Sensor Calibration Gas (Methane vs Pentane)
- Competent Person Activities
- Painting Issues
- Multi-employer worksites
- Tank Cleaning Operations

Green Degreasers

- Marine Chemist Scott Godfrey called to test two wastes/slop oil tanks on tug. Both tested greater than 999 ppm Hydrogen Sulfide. Immediate investigation found that company had changed to a soy based cleaner approximately 1 ½ months earlier.
- Marine Chemist Scott Godfrey returned to same company and inspected waste/slop oil tanks on two tugs, one which had been using the soy based cleaner and the other using petroleum base cleaner. The soy base cleaner tug waste oil tank was high in Hydrogen Sulfide and the petroleum base cleaner tug waste oil tank had zero ppm hydrogen sulfide.

From: Freeman, Carl - Zep Inc.
Sent: Monday, April 20, 2009 2:57 PM
To: Steadman, Bruce - Zep Inc.
Subject: Soy Response and Hydrogen Sulfide production.

Bruce,

I spoke with a safety engineer who deals with ships and the cleaning processes they use who had an interesting question. He has many ships that use the Soy Response to clean with, depositing the rinse into "slop" tanks which are later emptied and cleaned out. Scott, the engineer, noticed that ships that use our Soy product seem to develop a strong Hydrogen Sulfide odor faster than those that do not in these tanks. They always form it due to the high sulfur fuel they use, but he noticed that the ships that clean with us, do it faster. Any Thoughts? I found this very interesting.

*Eddie Freeman
Zep, Inc.
Principal Chemist
Technical Services
1420 Seaboard Industrial Blvd.
Atlanta, GA.,30318
Fax 404-603-7975
Phone 404-352-1413, ext 6420
1-877- I BUY ZEP*

From: Steadman, Bruce - Zep Inc.
Sent: Tuesday, April 21, 2009 9:51 AM
To: Freeman, Carl - Zep Inc.
Subject: RE: Soy Response and Hydrogen Sulfide production.

Eddie,

You're right! That is a very interesting observation!

Soy Response itself, of course, does not contain any significant level of sulfur-containing components so it is not contributing directly to the problem of Hydrogen Sulfide generation. However, the easily biodegradable components (Surfactants and Soy Methyl Esters) in the Soy Response residue will serve as a marvelous breeding ground for a wide variety of bacterial types. The bacteria count in the rinse water will rise dramatically. Conversely, the high sulfur petroleum fuel by itself is not easily digested by the tramp bacteria in the slop tanks and the Hydrogen Sulfide is not released very rapidly under these conditions, or when any relatively non-biodegradable cleaning product is used. Thus, the Soy Response is contributing indirectly to the problem, as would any easily biodegradable product that can provide 'food' for the bacteria.

Permit me the following crude analogy! I really don't like brussel sprouts very much. If I were served a big plate of brussel sprouts, I would probably nibble a little on them if I was really hungry, but most of the brussel sprouts would remain on that plate for a long time. However, if that plate also contained a big, juicy steak, a sweet potato with cinnamon and butter, and just a few brussel sprouts, I would probably clear the entire plate in a matter of minutes! Think of those brussel sprouts as the high sulfur fuel residue in the rinse water and the steak and sweet potato as the Soy Response residue. I, of course, represent those hungry but somewhat finicky bacteria!

Hope this helps!

----- Forwarded Message: -----

From: "Freeman, Carl - Zep Inc." <Eddie.Freeman@zep.com>

To: <sgodfreycmc692@bellsouth.net>

Subject: FW: Soy Response and Hydrogen Sulfide production.

Date: Tue, 21 Apr 2009 15:15:14 +0000

Here is an explanation for the problem you encountered. They could use Our Multi Clean Green 1249 as a degreaser, this would be more of an alkaline degreaser that is biodegradeable. It may reduce this problem.

Eddie Freeman

Zep, Inc.

Principal Chemist

Technical Services

1420 Seaboard Industrial Blvd.

Atlanta, GA.,30318

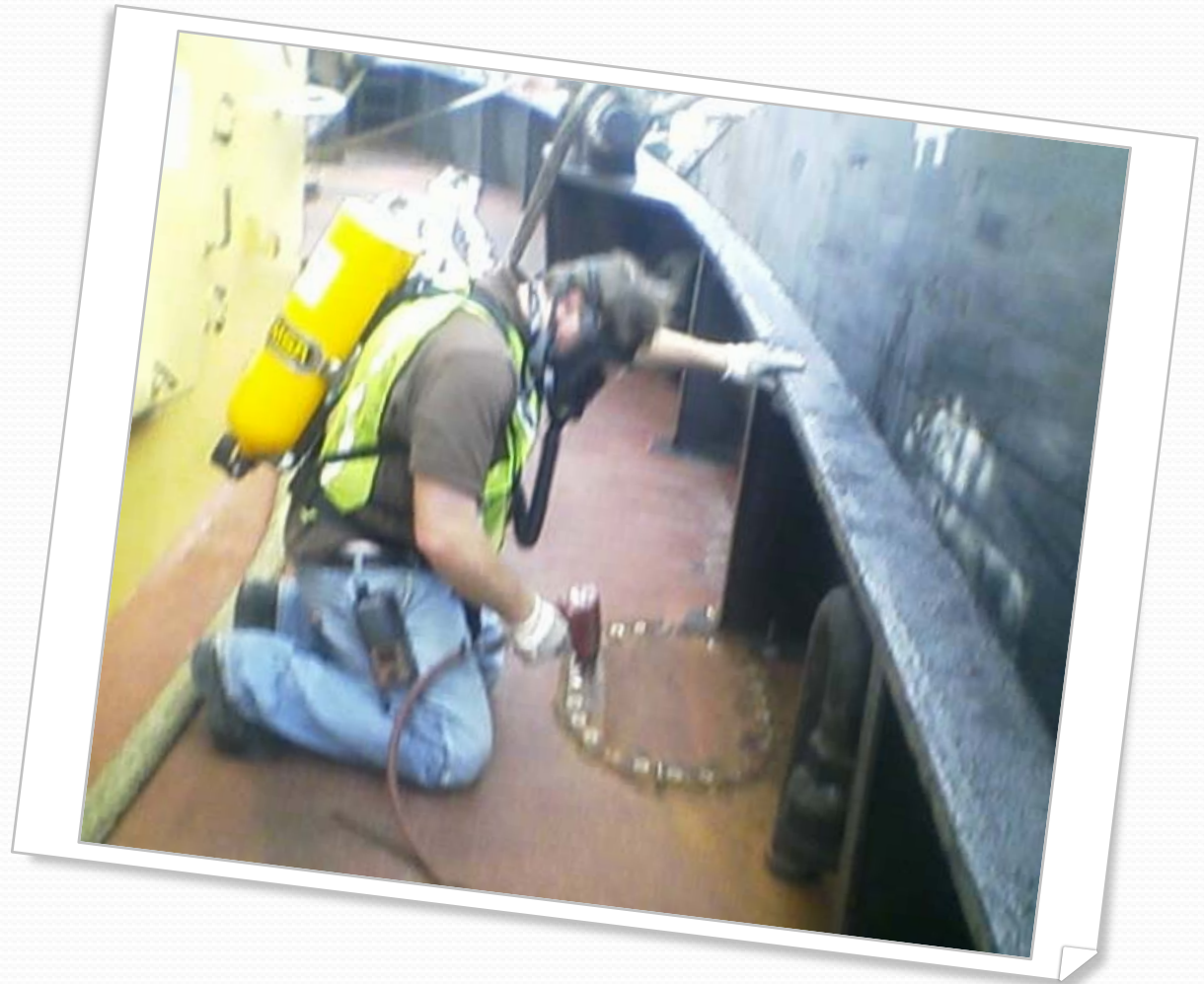
Fax 404-603-7975

Phone 404-352-1413, ext 6420

1-877- I BUY ZEP

Marine Chemist Testing Waste Oil Tanks

Scott Godfrey and John Edgar of Southern Marine Chemists tested two waste oil tanks and found 150 ppm Hydrogen Sulfide at the lid of each tank. Both tanks had IDLH atmospheres at the lid. Each of these tanks were also at 50% of the lower explosive limit.



Marine Chemist Testing Waste Oil Tanks cont.

As both tanks were IDLH, the only standard safety designation allowed was Not Safe for Hot Work and Atmosphere Not Safe for Workers.

The area was isolated and safety tape placed to prevent any access to the vessel and the tanks allowed to breath over night.



Marine Chemist Testing Waste Oil Tanks cont.

The following morning the atmosphere in the tanks was below 10 ppm in the head space. However, there was several inches of liquid residue in the tank which could possibly re-generate a toxic atmosphere if disturbed. Therefore, the marine chemist monitored the atmosphere for the entire period of the stripping operation.



Conclusions Regarding Green Cleaners

- 1. Green cleaners which claim increased rates of decomposition of petroleum hydrocarbons may be dangerous in the maritime industry.
 - Increased decomposition means the product is a good food source for bacteria and will increase bacteria consumption of both the cleaner and petroleum hydrocarbons.
- 2. High sulfur fuels found in the maritime industry will create a greater amount of hydrogen sulfide in a shorter period of time when the rate of decomposition is increased by using biodegradable cleaners.

Marine Diesel Fuel Testing

- Change of TLV for diesel required marine chemist to test all diesel tanks for ppm with either a detector tube or a PID.
- When calculated, a level of 60 ppm on the PID is considered to be 1% LEL for diesel.
- Marine Chemists observed relatively high levels on their PIDs and zero being measured on their four gas meter.
- This only occurred with the higher flash point marine grade diesels.

Marine Diesel Fuel Testing Continued

- Hit heavy during the Marine Chemist sectional seminars this year.
- NFPA will be looking at MC certs this year to see that MCs are using the 60 ppm = 1 % LEL concept on their certs.
- Marine Chemists and Competent Persons must use a PID to verify the LEL condition when marine grade diesel is involved.
- This condition has not been observed for highway diesel or jet fuel/kerosene.

LEL Sensor Calibration Gas (Methane vs Pentane)

- R. Wanek, R. Warn, Draeger Safety Inc., Pittsburgh, PA.
- There has been a movement to calibrate catalytic combustible gas sensors with pentane the past few years, with companies stating this will provide increased safety when detecting combustible gases.
- But is that really the case? It is possible for a catalytic sensor to calibrate and respond perfectly to pentane but have little or no response to methane.
- Calibration with pentane increases the sensitivity of the sensor and allows for more accurate readings for the heavier gases and higher readings for the lighter gases such as methane.

LEL Sensor Calibration Gas (Methane vs Pentane) cont.

- The advantage of calibrating with pentane to get increased safety margins really only applies to new sensors.
- Any new catalytic sensor, calibrated to a pentane calibration gas, will show higher than actual readings for methane.
- However, as the sensor ages its response characteristic will change. Sensitivity to lighter gases, such as methane, will decrease more rapidly throughout time than the sensitivity to heavier gases such as pentane.

Competent Person Activities

- Inspecting spaces for entry and hot work.
 - Testing for O₂
 - Testing for Flammability
 - Testing for Toxicity
 - Completing OSHA Log
 - Submitting WAFs for Hot Work
 - Authorizing and posting hot work for spaces which have not contained combustible or flammable liquids or gases.
 - Maintaining Marine Chemists Certifications
 - Testing and inspecting requirements, including adjacent spaces.

Painting Issues

- Most dangerous activity in a confined space when hot work is also scheduled for the space or adjacent space.
- The shipyard must maintain conditions within the toxic levels appropriate for the ppe used and below 10% of the lower explosive limit during the painting operation.
- Biggest issue. Is painting a change of conditions?
 - My opinion. If you feel you must red log the space during the painting operation, then there has been a change in conditions. If you feel you can allow hot work to continue during the painting operation, then there has not been a change in conditions.

Painting Issues cont.

- Paint mixing area distance from hot work.
- Routing of pressurized hoses thorough spaces and consideration of adjacent spaces.
- Similar to stopping all hot work on a vessel during fueling operations.

Multi-employer worksites

- Atlantic Marine Florida – requires all contractors working at their facility to run all hot work requests through their competent person program. Very good control of activities which could impact hot work, such as painting, tank cleaning, and abatement activities.
- Working aboard ship at Navy Base –
 - multiple contractors with different types of contracts working simultaneously aboard vessel.
 - Activities coordinated through vessel crews.
 - Each contractor competent person/marine chemist will authorize and monitor their work. **What other work cold and hot will occur in the space and adjacent space?**
 - **Competent person posts early, before the normal work day, and coordination meetings occurs later.**

Tank Cleaning Operations

- Meets the definition of Shipyard Employment.
- Tanks must be inspected by a shipyard competent person and results posted on OSHA log.
- As discussed earlier, for accurate results on marine diesel, a PID or equivalent must be used to verify the tank is less than and remains less than 10% of the lower explosive limit.