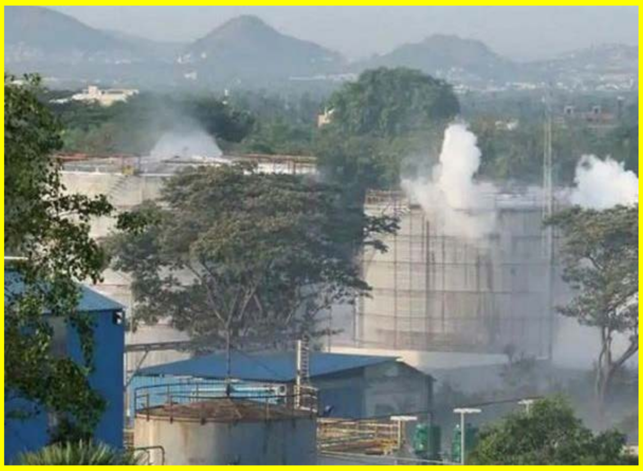

Learning from Incidents: Styrene Vapour Leak at Vizag

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A member of Technical Committee
Investigated the Styrene Vapor Leak at Vizag

THE ACCIDENT @ LGPL

On 7th May 2020, an incident of uncontrolled Styrene vapour Release occurred at LG Polymers, Visakhapatnam from one of the Styrene storage-tanks (M6 Tank).

This Styrene vapour release, widely referred to as "Vizag Gas Leak", is a unique major Styrene vapour release incident from a bulk storage tank anywhere in the world.

The accident took the lives of 12 persons in the immediate subsequent period and 585 people had to undergo treatment in hospitals, besides causing loss of livestock and vegetation.

IMPACT



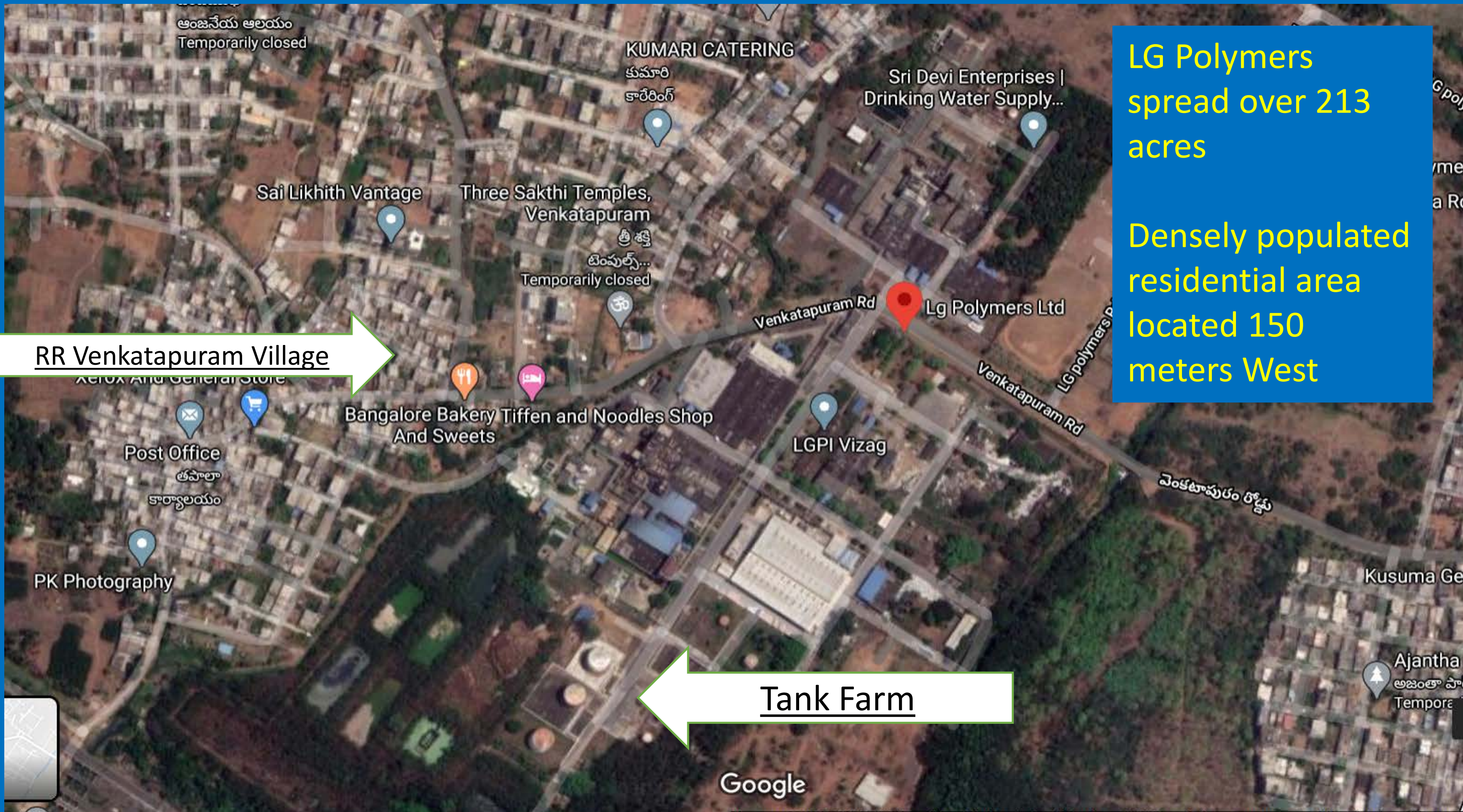






Nearly 20,000 people from 17,000 houses/residences of RRV Puram, Nandamuri Nagar, Kamparapalem, Padmanabha Nagar, SC/ BC Colony, Meghadripeta Colony were evacuated, and arrangements were made at 23 rehabilitation centres maintained by GVMC as well as Simhachalam Devasthanam authorities

LOCATION OF TANKS VS TOXIC IMPACT LOCATION



The region at 3 km radius was affected. At least 3000 people suffered from the effects of Styrene vapor.

COMPANY

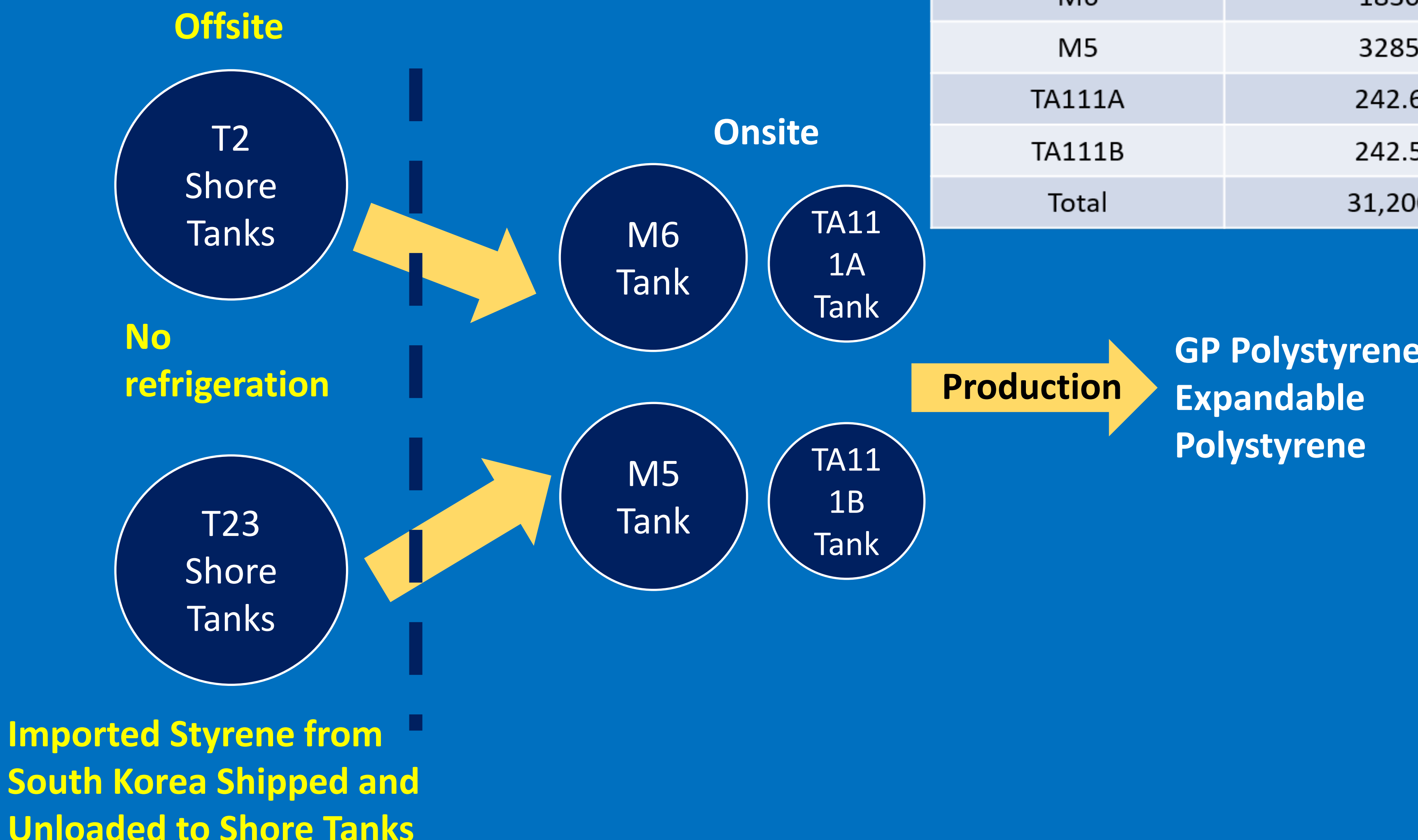
LG Chem.: Polymers India Private Limited (1997 – to date)

HISTORY

- Sri Rama Mills to manufacture alcohol from molasses – 1961
- Hindustan Polymers Ltd - 1962
- Hindustan Polymers Ltd to Manufacture Polystyrene & Co-Polymers – 1967
- Hindustan Polymers Ltd – 1973 (Initiated of Manufacture of Styrene Monomer)
- Hindustan Polymers Ltd. merged with McDowell & Co. Ltd – 1978 – Terminated manufacturing of Styrene monomer
- LG Chem.: Polymers India Private Limited - 1997

PROCESS DESCRIPTION

Tanks	Styrene Quantity tons
T2	12800
T23	12800
M6	1830
M5	3285
TA111A	242.6
TA111B	242.5
Total	31,200



Source: Report of the Joint Monitoring Committee in the O. A. No. 73 of 2020

PROCESS DESCRIPTION continued

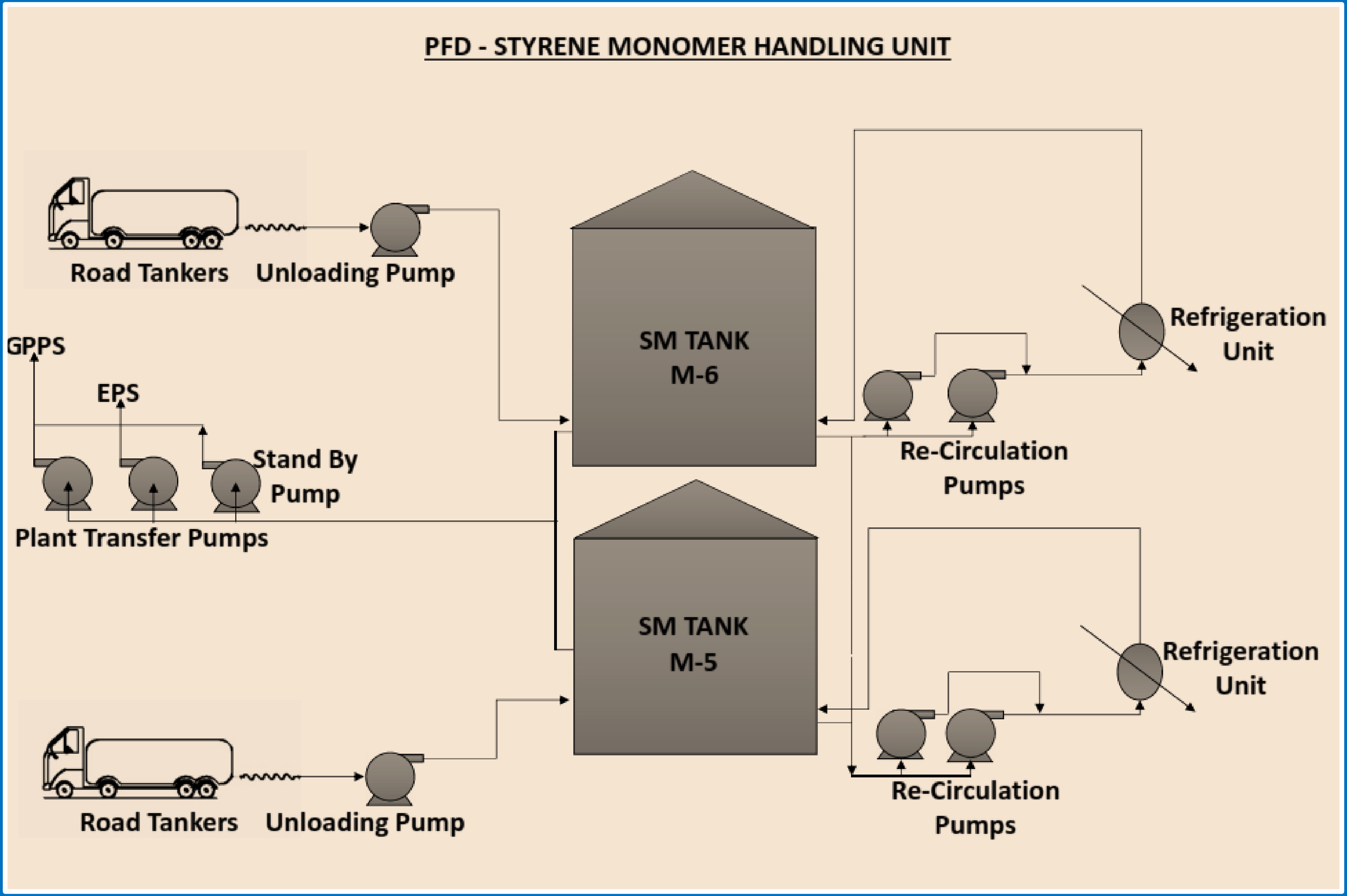


Figure 1: Schematic Diagram of Styrene Handling Plant

PROCESS DESCRIPTION continued

Figure 2: Roof Top of M6 Tank Showing Vents

Maximum Allowable Working Pressure is 0.1 barg [API 650 design]

HAZARD IDENTIFICATION

STYRENE MONOMER – CHEMICAL DATASHEET

NFPA 704

Diamond	Hazard	Value	Description
	Health	2	Can cause temporary incapacitation or residual injury.
	Flammability	3	Can be ignited under almost all ambient temperature conditions.
	Instability	2	Readily undergoes violent chemical changes at elevated temperatures and pressures.
	Special		

Interim AEGLs for Styrene (100-42-5)

Exposure Period	AEGL-1	AEGL-2	AEGL-3
10 minutes	20 ppm	230 ppm	1900 ppm
30 minutes	20 ppm	160 ppm	1900 ppm
60 minutes	20 ppm	130 ppm	1100 ppm
4 hours	20 ppm	130 ppm	340 ppm
8 hours	20 ppm	130 ppm	340 ppm

Lower Explosive Limit (LEL) = 9000 ppm

indicates value is 10-49% of LEL. Safety consideration against explosions must be taken into account.

Level of Distinct Odor Awareness = 0.54 ppm

(NAC/NRC, 2017)

ERPGs (Emergency Response Planning Guidelines)

Chemical	ERPG-1	ERPG-2	ERPG-3
Styrene (100-42-5)	50 ppm	250 ppm	1000 ppm

indicates that odor should be detectable near ERPG-1.

(AIHA, 2016)

PACs (Protective Action Criteria)

Chemical	PAC-1	PAC-2	PAC-3	
Styrene (100-42-5)	20 ppm	130 ppm	1100 ppm	LEL = 9000 ppm

indicates value is 10-49% of LEL.

Flash Point: 88 ° F (NTP, 1992)
Lower Explosive Limit (LEL): 1.1 % (NTP, 1992)
Upper Explosive Limit (UEL): 6.1 % (NTP, 1992)
Autoignition Temperature: 914 ° F (USCG, 1999)
Melting Point: -24 to -23 ° F (NTP, 1992)
Vapor Pressure: 4.3 mm Hg at 59 ° F ;
9.5 mm Hg at 86° F; 10 mm Hg at 95° F (NTP, 1992)
Specific Gravity: 0.906 at 68 ° F (USCG, 1999)
Boiling Point: 293 to 295 ° F at 760 mm Hg (NTP, 1992)
Molecular Weight: 104.16 (NTP, 1992)

IDLH: 700 ppm (NIOSH, 2016)

Reference: Cameo Chemicals

HAZARD IDENTIFICATIOM continued

PROPERTIES OF STYRENE

Although not considered highly toxic by inhalation, styrene causes moderate irritation of eyes and skin. **High vapor concentrations cause dizziness, drunkeness, and anesthesia**. (USCG, 1999)

Styrene has been involved in **several industrial explosions caused by violent, exothermic polymerization** [Bond, J., Loss Prev. Bull., 1985, (065), p. 25]. **The presence of an inhibitor lessens but does not eliminate the possibility of unwanted polymerization.** Violent polymerization leading to explosion may be initiated by peroxides (e.g., di-tert-butyl peroxide, dibenzoyl peroxide), butyllithium, azoisobutyronitrile. Styrene reacts violently with strong acids (sulfuric acid, oleum, chlorosulfonic acid), and strong oxidizing agents [Lewis, 3rd ed., 1993, p. 1185].

Reference: Cameo Chemicals

Sequence of events of the accident in the early hours of 7th May 2020

02:31 a.m.: No Styrene vapour release captured in the CCTV

Figure 3: M6 Tank (Normal Condition)

Sequence of events (Continued)

02:42 a.m.: Styrene vapour release captured in the CCTV

Figure 4: Vapor Release from M6 Tank

Sequence of events (Continued)

02:53 a.m.: Styrene vapour cloud formation captured in the CCTV

Figure 5: Styrene Vapor Cloud Formation

Sequence of events (Continued)

02:54 a.m.: Gas detector alarm noticed in Distributed Control System (DCS)

Figure 6: Display of the DCS

SETTING OF GAS DETECTOR ALARM

- There was 12 minutes time gap between the release at the top of the tank and the buzzing of gas alarm at the control room.

- The gas detectors were placed on the tank at 300 mm from the ground level. It had taken time for the styrene vapor to reach the gas detectors.

- Further, the gas detectors were not sensitive enough to detect the gas immediately as the gas detector alarm was tuned for 2200 ppm (20% of the LEL value).

METHODOLOGY

Inspection of the Site of the Incident

Data Collection

Data Analysis

Study of Major & Minor Parameters

Root Cause Analysis

ROOT CAUSE ANALYSIS

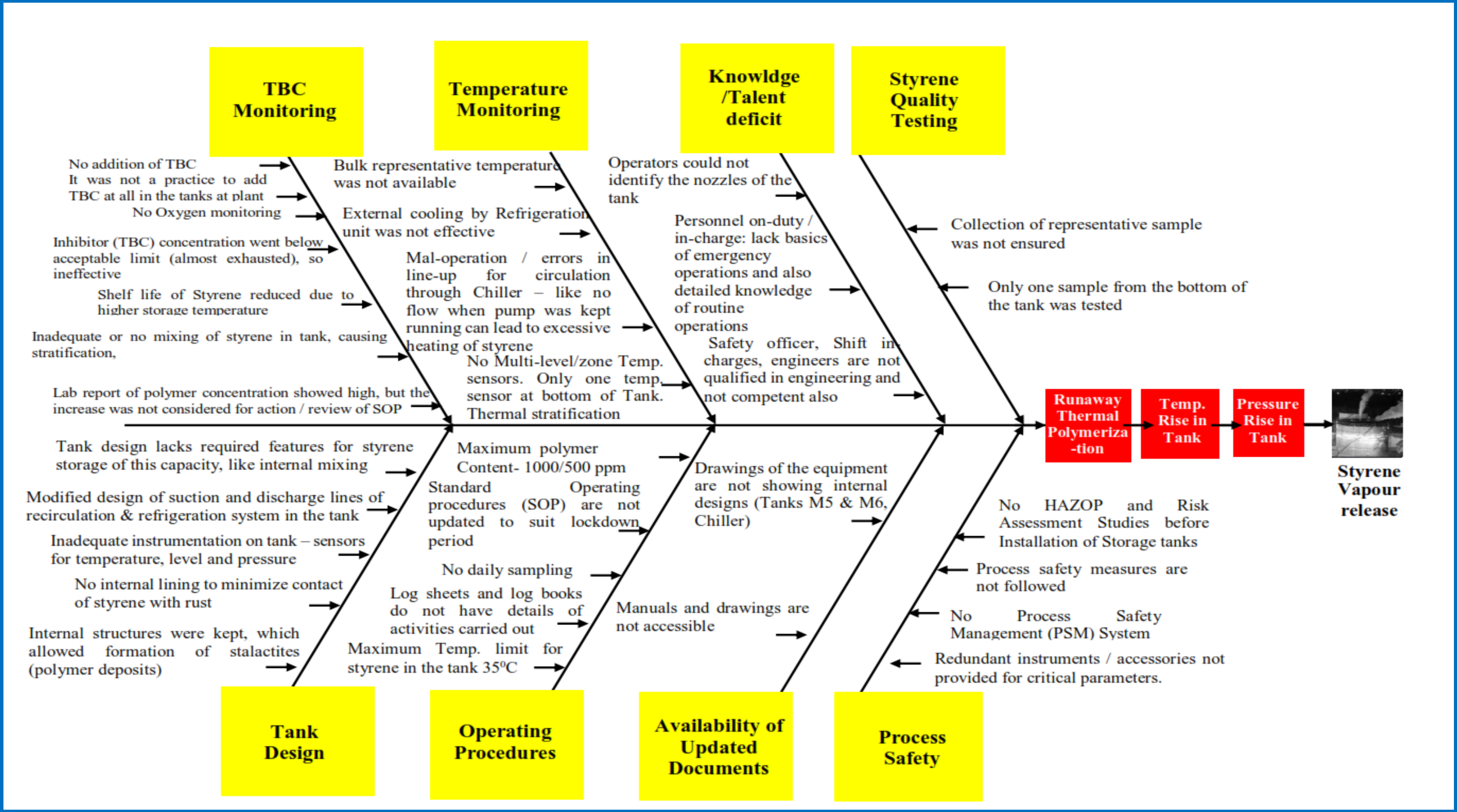


Figure 7: Ishikawa Fishbone diagram

ROOT CAUSE ANALYSIS (continued)

The major parameters that influenced the increase of temperature of styrene in the tank (M6) are mainly

1. **Tank Design**
2. **Tank Temperature Measurement and Control**
3. **TBC Monitoring [Inhibitor Depletion Characteristics]**
4. **Operating Procedures**
5. **Availability of Updated Documents**
6. **Knowledge / Talent Deficit**
7. **Styrene Quality Testing**
8. **Process Safety Management**

1. Tank Design

- **53 year old, Atmospheric Mild steel without any inside lining, insulated outside (Table 1) (Figure 8).**
- **17 Nozzles (Flame Arrester (N6), Dip Hatch (N1) used as Vents).**
- **Conical Roof on an Inside Structure**
- **Provided with a Recirculatory Cooling System**
- **Change of Design in the Suction and Discharge (Figure 9: A & B); No HAZOP and Risk Assessment for the Modified Design that falls under Management of Change under the OSHA PSM standard**
- **Last Cleaning and Maintenance of the Tank in 2015. Recommended cleaning is every 2 years.**

2. Tank Temperature Measurement and Control

- Single Temperature Measuring Probe at the Bottom of the Tank M6 (Figure 10).
- Temperature measurement is restricted to the bottom zone; top and middle zones might have different temperatures.
- Thermal stratification in the tank shown in Figure 11; Table 2.
- Temperature protocol of LG Polymers 35 ^{0}C.
- Tank top temperature at 41.7°C, estimated from DCS level percentage data recorded on 28.04.2020.
- Incorrect assumption of Bottom Temperature as Bulk Temperature of tank.
- Inadequate Time for Cooling

3. TBC Monitoring [Inhibitor depletion characteristics]

- No addition of TBC in the on-site storage tanks since last 10 years
- Unavailability of TBC Stock
- TBC Stratification in the tank due to inefficient mixing in Tank Design (1) (Figure 12)
- Decrease of TBC Concentration in Styrene (Figure 13) Unaware of inhibitor depletion characteristics
- Absence of monitoring of Dissolved Oxygen (Table 3).

LESSONS LEARNT FOR TANK DESIGN, TEMPERATURE MEASUREMENT & CONTROL, TBC MONITORING

1. **For the Indian point of view, it is imminent to review styrene storage tank design. (Figure 14) (Figure 15)**

   i. The tank must have suction swing pipe and eductor system for efficient mixing.

   ii. The tank should have effective cooling systems with back up cooling with a maximum temperature of 25 °C.

   iii. The number of nozzles in the tank should be kept to a minimum required.

   iv. The material of construction of the tank can be carbon steel with coating inside.

   v. The roof of the tank should be supported with outside structures.

LESSONS LEARNT FOR TANK DESIGN, TEMPERATURE MEASUREMENT & CONTROL

vi. Use a rust-resisting inorganic zinc silicate material to coat tank and nozzle internals, particularly the inside bottom of the tank and the lower 2 ft of wall.

vii. Rust and moisture should be excluded from styrene storage and handling facilities.

viii. Paint the outside of storage tanks white or aluminium; consider insulating storage tank.

ix. Tank life should be clearly defined; tank cleaning and coating should be carried out once in two years.

4. Operating Procedures

- Maximum polymer content- 1000/500 ppm
- Standard Operating Procedures (SOP) are not updated to suit lockdown period
- No daily sampling
- Log sheets and log books do not have details of activities carried out
- Maximum Temperature limit for styrene in the tank 35^0C

LESSONS LEARNT FROM OPERATING PROCEDURES

i. Standard Operating Conditions with upper and lower limits of each parameter need to be carefully reviewed.

ii. High Critical Standard Operating Procedures to be in place if high polymer content is observed.

iii. Understandable, useable, clear, and concise log book entries are good practice as part of operation discipline. Consider following boiler plate template.

iv. Sampling frequency to be increased when process is dormant (pandemic, turnaround, business cycles)

v. Procedures are to be reviewed and updated if necessary after a Management of Change.

5. Availability of Documentation

- Documentation was inaccessible
- Procedures and manual were not available during the time of the investigation
- Tank drawings do not show internal arrangements
- Validation of refrigeration system was unavailable
- A paucity of basic Process Safety Information was observed
- Process Safety Information is the foundation for a Process Safety Management program

6. Knowledge / Talent Deficit

- Operators could not identify the nozzles of the tank
- Personnel on-duty / in-charge: lack basics of emergency operations
- Personnel were unaware of detailed knowledge on Styrene handling and storage best practices
- Safety officer, Shift in-charges, engineers are not qualified in engineering and not competent also
- Process Safety Competency / Training is key driver to keep the workforce abreast in the latest in Process Safety Management

LESSONS LEARNED FROM INSUFFICIENT DOCUMENTATION & KNOWLEDGE / TALENT DEFICIT

- Thermal radical polymerisation (Table 4 & Figure 16)
- Overlooking Increase in Polymer Level on 24th April (Figure 17)
- Top layer of the tank was condensed styrene without TBC
- Temperature above 35 ^{0}C (Estimated 41.7 ^{0}C on 28.04.2020)
- The Runaway polymerization reaction started at about 34 ^{0}C (Harold Fisher)
- Hui and Hamielec Kinetic models are valid between 100 °C to 200 °C and under adiabatic conditions (Kaypear)
- Non-adiabatic (Volumetric vapor generation due to heat of reaction balances vent rate through relief devices)

7. Styrene Quality Testing

- Collection of representative sample was not ensured
- Only one sample from the bottom of the tank was tested

8. Process Safety Management Framework

- A disciplined framework for managing the integrity of hazardous operating systems and processes by applying good design principles of engineering and operating practices, CCPS Definition
- No HAZOP and Risk Assessment Studies before Installation of Storage tanks
- Little to no understanding of Risk Based Process Safety

CONCLUSIONS

* Technology and techniques should be continuously updated.
* Continual learning and keeping the equipment in good condition should be ensured.
* Senior professionals responsible for guiding should be adequately experienced & should ensure strict compliance of standard operating procedures.
* The operating personnel should be trained in on-site & off-site emergency response plans and procedures to handle emergencies for toxic chemical release along with fires & explosions.
* The awareness programs should be conducted for the neighbour-hoods on hazard nature of chemicals and their effects.
* Process safety management system, a systematic, comprehensive approach with 20 elements of risk based process safety should be implemented in toto.

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REFERENCES

- Cincinnati Styrene Release, Cincinnati, Ohio, USA 28th August 2005.
- Chin-Chuan Chen, Chi-Min Shu, Ron-Shin Chang, Mei-Ling Shyu and Shu-Ching Chen, Thermal Hazard Analysis of Styrene Monomer at Low Temperature, Conditions during Storage and Transportation, Corpus ID: 7937692, Materials Science, 2002 (www.academia.edu).
- Fisher, H. G & DIERS users Group, a Runaway Styrene Polymerization Incident with Inhibitor Effectiveness Study, AIChE Meeting, Pittsburgh, P. A., 1991.
- Fisher, H. G., Communication dated 07.06.2020
- Guidelines for Investigating Process Safety Incidents, 3rd Edition, Center for Chemical Process Safety, AIChE, John Wiley, NJ. USA, 2019
- Lin Zhao, Wen Zhu, Maria I. Padaki, M. Sam Mannan and Mustafa Akbulut, Probing into Styrene Polymerization Runaway Hazards: Effects of the Monomer Fraction, ACS Omega, 2019, 4, 5, 8136 – 8145.

REFERENCES (Continued)

- https://www.epa.gov/aegl/styrene-results-aegl-program(browsed on dated 23.06.2020)
- Product Handling Guide – Styrene Monomer, LyondellBasell, 2019
- Rahul Raman, Kaypear Consulting Chennai, 12th May 2020
- Safe Handling and Storage of Styrene Monomer, Chevron, Phillips Chemical Company LP, September, 2010
- Safe Handling and Storage of Styrene Monomer, Americas Styrenics LLC, USA, November 2016
- Shelf Life of Styrene Monomer, Chem. Eng. Prog. Vol. 65, No.4, April 1969
- Styrene: Chemical Response Guide, March 2004.
- Styrene Monomer: Safe Handling Guide, Plastic Europe, July 2018

Thank You

Any Questions?