

Manufacturing Chemists' Association, Inc.

(FOUNDED 1872)

1825 Connecticut Avenue, N. W.

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TO THE EXECUTIVE CONTACTS OF MEMBER FIRMS

SUBJECT: Case Histories of Accidents (including Fires and Explosions).

Member firms are urged to send the MCA Washington Office an account of accidents (or near accidents) which they believe should be included in this report. Factual information on such occurrences is desired whether or not occupational injuries are actually involved, and regardless of the exact nature of their results.

CASE HISTORY NO. 816

Vinyl Chloride Polymerization Explosion

Early in the morning, August 9, 1961, an explosion broke out at the Minamata Plant of the New Japan Nitrogen Fertilizer Co., claiming four lives and injuring ten people in or around its premises.

The plant is situated at Minamata, a city in the southwestern part of Kyushu, one of the four main islands of Japan. It occupies about 100 acres in which there are about 500 buildings accommodating manufacturing plants, warehouses, offices and many tanks. The total floor area of buildings is about 1,430,000 sq. ft. and the number of employees exceeds 3,500.

These buildings are principally of asbestos or stucco clad steel frame or stucco clad wooden frame construction, and some of them, including office buildings, are of wooden construction.

The plant produces varieties of chemical fertilizers and plastics including polyvinyl chloride, and the explosion occurred in the vinyl chloride polymerization plant, a building containing 18 pressure vessels, in which polyvinyl chloride is produced from vinyl chloride monomer under the pressure of 100 to 160 lb./in. at the temperature of 120 to 140 F. It takes between 10 and 15 hours to complete this polymerization in the pressure vessel. The characteristics of vinyl chloride monomer CH_2CHCl are as follows:

- boiling point: -13 C. (9 F.)
- specific gravity: approximately 2
- explosion range: between 4 and 22%

During the polymerization process, the vessel is cooled because heat is generated during the reaction. The temperature and pressure within the vessels are checked by the operators with gauges and meters in the controller's room. When the temperature has stabilized and the pressure has settled down, thus indicating completion of the reaction, they stop the churning of material, open the lid

on the top of the vessel. They then open the discharge valve at the bottom through which the liquid products are transported through a manually operated funnel and pipe to the drying and crushing plant, adjoining the polymerization plant.

About half past 6 o'clock in the morning, as the reaction in the polymerizing vessel No. 3 was completed, a foreman and three employees set to work to discharge the contents according to directions from the controller's room but in error they opened vessel No. 4 instead of No. 3. Thus the gaseous vinyl chloride monomer just in the process of polymerization burst out of the vessel, filled the room and shortly afterwards exploded, presumably ignited by a spark from electric machines or by static electricity generated by the bursting gas, or some other unknown cause.

The explosion was heard at the municipal fire department about a mile distant from the factory. A fireman on the watchtower saw black smoke clouds rising from plant buildings, but he did not see any flame.

When firemen arrived at the scene, there were thick white smoke clouds with a smell of gas around the polymerization plant, and near vessel No. 4 a little flame was found. The fire was extinguished after a few minutes. Then they worked to rescue the wounded employees and stayed there for a possible secondary explosion, which fortunately did not occur.

The foreman was found dead at the top of No. 3 tank and one of the two workers at the bottom was dead on arrival at the hospital. An employee in the controller's room died instantly and another worker in the burner plant, a building next to the polymerization plant, died after two days. Within the premises of the factory, 8 additional persons were injured, most of them not seriously, and outside the factory two persons were injured slightly by flying glass.

All the asbestos plates on the roof and walls of the polymerization plant fell out,

and parts of stucco walls were also blown down. Inside the building, the steel frame was dented or buckled by the shock of the explosion; iron floor plates in particular were seriously damaged, some of them cut off, others blown away. All the glass panes on the doors and the windows were blown off.

None of the 18 vessels were damaged seriously, with the exception of vessel No. 3 which was greatly dented on the side.

CASE HISTORY NO. 817

Sprayed with Hot Maleic Acid Solution

Description: An operator had been assigned the job of cleaning out a dehydrator system. He had completed the removal of the liquors in the system with the steam ejector and started the washes. When the first wash was completed, he requested the hook-up of a rubber steam hose from the discharge side of the dehydrator transfer pump to the storage tub which is used to store make-up water for the absorbers. (A steam hose had been used twice before for this job.) A department mechanic made the hook-up and also checked for leaks after the hose was in use. The operator stayed on the job until 12:00 noon when he left the plant. Another employee, who was an extra operator that day, was assigned to the job just before going to lunch. When he returned at 12:15, the chief operator gave him the line-up and also told him to check the hose connection to the discharge pump. He went up to the 12' level where the hose was connected and observed that the hose connection to the piping on the discharge side of the pump was leaking badly. The spray from the leak prevented him from closing the valve to the hose. He then went directly to the switch for the transfer pump and turned it off. He started back to check the leak again when the connection gave way and allowed the hose to drop to the floor. The hot solution continued to spray out due to the static head pressure of the liquid in the system. He was approximately 10' from the connection when the injury resulted. In the manufacturing of maleic anhydride, a section of the process requires the dehydration of maleic acid. The equipment used in this dehydration is cleaned out periodically. The exact time of the cleanout is dependent on a build-up of deposit of tars and residues which cause partial blockages and affect the vacuum. When a designated loss of vacuum is observed at the flash chamber, it means the equipment must be cleaned out. The first step in cleaning out the system is to suck all liquor in the system to the stripping still. After this is completed, water is introduced to the sys-

tem and heated. A large circulating pump is started and the hot water is continuously pumped through the whole system for a half hour. In the past, three separate washes were made on the system and on the completion of each, the liquor was pumped to the sewer. Through recent investigation, it was found that the first of the three washes contained maleic acid, so in an effort to better the yield, the liquor from the first wash is pumped through a rubber hose to the make-up water tank for the absorbers rather than being sewerred. The second and third washes are still pumped to the sewer. A project recently was submitted, approved and is scheduled for the near future which includes the installation of a storage tank for this liquor and the permanent piping necessary to pump the first wash to this storage tub. Cause: It is believed that rapid corrosion of iron fittings caused by maleic acid was the principal cause of this accident. It was found that there were iron fittings on the steam hose and the piping to the pump. Preventive Measures:

1. Hoses used for this operation be provided with 316 stainless steel fittings, and these hoses properly identified.
2. All blow-out and drain lines be changed to 316 stainless steel.
3. Inform personnel on location and use of special hoses and post sign INSTALL HOSES WITH 316 S.S. FITTING ONLY at each steam water mixer when stainless steel fitted hoses are attached.
4. Each department supervisor check hoses and fittings in his department from a corrosion standpoint. If it is found that the standard hose with steel or brass fitting is not suitable in all cases, production supervisor should: determine what material is suitable in each case, see that material required is installed, acquaint operators with resulting changes.

Armed Services Explosives Safety Board

CASE HISTORY NO. 818

Hydrogen Sulfide Release - Near Miss

Description: The operator and his supervisor went to investigate an H₂S odor coming from a reduction vessel. The fumes were so pungent the men experienced difficulty in breathing and immediately headed for an exit. When they got outside the operator collapsed but revived quickly and was taken to Plant Health. Cause: The scrubber unit to which this vessel