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Static Electric Discharge during Solvent Handling and Storage

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1.0 Introduction

On July 17, 2007, at about 9 a.m., an explosion and fire occurred at the Barton Solvents Wichita facility in Valley Center, Kansas. Eleven residents and one firefighter received medical treatment. The incident triggered an evacuation of Valley Center (approximately 6,000 residents); destroyed the tank farm; and significantly interrupted Barton's business. The initial explosion occurred inside a vertical above-ground storage tank that was being filled with Varnish Makers' and Painters' (VM&P) naphtha. VM&P naphtha is a National Fire Protection Association (NFPA) Class IB flammable liquid[5] that can produce ignitable vapor-air mixtures inside tanks and, because of its low electrical conductivity, can accumulate dangerous levels of static electricity.

This paper discusses the hazards associated with static-accumulating flammable liquids that can form ignitable vapor-air mixtures inside storage tanks. It urges companies to take extra precautions to prevent explosions and fires like the one at Barton. It also examines industry Material Safety Data Sheet (MSDS) hazard communication practices.

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[1] The U.S. Chemical Safety Board investigated the July 2007 Barton Solvents explosion and fire. Mr. McClure worked at the CSB from November 2002 to March 2009, and was the lead investigator for the Barton Solvents incident and primary author of the investigation report.

[2] Mr. Britton was a contractor consultant to the U.S. CSB for the Barton Solvents investigation.

[3] Mr. Holmstrom was the U.S. CSB Investigations Supervisor for the Barton Solvents investigation.

[4] Mr. Kaszniak was a U.S. CSB Investigator for the Barton Solvents investigation.

[5] Liquids most likely to form ignitable vapor-air mixtures during tank filling at ambient operating temperatures are normally those designated as Class IB or Class IC in NFPA 30 (flammability hazard rating of "3" in NFPA 704). In the American Petroleum Institute (API) classification system these liquids usually fall into the "Intermediate Vapor Pressure Products" category. A notable exception is motor gasoline, an NFPA Class IB liquid that is designated as a "High Vapor Pressure Product" in the API system, implying that (except at very low operating temperatures) the vapor-air mixture formed during tank filling rapidly becomes too rich to be ignitable. (See NFPA 30, Section 4.3 "Classification of Liquids" and NFPA 704 Chapter 6 for a detailed discussion of NFPA's classification and flammability hazard rating systems. See API 2003 (2008 edition), Section 3 "Definitions" for an explanation of "High," "Intermediate," and "Low" vapor pressure product classes.

2.0 Incident Description

The initial explosion occurred soon after the tank farm supervisor started the transfer of the final compartment of a tanker-trailer containing VM&P naphtha into a 15,000 gallon above-ground storage tank (Figure 1).

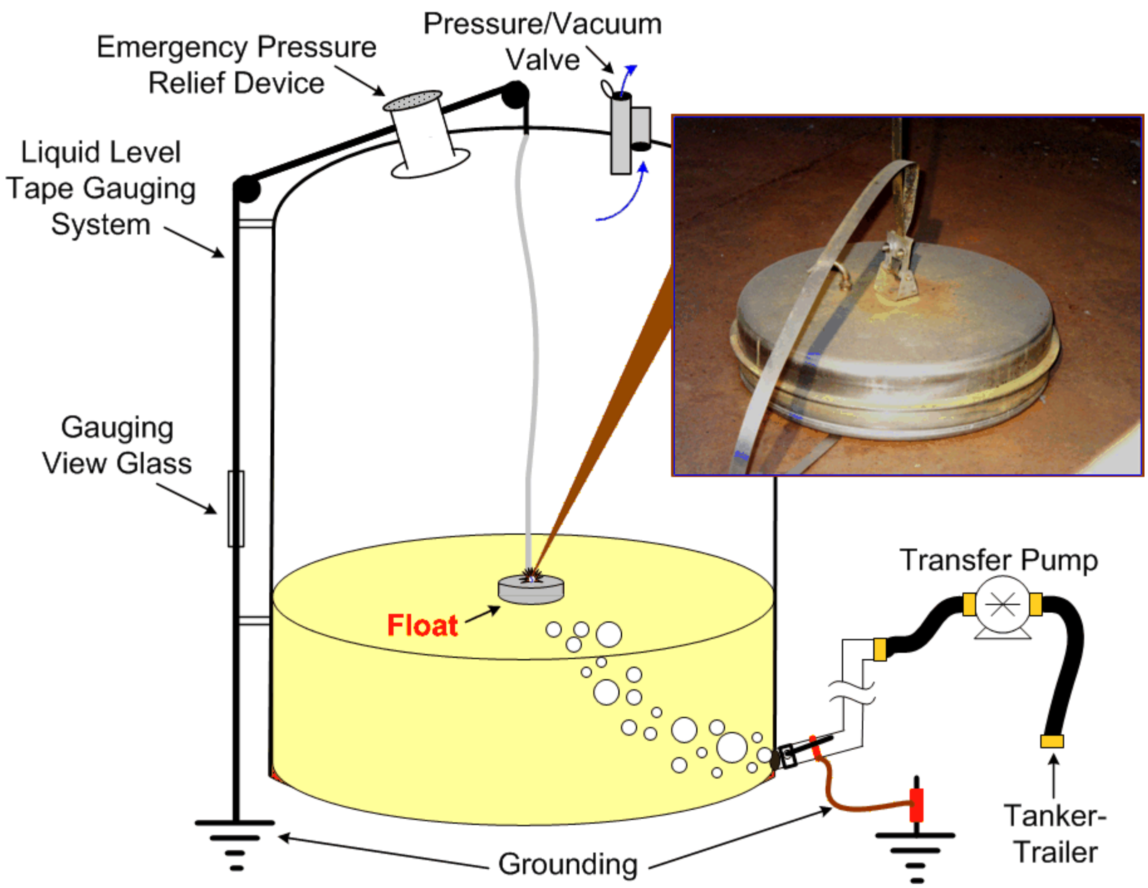

Figure 1 - VM&P naphtha tank and photo of an example float

The explosion sent the VM&P tank rocketing into the air, trailing a cloud of smoke and fire from the burning liquid; it landed approximately 130 feet away. Witnesses heard the explosion and saw the fireball from several miles away. Within moments, two more tanks ruptured and released their contents into the rapidly escalating fire that was concentrated inside the earthen spill containment area surrounding the tank farm.[6] As the fire burned, the contents of other tanks over-pressurized or ignited, launching steel tank tops (10-12 feet in diameter); vent valves; pipes; and steel parts off-site and into the adjoining community. A tank top struck a mobile home in the community (approximately 300 feet away) and a pressure/vacuum valve hit a neighboring business nearly 400 feet away (Figures 2 and 3).

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[6] Approximately 20,000 gallons of flammable liquid were released into the spill containment. The tank farm included 43 above-ground storage tanks with capacities ranging from 3,000 to 20,000 gallons. Tank heights ranged from approximately 15 to 40 feet.

Figure 2 - Tank top projectile

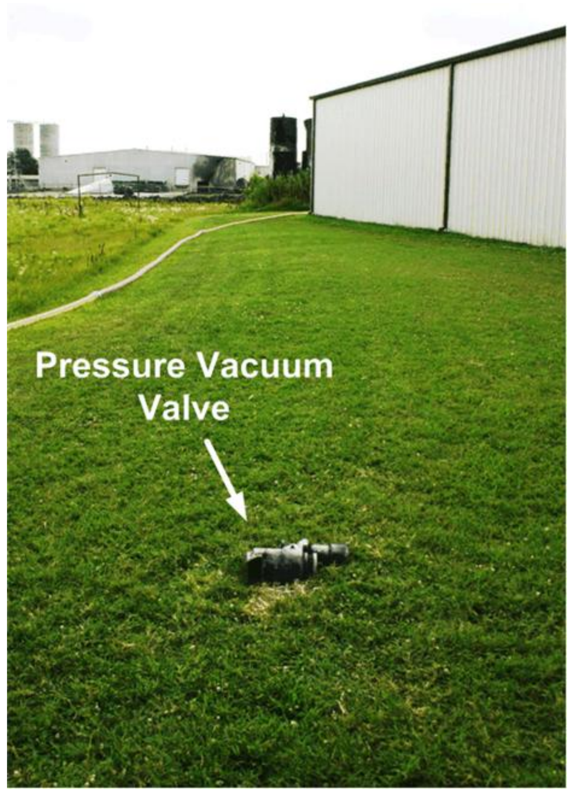

Figure 3 - Pressure vacuum valve

3.0 Flammable Liquids and Static Electricity

Fire occurs when there is an ignitable vapor-air mixture and a source of ignition, such as a static electric spark. At normal handling temperatures, flammable storage tanks, like those containing gasoline, may contain vapor-air mixtures that typically cannot be ignited by a static electric spark because the vapor-air mixture is too rich (i.e., contains too much fuel and not enough oxygen) to burn. VM&P naphthas, however, and other flammable liquids (e.g., many NFPA Class IB Flammables), may form ignitable vapor-air mixtures inside tanks at normal handling temperatures.

Static electricity is generated as liquid flows through pipes, valves, and filters while being transferred.[7] It can also be produced by entrained water or air, splashing or agitation, and when sediment in the bottom of the tank becomes suspended (Britton, 1999).

Because nonconductive liquids, such as VM&P naphtha and other flammable liquids, dissipate (or "relax") static electricity slowly, they pose a risk of dangerous static electric accumulation that can produce sparks inside tanks.

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[7] The rate of static charge generation during flow through pipe increases roughly with the square of the flow velocity. A liquid whose conductivity is less than 100 pico siemens per meter (pS/m) is generally considered nonconductive (Britton, 1999). The VM&P naphtha involved in the Barton incident had a conductivity of 3 pS/m. Some common nonconductive liquids are listed in NFPA 77 (Annex B – Table B.2). See the Resources Section at the end of this Case Study for web access instructions.

Common Static-Accumulating Flammable Liquids that May Form Ignitable Vapor-Air Mixtures

• VM&P naphtha	• Benzene	• Cyclohexane
• n-Heptane	• Toluene	• n-Hexane
• Xylene	• Ethyl benzene	• Styrene

4.0 Key Findings

Several factors likely combined to produce the initial explosion:

- ⇒ The tank contained an ignitable vapor-air mixture in its head space.
- ⇒ Stop-start filling, air in the transfer piping, and sediment and water (likely present in the tank) caused a rapid static charge accumulation inside the VM&P naphtha tank.
- ⇒ The tank had a liquid level gauging system float with a loose linkage that likely separated and created a spark during filling.
- ⇒ The MSDS for the VM&P naphtha involved in this incident did not adequately communicate the explosive hazard.

Normal Bonding and Grounding May Not Be Enough!

Companies that handle, transfer, and store flammable liquids should contact manufacturers to determine if these liquids can accumulate dangerous levels of static electricity, and if they can form explosive vapor-air mixtures inside storage tanks. If so, extra precautions—beyond normal bonding and grounding—may be necessary.

4.1 Flammability of VM&P naphtha

The VM&P naphtha involved in the Barton explosion was tested to determine if an ignitable vapor-air mixture could have been present inside the tank at the time of the explosion.[8] The results revealed that, at approximately 77˚F (25˚C) (the handling temperature of the VM&P naphtha at the time of the incident), the tank head space likely contained a readily ignitable vapor-air mixture. The energy from a static spark would have been adequate to ignite this vapor-air mixture.[9]

4.2 Tank Level Float Design

The design of the tank liquid level gauging system float used by Barton incorporates a loose linkage at the float/tape junction that can separate slightly, interrupting grounding (see Section

[8] Its flashpoint was 58°F (14°C); its vapor pressure was approximately 0.7 kPa (5 mmHg) at 68°F (20°C) using an Isoteniscope; and its flammable range was approximately 0.9-6.7% in air. The Reid VP of the VM&P naphtha was 3.1 psia (21.4 kPa) at 100˚F (38°C).

[9] The minimum ignition energy required for a spark to ignite the Barton VM&P naphtha was approximately 0.22 mJ (plus/minus 0.02 mJ).

4.3) and creating the potential for a spark (Figure 4).[10] Turbulence and bubbling during the stop-start transfer pumping, in addition to creating rapid static charge accumulation, also likely created slack in the gauge tape connected to the float, causing the linkage to separate and spark.[11]

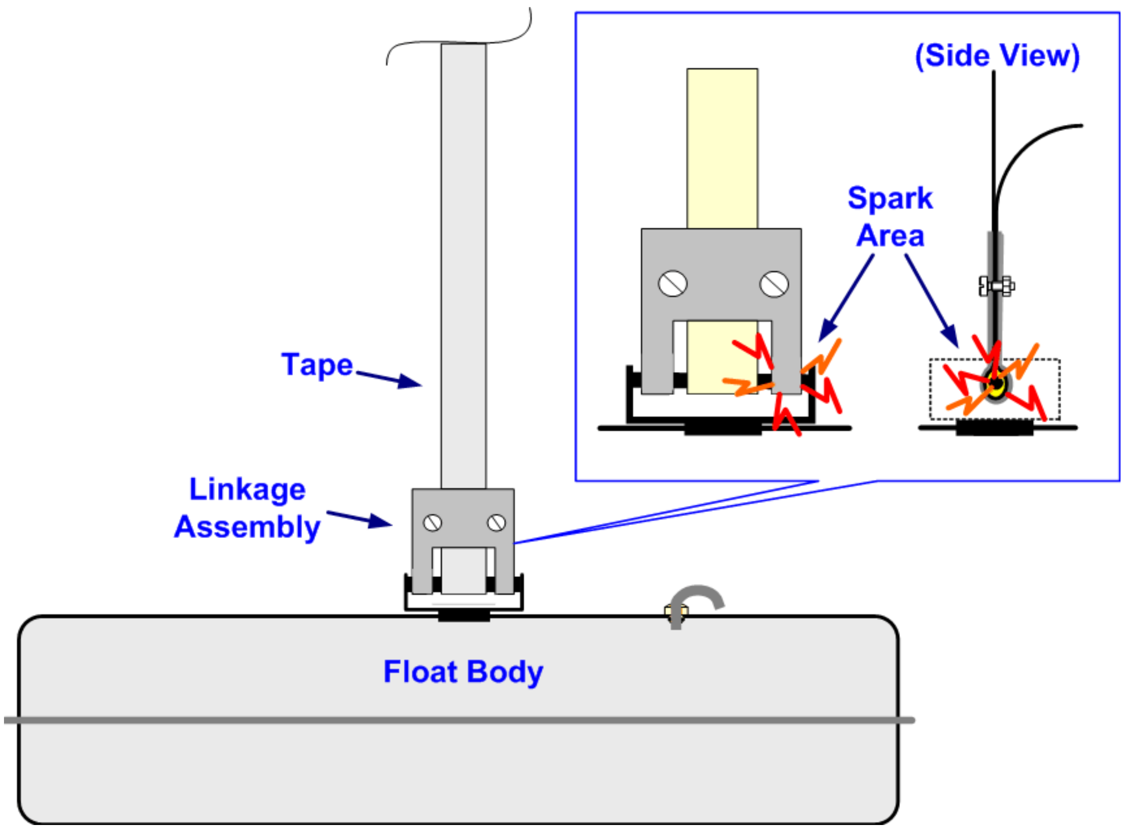

Figure 4 - Float linkage and area where the spark likely occurred

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[10] Electrical testing of an exemplar tank level float indicated that a loose linkage could produce a spark with sufficient energy to ignite a flammable vapor-air mixture inside a tank.

[11] While the loose linkage level float was a potential spark location, a spark from a "brush discharge" cannot be ruled out. Brush discharges encompass a variety of "non-spark" static discharges that occur between a charged liquid surface and a grounded conductive object, such as a dip pipe or other metal component acting as an electrode, or even the tank wall itself. Brush discharges can occur even when all equipment is properly bonded and grounded (Britton, 1999). See the Resources Section at the end of this paper for more information on brush discharge.

4.3 Bonding and Grounding

Bonding is the process of electrically connecting conductive objects, like tanker-trailers, to transfer pumps to equalize their individual electrical potentials and prevent sparking (Figure 5).

Grounding (earthing) means connecting a conductive object to the earth to dissipate electricity, like accumulated static, lightning strikes, and equipment faults, into the ground, away from employees/equipment and ignitable mixtures.

The tanker-trailer, pump, piping, and storage tank at the Barton facility were bonded and grounded at the time of the incident.[12] However, published safety guidance indicates that bonding and grounding measures applied to typical transfer and storage operations may not be enough if nonconductive flammable liquids are involved. Nonconductive liquids accumulate static electricity and dissipate (relax) it more slowly than conductive liquids, and therefore require additional precautions (see Section 5).

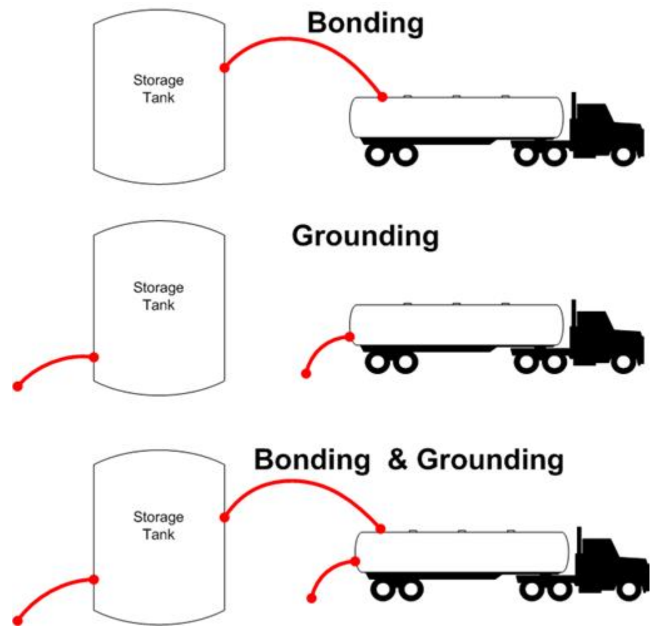

Figure 5. Bonding and grounding

4.4 Static Accumulation in the Pumped Liquid

Barton pumped the VM&P naphtha from three separate compartments in the tanker-trailer to the VM&P tank. Air pockets were introduced into the fill piping, and then transferred into the tank when the transfer hose was reconnected to the tanker-trailer after compartments were changed. Studies have found that static electricity accumulates rapidly during pump startup when nonconductive liquids are transferred to storage tanks (Walmsley, 1996).

In this case, the static electricity accumulation was likely exacerbated by the air pockets (bubbling) and the likely presence of suspended sediment and water in the tank.[13] In addition, the VM&P tank was approximately 30 percent filled at the time of the explosion, which would have produced a liquid surface potential (voltage) close to the maximum expected during filling.

4.5 Material Safety Data Sheets

According to the Occupational Safety and Health Administration (OSHA) Hazard Communication Standard (HCS),[14] employees both need and have the right to know the identities and hazards of the chemicals they are exposed to when working. The purpose of the

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[12] The transfer hose was severely damaged during the fire, preventing a conclusive determination that bonding and grounding were effective.

[13] Barton indicated that it had no records of the VM&P tank ever being cleaned, and the tank had no manway or access opening to facilitate cleaning. Employees stated that they scooped sediment from the bottoms of similar tanks to prepare them for inspection.

[14] 29 CFR 1910.1200.

HCS is to ensure that chemical manufacturers and importers evaluate the hazards and communicate them, along with appropriate precautionary measures, to employers and employees through a hazard communication program.[15] The primary method of communicating this information is via detailed technical bulletins called Material Safety Data Sheets (MSDSs).

The MSDSs supplied by the manufacturer of the Barton VM&P naphtha indicated that the material may accumulate a static electrical charge that could discharge and ignite accumulated vapors. It did not, however, provide critical physical and chemical property data and warnings that the material may form an ignitable vapor-air mixture inside storage tanks. Nor did it list any precautionary measures, beyond normal bonding and grounding practices, or reference relevant consensus guidance that Barton could have used to help prevent this explosion.

To prevent explosions with flammable liquids like VM&P naphtha, MSDSs should communicate

⇒ warnings that the material is a static accumulator and can form an ignitable vapor-air mixture inside storage tanks;

⇒ that bonding and grounding may not be enough;

⇒ specific examples of additional precautions (see Section 5) and references to the published guidance targeted at preventing static electric discharge; and

⇒ conductivity testing data,[16] so that companies know the degree to which the material will accumulate static and can compare it to the published guidance. Information about the published guidance is included in the Information Resources section at the end of this report.

Material Safety Data Sheets (MSDSs)

MSDSs do not typically communicate critical physical and chemical properties, and specific precautions or reference guidance for flammable liquids that may pose a static ignition hazard. Companies should contact the manufacturer (or an expert familiar with the relevant consensus guidance) for this information. Manufacturers should in turn update their MSDSs to provide this critical safety information.

4.5.1 Industry MSDSs Review

The team reviewed over 50 MSDSs of some of the most widely used nonconductive flammable liquids to determine if they provided the warnings, precautionary measures and references, and conductivity testing data discussed above.

⇒ <u>Static Accumulator and Storage Tank Ignitable Vapor-Air Mixture Potential</u>: Of the MSDSs reviewed, about half contained a warning about the potential for the material to accumulate static electricity. All of the MSDSs included a warning about ignitable flammable vapors, but only one specifically warned of the potential for the material to form an ignitable vapor-air mixture inside a storage tank.

[15] 29 CFR 1910.1200(a)(1) and (2).

[16] The units routinely used to report conductivity are pico Siemens per meter (pS/m).

⇒ Specific Precautions and References to Prevent Explosions: Of the MSDSs reviewed, most advised companies to properly bond and ground equipment, but only a few (less than 10 percent) indicated that bonding and grounding alone may not be enough to prevent a static discharge. Approximately a third of the MSDSs reviewed referenced NFPA 77 and API 2003,[17] but many of those did not specifically warn that bonding and grounding may not be enough. Only about a quarter of the MSDSs provided one or more specific precautionary measures such as adding nonflammable (inert) gases to tank head spaces, adding an anti-static agent, or reducing the pump flow velocity during transfer.

⇒ Conductivity Testing Data: Only three MSDSs (all prepared by the same manufacturer) included conductivity testing data.

5.0 Additional Precautions

Companies that handle, transfer, and store nonconductive flammable liquids, such as naphthas, toluene, benzene, and heptane, should take additional precautions to avoid an incident like the one at Barton.

Additional Precautions

⇒ Request additional manufacturer guidance

⇒ Add an inert gas to the tank head space

⇒ Modify or replace loose linkage tank level floats

⇒ Add an anti-static agent

⇒ Reduce flow (pumping) velocity

5.1 Request Additional Manufacturer Guidance

As discussed, MSDSs do not typically provide conductivity testing data or specific examples of additional precautions that should be observed, and do not typically reference the relevant consensus guidance pertaining to static electricity and storage tank vapor-air mixture hazards. Therefore, to determine if additional precautions to eliminate the potential for an explosion are necessary, companies that transfer flammable liquids should contact the manufacturers, or a qualified expert, to determine if the flammable liquid is

⇒ nonconductive (a static accumulator); and
⇒ capable of producing an ignitable vapor-air mixture inside a storage tank.

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[17] NFPA 77 and API 2003 are consensus standards that provide static electric safety guidance.

5.2 Add a Nonflammable, Nonreactive (inert) Gas to Tank Head Spaces[18]

Using an inert gas such as nitrogen, if done correctly, is effective in reducing the potential for an ignitable incident (explosion) as it renders tank head spaces incapable of supporting ignition from a static spark.[19] However, because this practice can produce oxygen-deficient environments inside tanks, extreme caution should be exercised when opening tanks for routine inspections and maintenance.[20]

5.3 Modify or Replace Loose Linkage Tank Level Floats

Companies with tanks that may contain ignitable vapor-air mixtures and that are equipped with conductive loose linkage level floats should take one or more of the following measures:

- ⇒ Use an appropriate gas to inert tank head spaces.
- ⇒ Inspect and replace, as appropriate, floats with level measuring devices that will not promote sparks inside the tank.
- ⇒ Modify floats so that they are properly bonded and grounded (see Figure 6).[21]
- ⇒ Reduce the liquid flow (pumping) velocity.[22]
- ⇒ Remove any slack in the tape connected to the float mechanism that could allow a spark gap to form.

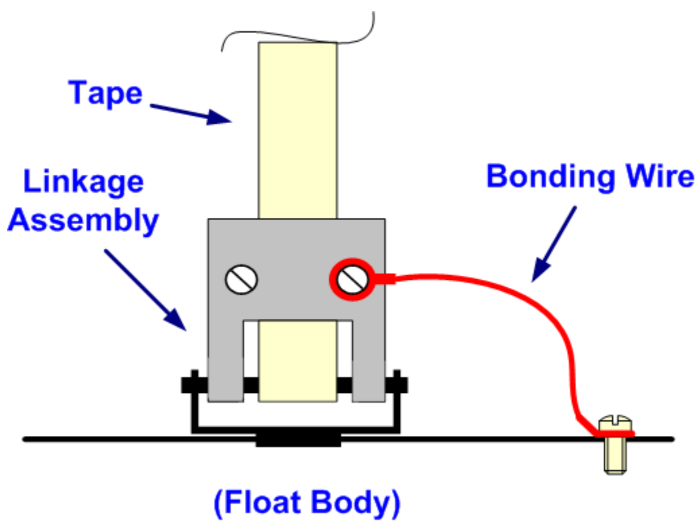

Figure 6 - Tank level float bonding wire

6.0 Anti-Static Additives

Anti-static (conductivity-enhancing) additives increase the conductivity of liquids, helping reduce static accumulation. Before relying solely on these additives, however, companies should

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[18] See NFPA 69 "Standard on Explosion Prevention Systems" (2008) for guidance pertaining to proper inerting practices.

[19] Before using inert gases in tanks, companies should contact the liquid manufacturer to determine if the proposed gas is appropriate for the particular liquid.

[20] Employers who require employees to enter confined spaces—particularly those with oxygen-deficient or other hazardous atmospheres—must comply with the requirements of the OSHA "Permit Required Confined Space Program" (29 CFR 1910.146).

[21] This figure illustrates the modification recommended by the manufacturer of the floats used at Barton's Wichita facility. Companies with floats equipped with loose linkages should contact the manufacturer for modification recommendations.

[22] NFPA 77 (2007); API 2003 (2008); and Britton (1999) recommend a flow (pumping) velocity of 1 meter per second when the risk of static ignition is high. Until the spark potential inside the tank is eliminated, companies should use a pump flow velocity at (or near) 1 meter per second to transfer nonconductive flammable liquids.

contact the flammable liquid manufacturer to determine if such an additive is appropriate and effective for the particular liquid.

7.0 Reduced Flow (Pumping) Velocity

Various guidance suggests that nonconductive flammable liquids capable of forming ignitable vapor-air mixtures inside tanks should be transferred at reduced flow (pumping) velocities to minimize the potential for a static ignition.[23]

Information Resources

The following references include additional information on the safe use of static-accumulating flammable liquids:

1. American Petroleum Institute (API), "API Recommended Practice 2003: Protection Against Ignitions Arising Out of Static, Lightning, and Stray Currents," 7th ed., 2008.

2. Britton, L.G., and J.A. Smith, "Static Hazards of Drum Filling," Plant/Operations Progress, Vol. 7, No. 1 (1988) pg. 53-78.

3. Britton, L.G., "Avoiding Static Ignition Hazards in Chemical Operations," AIChE-CCPS Concept Book, 1999.

4. National Fire Protection Association (NFPA), "NFPA 30: Flammable and Combustible Liquid Code," 2008.

5. NFPA, "NFPA 69: Standard on Explosion Prevention Systems," 2008 ed.

6. NFPA, "NFPA 77: Recommended Practice on Static Electricity," 2007 ed. NFPA 77 can be viewed, free of charge, on the NFPA website (www.nfpa.org). Access directions: At the NFPA Homepage, go the "Codes and Standards" pull down tab, then click on "Code development process" and scroll down to "Online access."

7. Walmsley, H.L., "The Electrostatic Potentials Generated by Loading Multiple Batches of Product into a Road Tanker Compartment," J. Electrostatics, Vol. 38, 1996, pg.177-186.

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[23] The guidance pertaining to reduced flow (pumping) velocities include API 2003 (2008), Sections 4.2.5.6 and 4.5.1; NFPA 77 (2007), Table 8.6 (footnote f); and Laurence Britton, "Avoiding Static Ignition Hazards in Chemical Operations", Chapters 2-1.6 and 5-4. While toluene and heptane are specifically identified in NFPA 77, Table 8.6 (footnote f), typical VM&P naphthas exhibit similar characteristics and should also be transferred at reduced flow rates. Recommended maximum flow (pumping) velocities provided in the various guidance differ. However, the most protective recommended flow (pumping) velocity is 1 meter per second.