TELEPHONE HUDSON 3-6126

Manufacturing Chemists' Association, Inc.

(FOUNDED 1872)

1825 Connecticut Avenue, N. W.

WASHINGTON 9, D. C.

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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 1 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 completi n of the reaction, th y 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 t the drying and crushing plant, adjoining th 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 c nnected 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 hos 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 system 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 sewered. 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.

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CASE HISTORY NO. 818

Hydrogen Sulfide Release - Near Miss

Description: The operator and his supervisor went to investigate an H_2S 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 Healt
Cause: The scrubber unit to which this vesse

was attached, had been charged with fresh solution before the reaction began. The scrubber blower, which is interconnected with an alarm, is shut during this procedure and the alarm tu d off manually. After the scrubber was returned to service, the alarm bell was not turned on. During the reduction step, the blower motor failed mechanically but since the alarm was shut off, the operator was not aware of the failure. The H_2S fumes escaped into the room creating the noxious situation.

The operator was attending a vessel in another part of the room and was not aware that the H_2S was escaping. This gas has the insidious property of causing olefactory fatigue and dangerous concentrations cannot be smelled after short exposure.

Preventive Measures: To prevent a recurrence, the batch sheet was revised to require the operator's signature that the alarm has been re-energized. In addition, it has been found that a lead acetate solution will absorb H_2S and detect it in the HCN detector in this room. This will ring an alarm when H_2S escapes into the room. Lead acetate paper also is available to be used when leaks are suspected.

CASE HISTORY NO. 819

Aluminum Triethyl Fire

De cription: A chemist dropped a gallon glass bottle containing about two liters of a 20 per cent solution of aluminum triethyl in kerosene when his feet slipped on slick mud on the walk at the entrance of a sample storage shed. The released solution flashed on contact with air and moisture, enveloping the chemist who had fallen to a sitting position. A plant safety inspector, fully dressed in protective clothing, mask, and gloves who was present to destroy discarded samples, immediately pulled the chemist to a dry area and extinguished his burning clothing. The safety inspector secured help from the adjacent laboratory and carried the chemist inside to a safety shower where clothing was removed and showering was continued for fifteen minutes under supervision of the plant nurse. The nurse also gave him a pain-killer. The local hospital was alerted and a team of doctors was waiting for the patient upon his arrival in the plant ambulance. They found the injured man to have second and third degree burns on both hands and f rearms, second or third degree burns on both buttocks, and first degree burns of the face. Treatment was spectacularly successful, with release from the hospital in 17 days with prognosis of no permanent disfigurement ar o necessity for skin grafting. The injured man returned to work with no limitations on the thirty-third day.

Cause:

1. Detailed safe-handling rules for aluminum triethyl had not been issued f r laboratory workers, although such rules were in effect in the plant.
2. The chemist wore no protective clothing, mask or gloves while handling the comparatively large container f aluminum triethyl.
3. The glass container was carried in the hand rather than being cushioned in an inert absorbent material in a bucket.

Preventive Measures:

1. Glass bottles containing more than eight ounces of aluminum triethyl solution will be carried only in a bucket cushioned with vermiculite or other inert material.
2. Approved protective clothing will be mandatory for anyone handling amounts of aluminum triethyl solution exceeding eight ounces.
3. Proper grading of the area will be done to prevent rain-washed mud from coating the concrete walk between the laboratory and sample storage house.
4. Detailed safety rules have been promulgated covering aluminum triethyl handling in the laboratory.

CASE HISTORY NO. 820

Blast Effect Injury

Description: A solution of 195 gm. of dibromomalononitrile in 600 ml. of ethyl ether was added to a solution of 197.5 gm. of sodium azide in 600 ml. of water (mechanical stirring) over a period of 45 min., while maintaining the temperature of the reaction at 5-8°C. by means of an ice-bath. After the addition was complete, the reaction mixture was stirred for an additional 2 hrs. at 10°C. The ether layer was then separated and discarded. The aqueous layer was extracted six times with 500 ml. portions of ether and these extracts discarded. The water solution was then acidified with 175 ml. of a 1:1 mixture of concentrated H_2SO_4 in water. An oily product separated out which was taken up in 500 ml. of ether. The water was extracted once with an additional 500 ml. of ether and the water discarded. The ether extracts were combined and dried over anhydrous sodium sulfate. After filtering off the drying agent, the product solution was p ured into a large evaporating dish in a hood late in the afternoon. The next morning the chemist stirred the oily product left in the dish and at about 10:00 a.m. noted that some crys-

tals had started to form. Several times later in the day, the chemist stirred the slurry with a metal spatula in order to induce more crystallization.

At about 4:05 p.m., the laboratory technician reached into the hood to adjust a rack. He did so without touching or otherwise disturbing the evaporating dish. Just as he withdrew his arm, the slurry in the evaporating dish (estimated to be 75-100 gm.) exploded with great violence breaking bottles containing solvents and sodium stored in the hood. The technician's shirt and safety glasses were blown off and he sustained multiple abrasions (blast effect) of chest and both arms, multiple puncture wounds of the chest, abdomen and right arm, ruptured right ear drum and scratch on right eye.

The reaction between dibromomalononitrile and sodium azide had been run previously using 1/5 the quantities used in the run which exploded. The products of these runs when isolated as an oil suspension of crystals did n t explode when struck with a hammer on a steel plate. The material would decompose rapidly when heated in a flame. Pure crystals f the product isolated by dissolution in ether followed by reprecipitation by the addition of chloroform were very shock-sensitive when dry.

Cause: The amount of material being handled was grossly in excess of that considered safe to be used in a laboratory hood. Even if shielding, remote handling devices and ear pr tection had been employed, it is probable that a serious injury would have been sustained. The fact that two of the four frontal hood shields were in the open position probably permitted the explosive force to be dissipated and resulted in lesser initial damage and less serious injury than would have occurred had all shields been lowered.

Pr ventive Measures: A maximum of 2 grams will be handled during any future reaction.

CASE HISTORY NO. 821

Firebox Explosion - Dowtherm Vaporizer

Description: At approximately 8:40 a.m. instruments in the control room indicated a flame failure of the Dowtherm vaporizer, F-5. Operating personnel immediately checked F-5 and found it was not operating. According to furnace start-up procedure, the firebox was checked before activating the control unit which automatically purges and lights the furnace. After the purge cycle, when the pilot ignited, there was a firebox explosion at 8:50 a.m. Extensive boiler casing and refractory damage resulted from the explosion. No other equipment or buildings were damaged. These events occurred s veral hours aft r a severe rain and electrical storm.

Cause: A short developed across the fuel selector switch which allowed the fuel gas valve to open during the purge cycle, thus purging the furnace with a mixture of fuel g and air. When the pilot ignited, the explos occurred.

There were no personnel injuries as a result of the explosion.

Preventive Measures: The fuel selector switch has been removed from the control circuit and all exposed connections have been weatherproofed. Consideration is being given to the installation of a roof over the front end of the boiler; the use of a continuous pilot flame and isolation of wiring circuits to reduce probability of "shorting." Damage was estimated at $15,000.

CASE HISTORY NO. 822

Ether Explosion in Laboratory

Description: A chemist was distilling ether from impurities when an explosion occurred, resulting in burns of the face, hand, arm and leg. The apparatus consisted of a distflla-tion flask, coupled with a water-cooled condenser draining the ether into a three liter bottle. The source of heat was a single steam bath. The hood contained some extraneous equipment of which there was a thermostatically-controlled hot plate with exposed contacts. The distillation was being carried on when the chemist added more ether to the flask. A bump caused by the steam raised the flask slightly. The chemist stepped over next to the hood to cut the steam back, and at that moment, the explosion occurred. The explosion caused the explosion-venting windows to open, but the venetian blinds were broken.

Cause: The connection between the flask and the condenser broke, permitting ether vap rs to fill the hood faster than they could be removed. The vapors were ignited by the hot plate.

Preventive Measures:

1. Sources of ignition should be removed from areas where flammable liquids can escape. Hot plates, open flames, unapproved electrical equipment, etc. are included in this category.
2. Laboratories should be designed so that it is not possible for persons to be trapped by fire.
3. Explosion venting windows should not be obstructed. Venetian blinds offer considerable resistance to explosion pressures.
4. Consider the hazards of a job and then choose the suitable conditions to carry it out.
5. Discuss new arrangements or procedur with the safety leader. His experience is valuable in recommending safe procedures.

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