INHIBITOR ADDING SYSTEM IN STYRENE MONOMER

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ABSTRACT

Due to human negligence and many other reasons, many industrial mishaps are happening across the globe in recent years one of the main reasons for mishaps are due to polymerisation reactions which is an exothermic reaction due to this exothermic nature lots of heat will release during reaction performing in many of the cases this heat leads to many thermal runaways hazards.

Thermal runaway occurs in situations where an increase in **temperature** changes the conditions in a way that causes a further increase in **temperature**, often leading to a destructive result. It is a kind of uncontrolled positive feedback.

Due to this thermal unstable behaviour, it is difficult to control this type of reactions in that we focused on styrene monomer thermal runaways because styrene is one of the most used chemicals across the world which is used to create many plastic products

One of the recent industrial hazards happened in India at LG polymer chemical plant which is located in Visakhapatnam

ABSTRACT

Based on Times of India

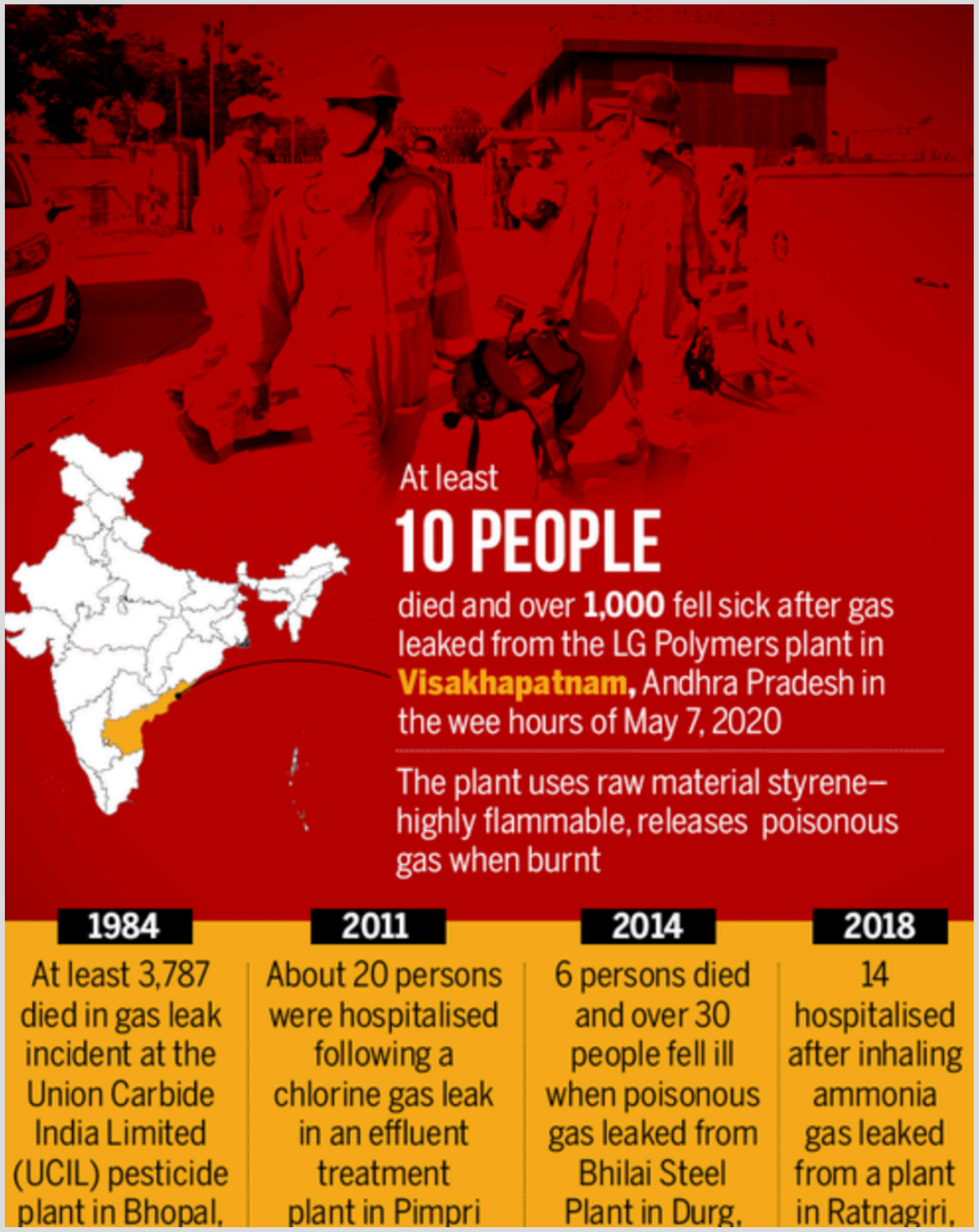
12 people died and several thousands of people affected due to the release of styrene gas from the chemical plant
Based on information given by Telangana forensic and Andhra Pradesh forensic teams

human negligence in adding auto polymerisation inhibiter in the storage tank and failing to maintain the temperature below 20c led to the mishap
that styrene should be mixed with tertiary butyl catechol to prevent self polymerisation they didn't add this one what ever-existing got inactive

the self polymerisation started and lead to a chemical reaction and subsequently generated an enormous amount of heat up to 150degree celsius
vapours started coming out through the breather
the boiling point of styrene is 146degree celsius

This type of thermal hazards not only occur in storage tanks of styrene but also while transporting styrene from one place to another.

SIMILAR INDUSTRIAL HAZARDS HAPPENED IN INDIA



SIMILAR INDUSTRIAL HAZARDS BASED ON STYRENE

Table 1. Selected Thermal Runaway Incidents Related to the Styrene Process

date	location	consequences	
		injury	fatality
07/05/1994	Kaohsiung, Taiwan	0	1
01/26/1996	Chiayi, Taiwan	1	0
01/21/1998	Kaohsiung, Taiwan	4	0
12/24/1998	Kanagawa, Japan	0	0
06/27/1998	Channahon, IL, US	1	0
06/23/1999	Pasadena, TX, US	21	2
10/06/1999	Chiayi, Taiwan	1	0
03/27/2000	Pasadena, TX, US	71	1
04/02/2003	Addyston, OH, US	0	1
04/08/2004	Jiangsu, China	8	6
06/30/2005	Mesa, AZ, US	0	1

OBJECTIVE

To control and to prevent this type of thermally unstable reactions we need to monitor the inhibitor level present in styrene and the temperature , the pressure of styrene tank.

Due to the manual methods of adding inhibitor and monitoring the temperature and pressure using a thermocouple temperature sensor, we cant effectively monitor the styrene present in the storage tank

Based on some chemical plant papers and their manuals ,this type of method is being used by many industries across the world including India

We are using advancement in technology and the internet of things concepts to solve this issue with the help of the internet of things we can able to monitor every each detail in the storage tank continuously we can also able to analyse the data received using this system for prevention of thermal runaways, tank ruptures etc. because by, monitoring the temperature rise in the tank and the inhibitor content of the tank there is a chance of almost 90% to stop these type of thermal runaways, tank ruptures and gas leak

PROPERTIES OF STYRENE MONOMER

Styrene is primarily used in the production of poly plastics and resins

Styrene polymerises slowly at normal ambient temperatures but very rapidly at elevated temperatures,Styrene polymerisation is initiated by heat, lack of inhibitor and dissolved oxygen, and contact with peroxides and other free-radical initiators, ionic initiators, and redox initiators

Polymerisation can take place in storage as well as under more controlled conditions. The polymerisation process is exothermic, evolving 288 Btu/Lb (17.8 kcal/gm mole). If this evolved heat cannot be dissipated rapidly enough, the temperature of the monomer will rise, increasing the rate of polymerisation and, with it, the rate of evolution of heat.

The temperature may rise to the point where the reaction becomes very rapid and self-sustaining (a runaway polymerisation)

Normally temperatures above 65°C (149°F) are needed to initiate runaway polymerisations. As the liquid polymerises and becomes more viscous, vapour bubbles may become trapped, expanding the liquid and causing spills or rupture off the tank. The important point is that polymerisation may occur spontaneously in storage tanks.

EXPOSURE TO STYRENE GAS

These are some of the disadvantages while exposure to styrene gas

Acute (short-term) exposure to styrene in humans results in mucous membrane and eye irritation, and gastrointestinal effects.

Chronic (long-term) exposure to styrene in human beings leads to serious multiple complications. Studies on its impact are inconclusive on the reproductive and developmental effects of styrene.

Several studies did not report an increase in developmental effects in women who worked in the plastics industry, while an increased frequency of spontaneous abortions and decreased frequency of births were reported in another study.

Several epidemiological studies suggest there may be an association between styrene exposure and an increased risk of leukaemia and lymphoma.

When it comes in contact with skin and mucosal membranes, its effects include blistering and irritation Many victims also reported a burning sensation in their eyes and a few complained of loss of vision. The gas also irritates the nose and throat, causes shortness of breath and chemical inflammation of the lung tissues. Exposure to deadly quantities of the gas can cause fluid to accumulate in the lungs and kill the person.

PREVENTION AND HANDLING RUNAWAY POLYMERISATIONS

Polymerisation during storage may be prevented by close attention to monomer temperature, inhibitor level, polymer content and oxygen content. Determinations of inhibitor content, oxygen level in the vapour space, polymer content, and monomer temperature should be made on a routine basis.

Styrene containing vessels should be protected from external sources of heat. Running pumps against closed valves (dead-heading) should be avoided. Care should be taken that vents, valves, pressure-relief devices, gauges, and controls do not become plugged with polymer.

The action to take will depend on how far the runaway has proceeded. The beginning of a runaway polymerisation may be identified by an increase in monomer temperature (particularly if monomer temperature exceeds ambient or rises more than 3°F in one day) The higher the temperature the further the runaway has progressed and the more difficult to stop.

Decisions concerning what actions to take must be made on-site. The following suggestions are listed approximately in the order recommended for halting a runaway polymerisation and dealing with an advanced runaway:

1. Add up to 0.5% TBC and aerate. Aeration can be accomplished by bubbling in air, or stirring the product while exposed to air. Facilities storing and handling styrene monomer should have TBC inhibitor on hand in case of emergency

PREVENTION AND HANDLING RUNAWAY POLYMERISATIONS

2. Reduce the temperature of the tank with water spray. If the tank is insulated, the insulation should be removed as quickly as possible and prior to spraying with water. Use ice, if feasible, but not in the product directly, as it will tend to remove the TBC. If placed in the product, ice should be in a sealed metal container.

3. Keep vessel vented.

4. Dilute with ethylbenzene or toluene if the tank is not venting and product temperature is below 231°F (110°C) to retard polymerisation and reduce viscosity.

5. If possible remove product from the tank before it solidifies, to save the tank. Use drums, diked area, or float on water

Inhibitors prevent polymerisation in two ways.

(1) They can react with and deactivate the free radical in a growing chain.

(2) They can act as an antioxidant and prevent polymerisation by reacting with oxidation products in the monomer. It should be noted that sufficient oxygen must be present for inhibition. In the absence of oxygen, polymerisation will proceed as if no inhibitor were present.

PREVENTION AND HANDLING RUNAWAY POLYMERISATIONS

OXYGEN REQUIREMENTS

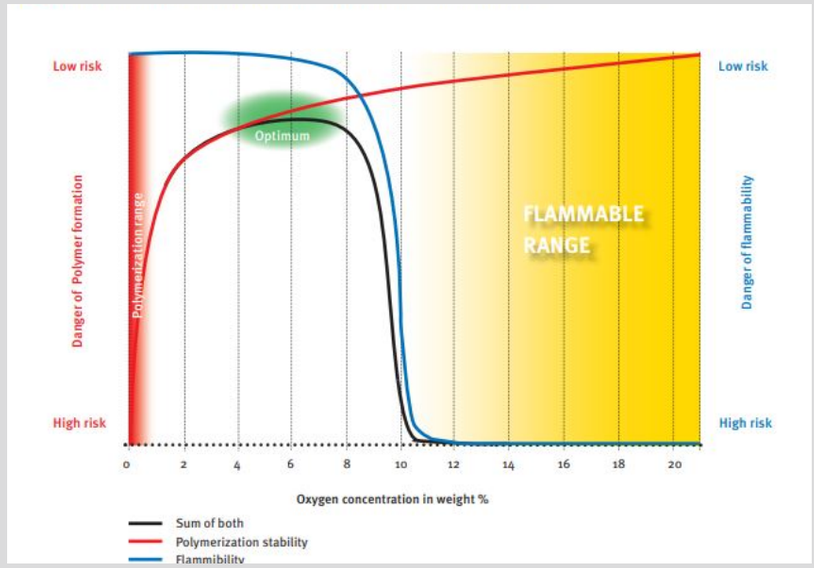
The problem presented by air is complex. TBC is not an effective inhibitor for styrene monomer in the complete absence of dissolved oxygen. Excessive amounts of oxygen in the storage tank, on the other hand, may lead to other serious storage and handling problems. Monomer vapours above the liquid level in the tank are uninhibited. These uninhibited vapours and condensed monomer droplets are readily oxidised on contact with air.

These droplets containing oxidation products will polymerise quite rapidly and adhere to the rusted, porous surfaces of unlined steel tanks. They form stalactites on the roof and coat the sidewalls above the liquid level. Complete elimination of oxygen from the vapour space will lead to depletion of dissolved oxygen from the liquid monomer. If this dissolved oxygen is greatly reduced, the TBC inhibitor becomes ineffective and rapid polymerisation of the stored monomer will take place.

If an inert gas blanket such as nitrogen is used, provisions should be made to aerate the monomer once a week for approximately 30 minutes, or until the oxygen level again reaches saturation. An alternative is to recirculate product and inject air at a rate of approximately 1-2 ft3 /hr/million pounds of styrene monomer.

PREVENTION AND HANDLING RUNAWAY POLYMERISATIONS

3-8 volume % oxygen in the vapour phase. Less than 3 vol% is not recommended because the increased risk of polymerisation leading to a shorter shelf life. Higher than 8% will lead to an atmosphere above the lower explosion limit. Extra measures have to be taken to prevent sparks.



Optimum oxygen concentration in vapour phase

ADDITION OF TBC TO STORED MONOMER

Styrene monomer in storage should be checked periodically for TBC content and additional inhibitor added as required (see previous section on Inhibition). A good policy is to add additional inhibitor when the level drops to the minimum specification level. The TBC content of styrene monomer in storage should never be allowed to be depleted or remain below the 10 ppm-level. The storage tank (or drum) should always be recirculated or mixed after inhibitor is added. This ensures uniform blending of the TBC and supplies an adequate amount of dissolved oxygen in the monomer for effective inhibition. Caution must be exercised in handling TBC. See information on toxicological properties and safe handling of TBC as well as manufacturer's MSDS.

TBC INHIBITOR

Manually adding TBC polymer to the storage tank could direct to many health related problems

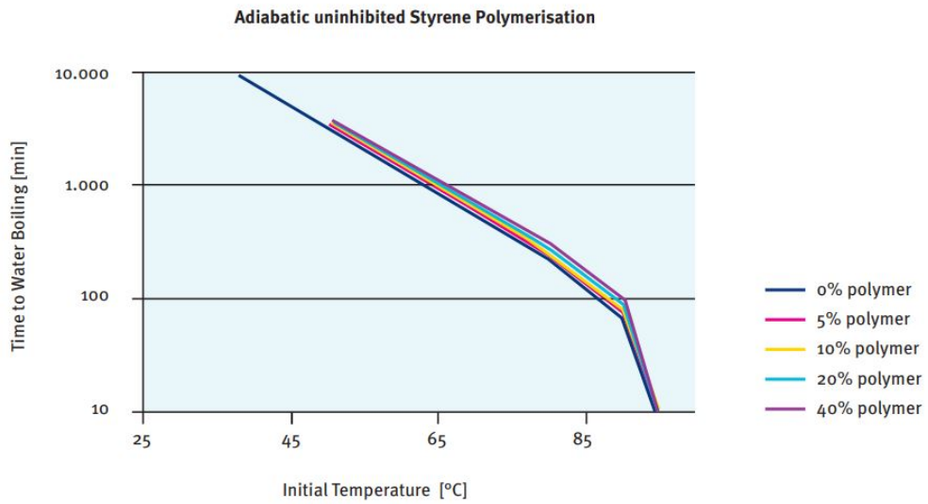
Hazards of TBC Inhibitor

TBC is a polymerisation inhibitor and an antioxidant for styrene. It forms hygroscopic crystals or flakes and is poorly soluble in water, but soluble in ether, alcohols and acetone.

TBC is harmful if inhaled, ingested or absorbed through the skin. It is severely irritating to skin (some producers even classify it as corrosive), eyes, respiratory and gastrointestinal tract. It could cause allergies following skin contact.

There is no evidence for carcinogenicity or genotoxicity, but effects on blood 44 45 (formation of methemoglobin) have been observed. Due to its close to corrosive effects, TBC might have negative effects on aquatic organisms.

Figure 7: *Predicted moment of storage vessel failure*



Predicted moment of storage vessel failure

Suggested Inspection Schedule for Styrene Bulk Storage

Inspection	Frequency
Air Vents Vacuum pressure relief Flame arrester Foam reservoir should be inspected for polymer	Quarterly
Tank interior	Every 3 years, if coated Annually, if uncoated

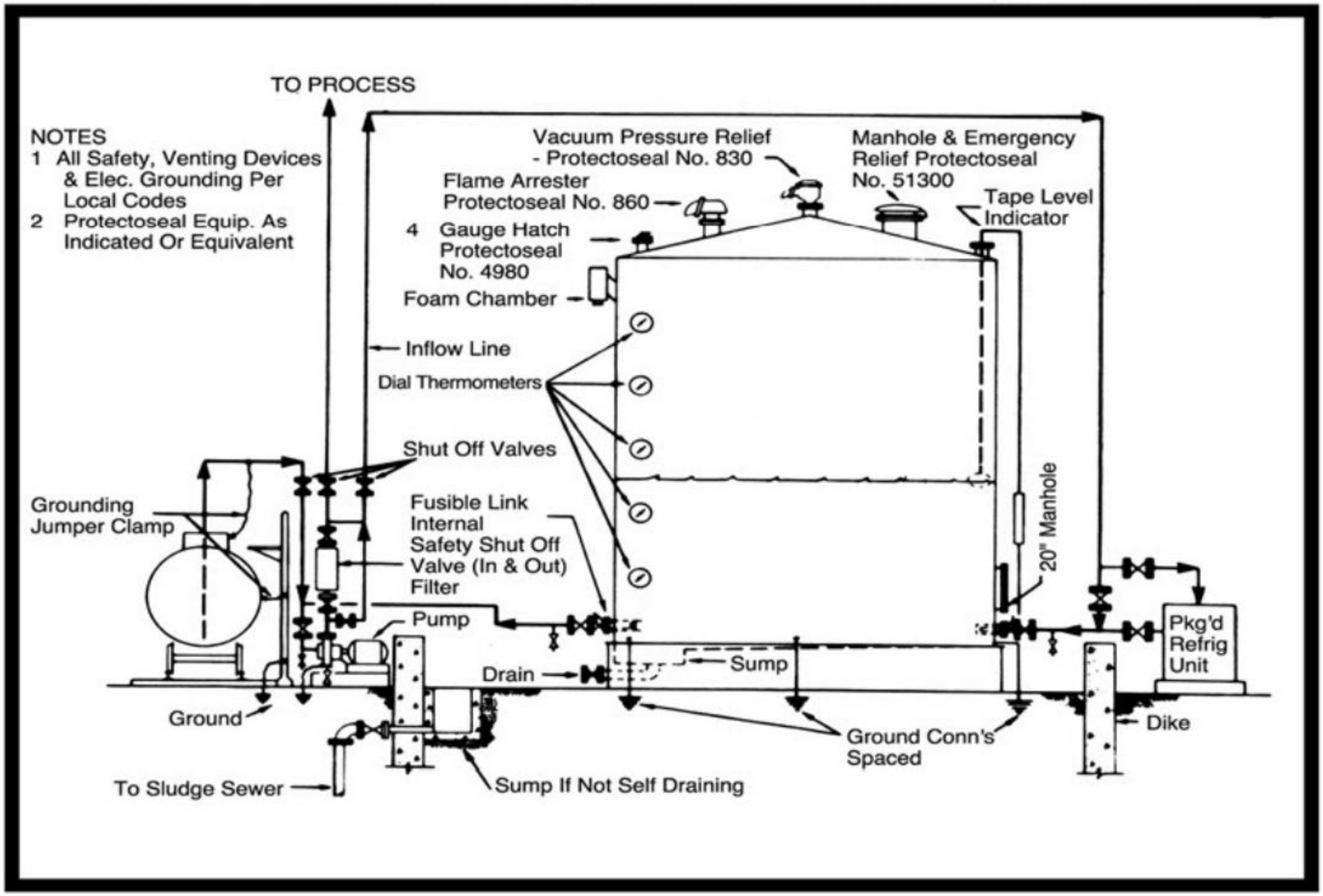
Inspection schedule for styrene Bulk Storage

Suggested Testing Schedule for Styrene Bulk Storage

Monomer Temperature	Frequency	Key Properties	
26.7°C (80°F) or higher	Weekly	Polymer	ASTM D2121
		Inhibitor	ASTM D4590
21.1 - 26.1°C (70 - 79°F)	Bi-weekly	Color	ASTM D5386 or D1209
		Appearance	Visual
Below 21.1°C (70°F)	Monthly	Aldehydes	ASTM D2119
		Peroxides	ASTM D2340

Testing Schedule For Styrene Bulk storage

FIGURE 1 – STYRENE MONOMER STORAGE TANK



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PLAN OF ACTION

Required components :inhibitor content analyser, dissolved oxygen analyser, no contact temperature sensor , high efficient pressure sensor and motor with three blades

We cross checked each and every information which is mentioned above

We gathered all the information regarding handling and prevention of runaways and tank ruptures for many chemical plant papers and manuals

We referred many videos regarding thermal explosion and explosion of storage tanks while transporting

We gathered every property of styrene polymerisation and styrene monomer and vapour gas

Research : about the maximum possibilities

We still need to gather information whether we can use any chemical sensors instead of inhibitor content analysers and dissolved oxygen analyser

INHIBITOR CONTENT ANALYSER

In hazardous environment ,where concentration of flammable gas, dust or vapour occur, It is vital that the instrument be safe to operate and do not initiate an explosion. For these environments the ADI 2045TI Ex proof fulfils EU Directives 94/9/EC (ATEX95) and is certified for Zone1 and Zone2 areas.

It analyses the inhibitor content based on standard method ASTM D4590

ADI 2045TIEx proof analyser

START

INITIALISATION OF SETUP

Sensed data will be sent to main server for analysing

IF

IF(Temp>65)

IF(Inhibitor<10ppm)

IF(Temp increase by 2-3 per day)

IF(dissolved oxygen < 3-8% of oxygen in gas form in tank)

Inhibitor should be added with the sufficient amount of dissolved oxygen and it should be supplied homogeneously

REFERENCE VIDEOS AND WEBSITES

Explosion of styrene storage tank while transportation YouTube link - https://youtu.be/vGtX89vUiPE

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