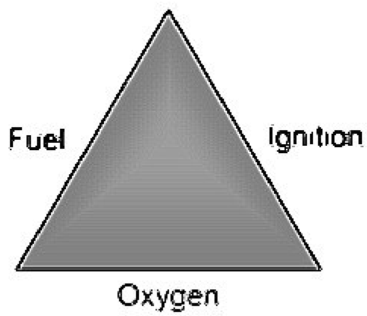
Explosions Involving Nonconductive Flammable Liquids

Almost every firefighter and responder has been introduced to the classic fire triangle.



For a fire to occur, all three elements (a fuel, oxygen, and an ignition source) must be present. The oxygen can come from the air, which is composed of 21% oxygen. In a few situations, the oxygen can come from a chemical that is in contact with the fuel, for example nitrates and ethers. The ignition source could be static electricity, lightning, another fire, a lighted cigarette, or sparks from equipment. The fuel is anything that will burn.

What is sometimes not recognized is that under certain circumstances the pouring or movement of nonconductive flammable liquids poses a special hazard. This hazard is often not mentioned on chemical Material Safety Data Sheets (MSDS) or even in company standard operating procedures for the handling of these liquids. Even the grounding of tanks and transfer vessels containing these liquids may not be sufficient to correct the hazard. Let's look at some real-world examples.

Examples

Writer's Experience

John Nordin was first introduced to the problem as an undergraduate attending an organic chemistry class lecture at the University of Minnesota many years ago. During the classroom lecture held on the upper floor of the chemistry building, the fire alarm sounded. Dense black smoke quickly came into the room through the building ventilation system. Everyone was safely evacuated. Fortunately the building had wide hallways and several exits, and although the hallways/stairwells were filled with smoke, the people could see their way. The Minneapolis Fire Department responded quickly; the building was saved although there was extensive damage. The root cause of the fire was a buildup of static electricity as a flammable aromatic liquid (benzene or toluene) was being transferred from a central storage drum to smaller containers for use in chemistry laboratories. The people working in these areas or their supervisors should have been aware of the hazards involved, but since this incident took place about 45 years ago safety procedures probably had not been developed or written for the operations.

ConocoPhillips South Tank Farm, Glenpool, OK

Summary:
On April 7, 2003, at about 8:55PM, an 80,000 barrel capacity storage tank (tank 11) at ConocoPhillips Company's Glenpool tank farm exploded and burned as it was being filled with diesel fuel delivered by pipeline [Comment: one barrel = 42 gallons]. At the time of the explosion, tank 11 contained between 7,397 and 7,600 barrels of diesel. Tank

11 had been used to store gasoline, which was transferred to another tank (tank 12) earlier that day to make room for the diesel. The resulting fire burned for 21 hours and damaged two other storage tanks in the area. There were no injuries or fatalities. Nearby residents were evacuated, and schools were closed for two days. The total cost of the incident including emergency response, lost product, property damage, claims, and remediation was $2,357,483.

Sequence of Events:
Transfer of about 8710 barrels of gasoline from ConocoPhillips' Tank 11 to Tank 12 started during the afternoon on April 7 and was completed at about 6:10 PM.

Pipeline delivery of diesel to tank 11 started at 8:33PM on April 7, about 22 minutes before the explosion. Two operators were on duty. The initial filling rate was 24,000 to 27,500 barrels per hour. An outside operator in the tank farm saw a flash followed by smoke and fire at the time of the explosion. The other operator reported that the high product level alarm went off at 8:55 PM at the time of or a few seconds before the explosion, which blew off the fixed roof from the tank shell. At 8:59 PM, the valve was closed stopping pipeline delivery to tank 11, with the diesel diverted to other tankage in the tank farm, thus isolating ConocoPhillips from the pipeline.

The Glenpool Fire Department received a 911 report at 9:00 PM, about 5 minutes after the explosion, and arrived on scene by 9:06 PM, at which time tank 11 already had collapsed and was engulfed in flames. Eventually 13 fire departments were involved providing mutual assistance. The 28-inch pipeline itself was shut off at 9:35 PM, and by 9:45 PM all tank and header valves were close. Firefighting efforts included application of foam, and also water cooling of nearby tanks 12 and 7.

Because of the proximity of the fire to nearby electrical transmission lines, American Electric Power (AEP) was notified, but they said they had already seen reports on the local TV and were aware that their transmission lines were located nearby. ConocoPhilllips called again saying that flames were impinging on the power lines, and American Electric Power sent an inspector out to the site who arrived at 1:14 AM, but the inspector noted that there was no sag in the transmission lines and returned home. The fire became worse overnight, the on-scene personnel notified AEP again, and the AEP servicer revisited the site at 5:50 AM, who noted some sag in the transmission lines, but no decision on the part of AEP was made to shut off power to the transmission lines. About 20 minutes later one or more lines fell into the diked area east of the tanks igniting the diesel fuel contained within the diked area, severely damaging another tank.

Followup Investigation by National Transportation Safety Board
A detailed investigation of the accident was conducted by the National Transportation Safety Board (NTSB), and their findings have been published as Pipeline Accident Report NTSB/PAR-04/02, [PB2004-916502 Notation 7666], which is available at http://www.ntsb.gov/publictn/2004/PAR0402.pdf. [Comment: Because the fuel is delivered by pipeline, the accident is considered a transportation incident, and was not investigated by the U.S. Chemical Safety Board].

According to the NTSB report, the specific cause of the explosion and fire was a buildup and discharge of static electricity that ignited a flammable fuel-air mixture within the tank being filled. The NTSB report claimed that the tank was being filled at flow velocities significantly higher than that recommended both by the company's own procedures and industry-recommended practices, and this resulted in the buildup of excess static electricity. There was also some blame cast to American Electric Power employees who failed to recognize the risk the tank fire posed to nearby power lines and take effective emergency action.

Diesel fuel by itself has a low vapor pressure (about 0.3 mm of Hg @68^{o}F) and would not be expected to form an explosive vapor mixture with air (the flash point exceeds 125^{o}F, and a conservative lower explosive limit is 0.3%). The flash point of the diesel being delivered to tank 11 was 162^{o}F (ASTM test procedure D-93). The concentration of diesel fuel in the air space in the tank would be expected to be 0.3*(1/760)*100% = 0.04% at 68^{o}F. The temperature at the time of the explosion was about 52^{o}F meaning that the concentration of diesel fuel in the air would be expected to be even less than 0.04% as the vapor pressure decreases with temperature. An explosion would not be expected in the tank for diesel vapor in air.

But when National Transportation Safety Board (NTSB) investigators questioned ConocoPhillip representatives, the company said that even though no gasoline remained in the tank 11 lines, about 55 barrels of gasoline remained in the tank 11 sump between the sump floor and the bottom of the 30-inch-diameter fill/drain pipe (diagrams are provided in the NTSB report). The tank 11 construction itself had a floating roof (diagrams in NTSB report). The NTSB concluded that the previous draining and filling of tank 11 allowed a large amount of gasoline vapor to be generated between the diesel added during filling and the floating roof and between the floating roof and tank top to create a flammable fuel-air mixture. The damage to the tank was consistent with a vapor cloud explosion occurring within the tank set off by an ignition source. The NTSB also ruled out lightning, electrical arcing, and human activity as the source of the ignition.

The NTSB report stated that the high velocity of the diesel in the tank fill piping and the turbulence created in the sump area resulted in the generation of increase static charge and, combined with the very low electrical conductivity (static accumulating) liquid (the diesel fuel), there was an elevated risk for a static discharge inside the tank. (from "Conclusions", page 39 of report).

American Petroleum Institute procedure API RP 2003 recommends, for tanks that may contain a flammable liquid mixture in the vapor space such that can occur during swatch loading (e.g. gasoline followed by diesel), protective measures must be taken to control the electric charge in the storage tank, which includes:

"Limit the fill line and discharge velocity of the incoming liquid stream to 1 meter/second (3 feet per second) until the fill pipe is submerged either two pipe diameter or 2 feet, whichever is less. In the case of a floating roof, observe the 1 meter/second (3 feet per second) velocity limitation until the roof becomes buoyant".

NTSB calculated that the fill velocity for tank 11 was exceeded by a factor of four.

Laboratory analysis of the diesel used to fill tank 11 had a conductivity of less than 1 pS/m. API RP 2003 identifies any liquid with a conductivity of less than 50 pS/m as a static accumulator.

Figure 1. General View of site several days after accident (note water from firefighting) looking south, tank 11 wreckage at right center, earthen dike at left center, AEP transmission lines at left, photo from NTSB report.

Barton Solvents Distribution Facility Explosion and Fire at Valley Center, Kansas

Summary:

On July 17, 2007, an explosion and fire occurred at the Barton Solvents facility in Valley Center, Kansas, north of Wichita as a tanker trailer was transferring VM&P Naphtha into a 15,000 gallon (above ground) storage tank. The force of the explosion blew the tank 130 feet into the air, and within moments two more tanks ruptured and released their contents, which ignited. Debris was launched into the air where some of it struck a mobile home and a neighboring business. Six thousand residents were evacuated. No one was killed, but 11 residents and one firefighter sought medical attention. The tank farm was destroyed.

Followup Investigation by the U.S. Chemical Safety Board

The U.S. Chemical Safety Board (CSB) released their final report on the incident on June 26, 2008. The report is available at http://www.csb.gov/completed_investigations/docs/CSB_Study_Barton_Final.pdf.

The CSB report concluded that a static spark occurring within the 15,000 gallon storage tank as it was being filled ignited the vapor in the air space above the liquid. The CSB investigation concluded that the transfer equipment from the truck tanker to the storage tank was properly bonded and grounded to prevent the generation of static electricity. However, the float device inside the 15,000 gallon storage tank presented a hidden danger. The static spark was generated from a loosely-linked level-measuring float within the tank. The spark ignited the air-vapor mixture inside the tank as it was being filled.

The CSB Lead Investigator Randy McClure said, "When transferring liquids, it is standard industry practice to bond and ground storage vessels, tankers, and other equipment to prevent static discharges. But our investigation illustrates how normal bonding and grounding may not be enough to prevent ignition from static electric sparks."

The CSB determined that the liquid flow and turbulence created by filling the tank likely resulted in the metal float accumulating a static electrical charge. As the float moved, a gap is believed to have formed with the linkage of the tape and the float. A spark likely jumped between the metal parts and ignited the explosive mixture of vapor and air that had accumulated above the liquid.

The 15,000 gallon storage tank was approximately 30% filled with VM&P naphtha at the time of the explosion. The temperature of the system was 77^{o}F (25^{o}C) at the time of filling, well above the flash point of 58^{o}F (14^{o}C). The flammable range in air was approximately 0.9 to 6.7%. The VM&P naphtha used to fill the tank had a conductivity of 3 pS/m, which is considered as "nonconductive", meaning that the liquid poses a risk of dangerous static electric accumulation that can produce sparks inside tanks.

The CSB investigation computed that the length of transfer piping from the pump to the storage tank was approximately 215 feet (66 meters), the piping was 2.5 inch NPS Schedule 40, and that the pump flow velocity 15 feet per second (4.6 meter per second). The company was following correct procedures in bonding and grounding the tanker-trailer, pump, piping, and storage tank, but this grounding was not enough as what was learned after the incident.

The loose linkage at the float/tape junction separated slightly, interrupting grounding, and created a potential for spark (figure 3). The turbulence created during tank filling caused rapid static charge accumulation, and also created slack in the gauge tape connected to the float (more details in CSB report).

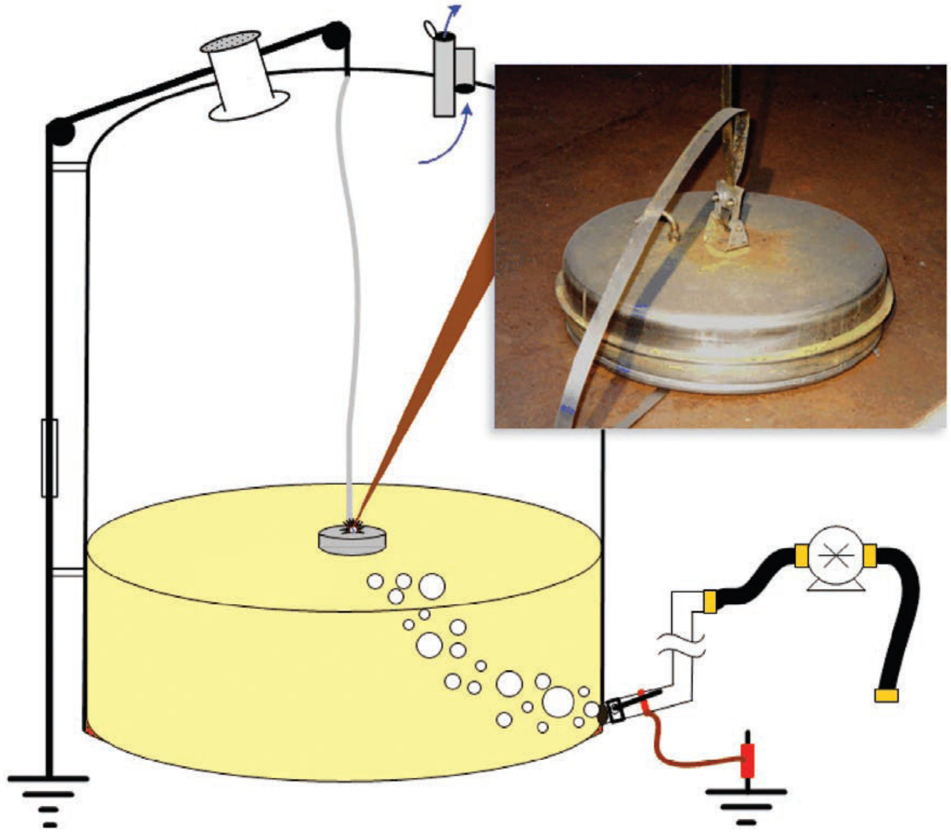


Figure 2. Chemical Safety Board sketch of the 15000 gallon storage tank during filling showing grounding of the tank and transfer line (lower right), but no grounding of float device (with photo insert of float device).

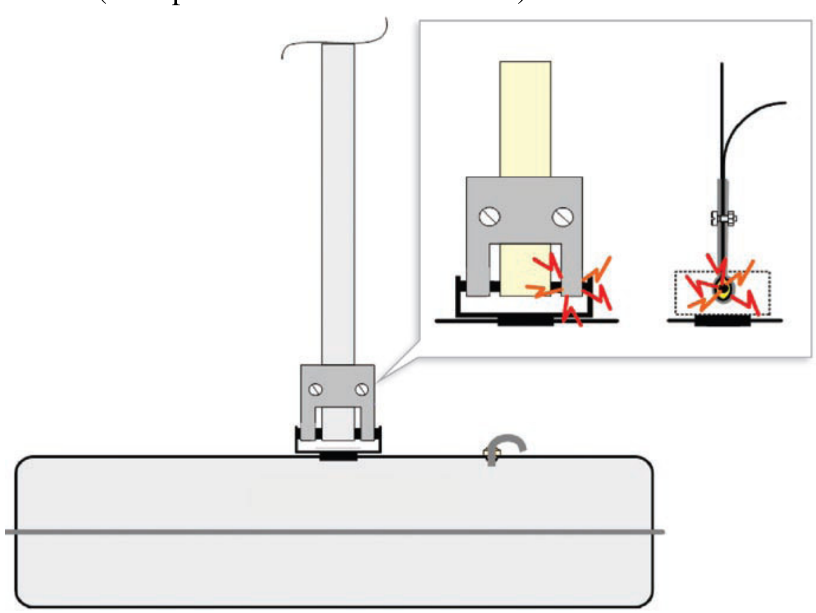


Figure 3. Chemical Safety Board sketch of Float Linkage with front and side view insert where spark likely occurred (in red).

The Chemical Safety Board has prepared a free safety video on the subject of flammable, non-conductive solvents following the Barton explosion and fire investigation. The safety video is available at **http://www.youtube.com/watch?v=tVZzdtnZaJk**.

What Do These Accidents Have in Common?

- A non-conductive liquid is involved
- The rapid and turbulent movement of the non-conductive liquid results in a buildup of an electrical charge
- The electrical charge ignites the vapor-air mixture inside a storage tank or in process equipment creating an explosion.

Some common examples of non-conductive liquids that also may form ignitable vapor-air mixtures include:

- VM&P naphtha [Varnish Maker's and Painters' naphtha]
- Benzene
- Toluene
- Xylene
- Ethyl benzene
- Styrene
- n-Hexane
- n-Heptane
- Cyclohexane

There are also examples of non-conductive liquids that have low enough vapor pressures and high enough flash points that they do not form ignitable vapor-fuel air mixtures. A common example is fuel oil and diesel fuels. There may be a static buildup of charge as this liquid is pumped, but if the concentration of vapor in the air space in the tank is below the lower explosive limit (or if the flash point is higher than the actual temperature), there is no ignition.

The most familiar example of a liquid that forms a vapor-air mixture that is too rich (too much fuel and not enough oxygen) to ignite inside a tank is gasoline. Gasoline also contain additives that increases its conductivity.

But as the ConocoPhillip example showed, if there is enough residual flammable liquid with a high vapor pressure left inside a tank or process equipment (gasoline), an explosion can still occur if another non-conductive liquid (diesel) with a low vapor pressure is later moved in the system. The ignitable air-vapor mixture does not have to originate from the non-conductive fluid being pumped; it just needs to be present.

The most common way for a buildup of static charge is by flow of the non-conductive liquid through piping, valves, and filters as it is being transferred. The rate of static generation as a non-conductive liquid increases roughly as the square of the flow velocity. Static charge can also be produced by entrained water or air or agitation or even by suspension of sediment in the bottom of a tank or process equipment. [see Britton, L.G., "Avoiding Static Ignition Hazards in Chemical Operations", AIChE-CCPS Concept Book, 1999.].

MSDS Sheets

The standard Material Safety Data Sheets (MSDS) often do not contain a warning that the chemical is a static accumulator that can ignite flammable vapors inside tanks. The MSDS typically will display a flash point, lower explosive limit, upper explosive limit, the NFPA diamond triangle, and sometimes say that the chemical is a static accumulator, but do not put the information to a format which warns the user of the hazard.

The Chemical Safety Board reviewed 62 MSDSs for widely used nonconductive flammable liquids. Almost all (97%) contained a warning about ignitable flammable vapors. About 67% contained a warning about the potential for the potential to accumulate static electricity, but only three MSDSs included conductivity testing data. Only one MSDS warned specifically of the potential for the chemical to form an ignitable vapor-air mixture inside tanks. Eight of the 62 MSDSs mentioned one or more precautionary methods such as adding an inert gas to tank head spaces, reducing the pump flow velocity, or bonding and grounding, or adding an anti-static agent, but sometimes even this information was incomplete (e.g. bonding and grounding alone may not be enough).

Prevention of Explosions and Fires Involving Non-Conductive Flammable Liquids

The specific standards for the industry need to be communicated to the people who handle and use the chemicals. In general, one or more precautions must take place to avoid an incident.

- Manufacture guidance, in addition to the MSDS which probably will not be enough
- Add an inert gas to tank head space [contact liquid manufacturer to see if appropriate, and also comply with OSHA requirement 29 CFR 1910.146 for entering confined spaces]
- If applicable, add an anti-static agent to the liquid [comment: anti-static agents are required for all Jet fuel worldwide except the United States and Chile].
- Reduce pumping flow velocity during filling or transferring non-conductive liquids. NFPA 77 (published 2007) recommends a pumping flow velocity of 1 meter per second.

- The tank, transfer lines, pump, floats, etc. must be properly bonded and grounded. Inspect and replace, as appropriate, floats with level measuring devices which will not promote sparks inside the tank [from CSB report on Barton Solvents explosion].