Violent Self-Polymerization Reactions

Polymers are an essential part of modern day living. Examples include the many plastics, synthetic rubber, Teflon®, polyethylene, polyesters, nylon, rayon, and even the polyvinyl alcohol in Elmer's glue. Nature produces its own polymers such as proteins and starches. Polymers are very large molecules made up of smaller parts called monomers. The process of joining the smaller parts to form the very large molecule is called polymerization. Another chemical, called a cross-linking agent is required to bring the parts together to form the very large molecules. In the case of synthetic (man-made) polymers, the cross-linking agent could be a peroxide or maybe a metal ion or other chemical. Nature uses enzymes in the cross-linking process.

A lot of heat can be released in the manufacture of synthetic polymers. The reaction also can occur quickly, even in a second. The quick heat release can vaporize the monomer or other flammables resulting in an explosive vapor cloud. The buildup of flammable gases can "explode" the reaction vessel or container, or if the vapors are released by a "safety valve", a spark can ignite the vapors creating a vapor cloud explosion. During the manufacture of polymers the heat release is controlled by slowly adding the reactants according to prescribed procedures and by cooling of the reaction vessel. Even then, sometimes systems fail resulting in industrial accidents.

This PEAC newsletter examines the situation where certain chemicals can "self-polymerize" or "auto-polymerize" in storage or during transport. The release of heat can vaporize the chemical resulting in an explosion. The cross-linking agent (polymerization initiating agent) could be iron or other metal contamination or a peroxide produced from exposure of the chemical to sunlight or moisture.

Let's look at an example.

Cincinnati Styrene Release, 28 August 2005

Source: http://www.isitech.com/en/chemical-accidents/styrene-usa.html.

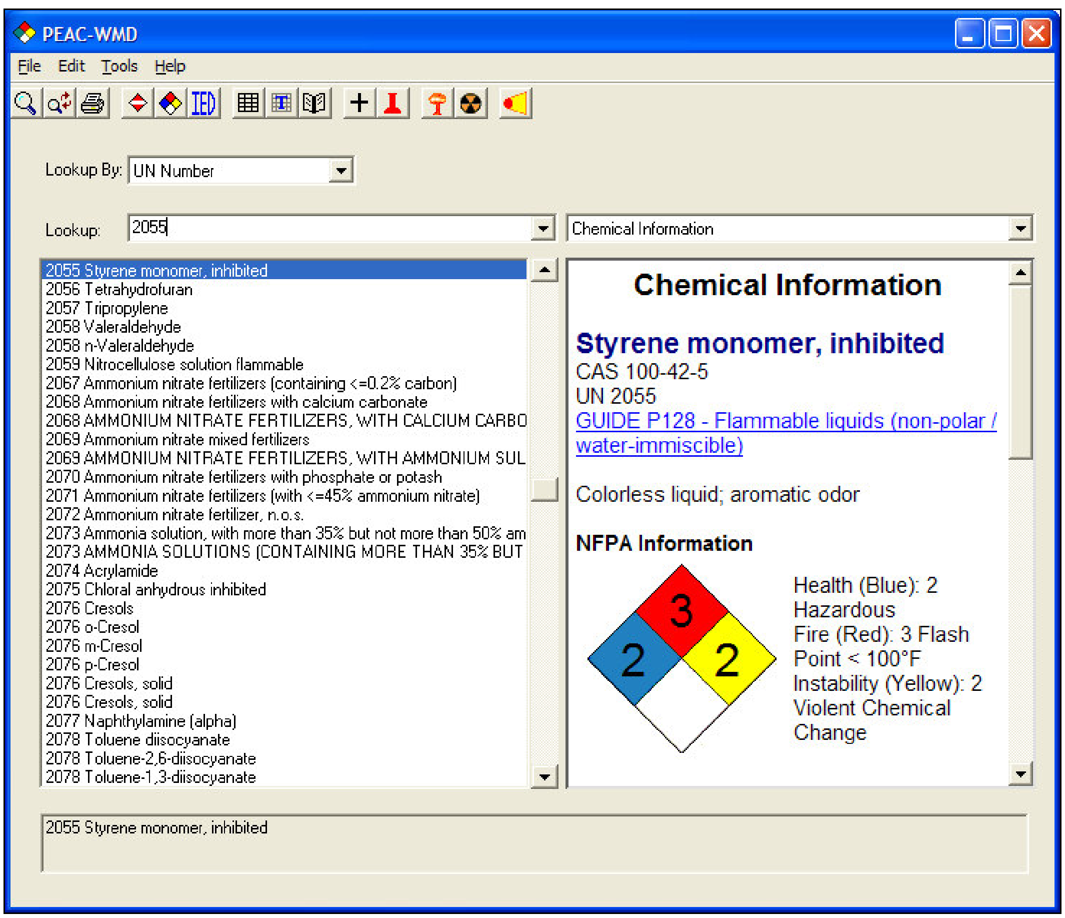
Left: Stationary railroad tank car containing styrene monomer escaping from tank. Center: USGS satellite photo of evacuation zone. Photos from website.

On 28 August 2005 at approximately 5 PM, a white vapor cloud was observed escaping from a stationary railway tank located near the Lunken regional airport near Cincinnati

Ohio. From tank markings and from information supplied by the railroad, the contents of the railcar was identified as approximately 24,000 gallons of styrene monomer. A safety valve at the top of the tank had opened allowing the gas to escape. The population within a radius of 0.5 miles around the tank was evacuated. A curfew with a radius of 1 mile was imposed. The Lunken regional airport was temporarily closed. Two policemen were hospitalized and later released after they had inhaled the gas. There were no reports of further injuries.

The railcar would have been marked with UN number 2055. The 2008 Emergency Response Guidebook (and the 2004 edition, which was available at the time of the accident) identify the contents for UN2055 as Styrene monomer, stabilized, which is linked to Guide Number 128P. The letter "P" in Guide 128P means that the chemical can undergo "auto-polymerization", and that it is shipped with a stabilizing agent added. Guide 128 covers Flammable Liquids (non-polar/water-immiscible). In anticipation of a possible fire, Guide 128 recommends: "If tank, rail car, or tank truck is involved in a fire, ISOLATE for 800 meters (1/2 mile) in all directions; also consider evacuation for 800 meters (1/2 mile) in all directions".

The 2008 Emergency Response Guidebook information can also be pulled up in the PEAC tool. The PEAC tool user can enter 2055 which links up to Styrene monomer, stabilized, as follows:



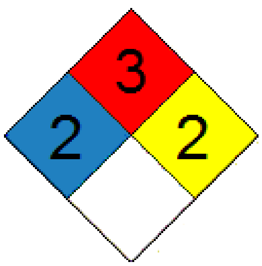
Information about the styrene monomer is obtained by clicking on the ‘maximize” box at upper right or the icon at the left.

Styrene monomer, inhibited

CAS 100-42-5
UN 2055
GUIDE P128 - Flammable liquids (non-polar / water-immiscible)

Colorless liquid; aromatic odor

NFPA Information



Health (Blue): 2 Hazardous
Fire (Red): 3 Flash Point < 100°F
Instability (Yellow): 2 Violent Chemical Change

Physical and Chemical Properties

Formula: $C_6H_5CH{=}CH_2$
Molecular Weight: 104
Flash Point: 88°F
Lower Explosive Limit: 0.9%
Upper Explosive Limit: 6.8%
Auto Ignition Temp.: 914°F
Boiling Point: 293°F
Melting Point: -23°F
Rel Vapor Density @68°F: 1.1 (Heavier than air)
Vapor Pressure @68°F: 0.01 atm
Liquid Specific Gravity: 0.91 (Lighter than water)
Ionization Energy: 8.43 eV
RAE Systems PID correction factor for 9.8 eV: 0.45
RAE Systems PID correction factor for 10.6 eV: 0.4
RAE Systems PID correction factor for 11.7 eV: 0.4
Yield Factor: 0.03

Toxic Levels of Concern

IDLH: 700 ppm (2977.51 mg/m^3)
TWA: 50 ppm (212.68 mg/m^3)
STEL: 100 ppm (425.36 mg/m^3)
ERPG-1: 50 ppm (212.68 mg/m^3)
ERPG-2: 250 ppm (1063.39 mg/m^3)
ERPG-3: 1000 ppm (4253.58 mg/m^3)
TEEL-1: 50 ppm (212.68 mg/m^3)
TEEL-2: 250 ppm (1063.39 mg/m^3)
TEEL-3: 1000 ppm (4253.58 mg/m^3)

The NFPA 704 Hazard Clarification information displays a “2” for “health”[blue quadrant], “3” for flammability [red quadrant], and “2” for reactivity [yellow quadrant]. The PEAC user can click on any of the highlighted words to get definitions or additional information. For example, if the user clicks on Guide 128P, the 2004 Emergency Response Guidebook information is displayed, a portion of which is printed below (the 2008 edition is in the PEAC tool being updated):

PROTECTIVE CLOTHING

* Wear positive pressure self-contained breathing apparatus (SCBA).
* Structural firefighters' protective clothing will only provide limited protection.

EVACUATION

Large Spill

* Consider initial downwind evacuation for at least 300 meters (1000 feet).

Fire

* If tank, rail car or tank truck is involved in a fire, ISOLATE for 800 meters (1/2 mile) in all directions; also, consider initial evacuation for 800 meters (1/2 mile) in all directions.

EMERGENCY RESPONSE

FIRE

CAUTION: All these products have a very low flash point: Use of water spray when fighting fire may be inefficient.

CAUTION: For mixtures containing a high percentage of an alcohol or polar solvent, alcohol-resistant foam may be more effective.

Small Fires

* Dry chemical, CO_2, water spray or regular foam.

Large Fires

* Water spray, fog or regular foam.
* Use water spray or fog; do not use straight streams.
* Move containers from fire area if you can do it without risk.

Fire involving Tanks or Car/Trailer Loads

* Fight fire from maximum distance or use unmanned hose holders or monitor nozzles.
* Cool containers with flooding quantities of water until well after fire is out.
* Withdraw immediately in case of rising sound from venting safety devices or discoloration of tank.
* ALWAYS stay away from tanks engulfed in fire.
* For massive fire, use unmanned hose holders or monitor nozzles; if this is impossible, withdraw from area and let fire burn.

The PEAC user can also click on the Protective Action Distance icon . This will enable the user to calculate a protective action distance based on toxicity. The worst case is if all of the chemical is released at once. The result could be a vapor cloud explosion and fireball. Guide 128P recommends a half-mile evacuation distance. It is unlikely that all of the chemical would be released at once, but based on an instantaneous release of 150000 lbs and modeled to an Immediately Dangerous to Life and Health (IDLH) concentration level of 700 parts per million, a protection action distance of one mile is predicted. [We assumed a wind speed of 5 mph and urban terrain].

What caused the rail car to vent styrene monomer? The venting occurred because of an increase in pressure inside the tank. The website listed above explained that the increase in pressure was due to heat generated within the tank due to polymerization of the styrene monomer within the tank. Normally, a chemical inhibitor such as 15 parts per million of 4-tertiary-butyl-catechol (TBC) is added to the tank during transport to prevent polymerization. This inhibitor scavenges rust and other impurities within the tank that can act to initiate polymerization. Oxygen (about 10 ppm) is also required to be dissolved in the styrene monomer for the TBC to do its job. The TBC concentration decreases with time as it scavenges impurities; 15 ppm concentration would probably be

mostly used up in possibly 3 months (even less time if ambient temperatures are warmer). The website mentioned that the rail car had been sitting there for 9 months. Without the inhibitor, the styrene monomer can polymerize with oxygen to form a styrene-oxygen copolymer or benzaldehyde and/or formaldehyde and polymerize with the release of heat. The heat further accelerates the polymerization releasing more heat.
Fortunately, no explosion occurred, the chemical was not released all at once, and people were evacuated to safe distances. The safety valve did the job it was designed to do, to release excessive pressure buildup slowly avoiding a catastrophic explosion. The error was that the rail car was allowed to sit there for nine months, during which time the inhibitor became depleted.

2008 Emergency Response Guidebook (ERG) Listings of Chemicals Likely to Undergo Self-Polymerization

The 2008 ERG lists a number of chemicals as being shipped "inhibited" or "stabilized" and have a "P" listed with a Guide Number meaning that the chemical can polymerize. It is illegal to ship some of these chemicals in bulk without an inhibiting or stabilizing chemical or chemicals. The inhibitor or stabilizer can also be used up over time. The science of this has been worked out for these chemicals, where an inhibitor can be tested and more inhibitor added if necessary. The problem occurs if the inhibitor is used up as in situations where the chemical sits unused or is exposed to unnecessary heat, sunlight, or moisture, or trace metals.

The inhibiting or stabilizing agent used depends on the chemical to be shipped and anticipated storage temperature. The container also makes a difference. The inhibiting agent used for styrene monomer, UN2055, is 10 to 50 ppm of tertiary butylcatechol (4-tertiary-butyl-catechol), with the greater concentration used for a higher storage temperature.

Example Chemicals

Butadienes, UN1010, readily self-polymerizes and can also form explosive peroxides with air unless inhibited, and it is illegal to ship butadienes without an inhibiting agent (tributylcatechol, di-n-butyl amine, or phenyl-betanaphthylamine). For an account of a butadiene explosion involving a 500 kg cylinder at a Japanese chemical plant, see http://shippai.jst.go.jp/en/Detail?fn=0&id=CC1200052&kw=Environment. The butadiene polymerized within the safety release valve of the partly full cylinder, which caused it to clog. When the cylinder was left outside exposed to sunlight, the pressure built up within the cylinder and it exploded.

A summary of salvage operations following the gas tanker Igloo Moon incident, where the tanker ran aground outside Key Biscayne, Florida, within the Biscayne National Park boundary, on 6 November 1996 is at http://www.kustbevakningen.se/ra/volume2/annex3accidents/igloo.htm.

The gas tanker contained 6589 tonnes of compressed and liquefied butadiene. Many different salvage operations were considered, and plans for public evacuations were set up for various situations that could go wrong. The salvage plan chosen included bringing another vessel (the Selma Hosan) alongside the Igloo Moon which had runaground; approximately 1000 tonnes of butadiene were transferred between November 20 and 21 to the Selma Hosan, which was enough to lighten the load so that the stricken gas tanker could be refloated during the flood tide. The plan included monitoring the inhibitor concentration so the butadiene would not polymerize, which would have been catastrophic. No chemicals were released to the water.

Ethylene oxide, UN1040, may self-polymerize in the presence of a small amount of water, and many common metals (except stainless steel and nickel containers) can initiate the polymerization; sometimes 0.1% hydroquinone (an anti-oxidant) is added as an inhibitor.

Propyleneimine, UN1921, and **Ethyleneimine**, UN1185, readily polymerizes in contact with acid or acid fumes, and is sensitive to air, sunlight, and/or heat; solid sodium or potassium hydroxide is added as an inhibitor to scavenge any acid.

Furural or **furfuraldehydes**, UN1199, can undergo exothermic polymerization in contact with acid or alkali; ignition can occur spontaneously with sodium bicarbonate (baking soda). Exposure to light and air darkens the chemical. The inhibiting agent for this chemical may be dialkylphenylenediamine or butylated hydroxytoluene (BHT).

Vinyl acetate, UN1301, is another chemical that can undergo bulk polymerization in storage vessels. This polymerization is extremely violent and may generate a pressure surge of over 40 atmospheres due to the monomer vapor pressure, enough to explode the vessel. The polymerization may be initiated by exposure to small amounts of peroxide; the peroxide may be formed by exposure of the chemical to oxygen in the air. The inhibitor is usually 3 to 20 parts per million (ppm) of hydroquinone or methyl hydroquinone to scavenge free radicals (peroxides). Less hydroquinone is added if the vinyl acetate is to be used soon, and more hydroquinone is added if the vinyl acetate is to be stored for several months before use. Diphenylamine might be used as an inhibitor for prolonged storage. Details on this chemical may be found in a rather technical paper, Jean-Louis Gustin and. F. Lahanier, "Understanding Vinyl Acetate Polymerization Accidents", Organic Process Research & Development, 2005, vol 9, p 962-975, which can be obtained from the Internet at http://pubs.acs.org/cgi-bin/sample.cgi/oprdfk/2005/9/i06/pdf/op050097f.pdf.
An account of an exploding drum of vinyl acetate stored in an industrial facility is at http://shippai.jst.go.jp/en/Detail?fn=0&id=CC1000176.

Hydrogen cyanide, UN1051, is another chemical that can undergo self-polymerization releasing heat. The container could fail because of increasing container pressure as it is heated releasing lethal hydrogen cyanide gas. If the temperature exceeds about 260-265°C (about 520°F), the chemical can detonate. A mineral acid inhibitor (such as phosphoric acid) is usually added to prevent polymerization.

Summary

The situation for each chemical is different. Some chemicals can self-polymerize violently causing an explosion. Some form peroxides upon exposure to light and air, the peroxides formed may initiate the polymerization. For some chemicals the reaction is slow allowing excessive heat to dissipate forming no special hazard to responders but ruin the chemical and container creating a disposal problem. Companies who store or use or transport these chemicals must be cognizant of the hazards involved. The chemical industry is aware of the potential for self-polymerization of these chemicals, but incidents do occur.

One particular hazard is the storage of chemicals in laboratories, including colleges, high schools, industry, and clandestine operations. Certain chemicals over time may form explosive peroxides or can polymerize violently. An example account has been written up in the American Chemical Society magazine Chemical and Engineering News, and is available at http://pubs.acs.org/cen/safety/19960603.html. The sample size stored on the shelf was only 100 grams, but it self-polymerized because the chemical sat on the shelf for a long time and the inhibitor was used up.

The inhibitor for the styrene monomer was used up in the Cincinnati example because the railroad tank car had sat idle well after the estimated useful lifetime of the inhibitor. The safety valve was able to release the buildup of pressure within the tank car.

But safety valves can become clogged and fail because of the polymerization. There can also be chemical in dead space in an industrial process line, which is not purged and is forgotten, and polymerizes blocking flow or rupturing the piping or vessel. These issues must be included as a part of a safety-training program.