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TO THE EXECUTIVE CONTACTS OF MEMBER FIRMS

SUBJECT: Case Histories -- Accidents, Including Fires and Explosions, Worth Noting. Report for the Month of April 1960.

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, i.e., whether there be personal injury, fire, explosion or other injurious effect.

CASE HISTORY NO. 622

Explosion - Maleic Anhydride

Description of Accident:

On January 9, 1960, a vessel containing partially solidified maleic anhydride exploded violently. The explosion injured five operators. Two of the men died of injuries and burns a few hours after the accident. Damage to plant facilities in the blast area amounted to about $250,000. The damage resulted primarily from the force of the explosion and not by fire.

The vessel which exploded was of Type 304 stainless steel construction, fully insulated, and had a capacity of 800 gallons. The diameter was 4 ft. 6 in., shell length was 6 ft. 0 in., shell thickness was $\frac{1}{4}$-inch, thickness of heads was 5/16-inch, and the vessel was designed for 100 psig pressure or full vacuum and a maximum temperature of 250°F. One 2-inch by 3-inch relief valve was set at 90 psig. This valve had functioned properly prior to the explosion, but was inadequate in size to cope with the volume of gas evolved.

Cause:

An extensive investigation into the cause of the accident has revealed that the explosion was caused by decomposition of maleic anhydride, catalyzed by sodium ion (in the form of caustic) and heat (300°F or more). Sodium introduced as sodium hydroxide or other sodium compounds into maleic anhydride causes an exothermic decomposition which rapidly produces large volumes of gas (carbon dioxide). This reaction was generally unknown at the time of the explosion.

The vessel was connected with a process unit which was periodically cleaned with a weak caustic solution. Since the vessel contained maleic anhydride, top and bottom valves had been closed so that the caustic solution could not enter the vessel while other parts of the processing unit were being chemically cleaned with this material. However, sodium was found in samples from both sides of the valve at the bottom of the vessel and also in a sample taken from the seat of this bottom valve. It is concluded that at some time prior to the explosion the bottom valve had been open enough to allow the caustic cleaning solution to enter into the vessel. This could have happened several hours prior to the explosion, or perhaps a few minutes prior to the explosion. The heat evolved by the neutralization of the maleic anhydride with the caustic, and heat which possibly may have been supplied by steam, raised the temperature to a point where the sodium ion-induced decomposition of maleic anhydride further increased the temperature. Since the vessel was insulated, very little heat was lost. Once the decomposition started, the heat released from this exothermic reaction caused an autocatalytic runaway decomposition which could be described as a thermal explosion. Large amounts of carbon dioxide gas were liberated which built up the pressure in the vessel very rapidly. The rate of gas evolution was too rapid for the relief valve to handle completely, and the pressure increased beyond the bursting point of the vessel. It is believed that the gas pressure from this thermal explosion ruptured the vessel.

It has been found as a result of the investigation following the explosion that other alkali and alkaline earth compounds, such as potassium, lithium, calcium, barium and magnesium compounds, may also bring about the decomposition of maleic anhydride. It was found that amines and other nitrogen compounds also will trigger the decomposition of maleic anhydrid

Preventive Measures:

In order to prevent future accidents of this nature, caustic cleaning solutions and other alkali compounds and amines have been prohibited for use in equipment in maleic anhydride service. The replacement vessel has been redesigned and has been equipped with improved warning devices and also larger pressure relief facilities.

CASE HISTORY NO. 623

Chlorine Exposure

Description of Accident:

On January 19, 1960, a section of 200 psig steam header was blocked in for maintenance work. A tap from this section of header reduces the steam to 12 psig for use in heating a chlorine header. Since this section of header was blocked in making no steam available for chlorine heating, the chief engineer closed the chlorine feed regulator at the chlorinator.

After completion of the maintenance work on the 200 psig system the header was warmed up. Shortly thereafter the chief engineer smelled chlorine in the chlorinator room and blocked in the chlorine supply line just outside the door. About 45 minutes later, an operator reported to

the chief engineer that he smelled chlorine outside the chlorinator room. The chief engineer, believing that the one chlorine valve which he had closed must be leaking, closed the second valve in the system. A few minutes later, the diaphragm type pressure gauge blew off, allowing chlorine to issue from the 3/16" orifice in the lower portion of the pressure gauge. The chief engineer, a boilermaker, an adjacent area chief operator and supervisor inhaled chlorine gas. All four men were treated in the dispensary and three of these were sent to the medical clinic for examination. All were released shortly thereafter.

Cause:

Liquid chlorine was trapped in the system between the closed block valves. When steam entered the chlorine heater, a vapor pressure exceeding the maximum pressure of the gauge (150 psig) was exerted on the system and caused the gauge to rupture.

Preventive Measures:

1. Repairs were made to the system and new 0-300 pressure gauges were installed in place of the damaged ones.

2. An Engineering Work Order has been initiated for study of the chlorine system in the power departments with special instructions on pressure control, pressure relieving facilities and chlorine heating control.

3. This incident is to be used in safety meetings to emphasize the proper handling of chlorine and written instructions will be developed and incorporated into the department's operating manual.

CASE HISTORY NO. 624

Valve Repair Men Injured

Description of Accident:

Two men were assigned the job of repairing a 3-way valve. They were advised by their foreman that it was leaking internally. They checked with the Biphenyl operator about pumping the product from the high boiler catch tank and, when advised that there would be no transfer, physically checked the pump and valves, and found the pump off and valves closed. They then proceeded to the 3-way valve located at the southeast corner second level of the department. External adjustments were made to the valve to stop leaking. The operator entered the area and was called to the job site and asked if the line was okay. The operator indicated that he was not pumping through the line. The valve packing gland was then removed and the packing checked. The packing was found to be in good condition and the pipefitter started to replace the gland. At this instant there was a sudden discharge of hot product.

Both pipefitters were spray d about the head and shoulders and suffered face and neck burns. The product sprayed out for a very short period of time (seconds) in an umbrella effect. The fact that they both wore safety goggles undoubtedly prevented the incident from being more serious. The men were taken to the dispensary by their foreman and given emergency treatment.

Cause:

There were two contributing causes for the accident:

1. Lack of complete communication in establishing the scope of the work.

2. The location of valve in the lowest section of a series of transfer lines.

The liquid material that sprayed the area was apparently contained in a vertical section of 2" pipe, 4 feet high, immediately west of the 3-way valve. The material was suddenly released when the valve plug or packing moved.

The plant tagging procedure was not used, although personnel involved physically checked pumps and valves to determine whether they were in a safe position.

Preventive Measures:

The Committee recommends immediate action on the following:

1. Maintenance and Production personnel be made fully aware of the complete scope of every job, thereby enabling every man to fully evaluate all the potential hazards involved in a job.

2. Install drain lines with flanged gate valves on the east and west process lines at the 3-way valve.

3. The Maintenance procedure for working on a valve located in a trapped section of line shall be:

   The mechanic will wear a face shield and chemical goggles, break the flange closest to the valve using the standard safe method, i.e., open the flange away from himself.

4. All plant personnel should be re-instructed within the next two weeks on the use of the plant safety tag-out procedure.

Secondary Recommendation:

Investigate the process piping system centered at the 3-way valve and determine the possibility of simplifying transfer operations.

Superintendents will report status of recommendations to the Plant Manager bi-monthly, with copies to the Investigating Committee, until all phases of recommendations have been completed.

CASE HISTORY NO. 625

Vinyl Chloride -- Laboratory Accident

Description of Accident:

The employee was disposing of excess vinyl chloride sample quantities by discharging the material into the air stream of a conventional bench type laboratory hood. The sample containers are stainless steel tanks. round end - about 4" x 6". Connections are provided at each end to facilitate filling. The residual quantity usually amounts to from 200 to 400 cc. and at ambient laboratory temperature has a vapor pressure of about 60 p.s.i.

One such sample container had been inverted in a ring stand at the right side of the hood and the valve "cracked" to allow the vinyl chloride to drip into a beaker for evaporation. A two liter open-top Dewar cooling bath containing dry ice and isopropanol stood at the left. A sheet lead pan covered most of the bottom of the hood. The employee held a second sample in one hand, sloped the outlet downward and opened the valve; discharging VCl as a vapor-liquid spray onto the bottom of the hood. Within 5 to 10 seconds the vapors in the hood ignited and for a short period the upper half of the employee's body was enveloped in flames.

At this point the injured dropped the container to the bottom of the hood and retreated from the room. He was wearing a short sleeved shirt and the arm burns extended above the elbows. His face was burned but his eyes were protected by safety spectacles. His cotton work clothing did not catch fire nor was it scorched.

The injured then walked 60 feet down the hall to the lunch room to tell fellow employees of the fire and that he had sustained burns. He then went to the change room, 50 feet, to rinse his face and arms. Meanwhile the fellow employees summoned assistance which arrived within 5 minutes. The fire alarm system was not activated.

(Security personnel transported the injured to Medical immediately for treatment and subsequently to the City General Hospital by car where he was confined for one month under treatment by his personal physician.)

The fire in the laboratory room (door closed) continued unabated and undisturbed as the employees had heard two dull thuds issue from the fire area, perhaps two to three minutes apart, and did not wish to chance entering the room. These reports came from rupture of the stainless steel sample containers that were in the hood. The two containers "tore" into several pieces each, possibly indicating an accelerated rise to the area of or above the critical pressure (775# at critical temperature of 317°F) f vinyl chloride. These pieces were thrown across and around the laboratory room and produced some damage.

When the fire subsided, extinguishment was accomplished by the use of one 20# extinguisher.

Cause:

There are no electrical service connections in this hood and the hood contained no electrical equipment. The overhead light in the hood was protected by a "vapor-proof" globe but this was intact before the fire - the switch is external. The employee reports that whil discharging a sample in the same manner about one-half hour previously he noted a "tickle" in the palm of the hand holding the container, indicating a static discharge. He had never noted such an event and attached no importance to the incident. Such was not noted at the time of the accident but static appears to be the most reasonable ignition source.

It has since been established that a "fogging" discharge of vinyl chloride from such a container is capable of building a static charge of consequence. True gaseous discharge did not produce a charg that was measurable with the equipment available.

Preventive Measures:

1. All Control Laboratory employees have seen the USBM-AGA film on static electricity.
2. Flammables are being disposed of in open air with static grounds as needed.
3. Special disposal facilities are to be provided
4. In laboratory quantities of flammables are being held to an absolute minimum.
5. Long sleeves specified.
6. Hood ventilation being studied
7. Eye protection re-emphasized.
8. Sampling methods under study.
9. Problem of sample container pressure relief being studied.

CASE HISTORY NO. 626

Chemical and Thermal Burns

Description of Accident

A phenolic kettle operator opened the #3 kettle manhole during a class A cleanup and thereby permitted 100°C caustic solution (3-5%) to

boil over from the open vessel. Second degree burns were sustained on both legs (below the knees). Immediate flushing with water and medical treatment permitted the employee to return to work without loss of time.

According to standard practice a class A cleanup of the #3 phenolic kettle was initiated following the last of a series of 497 Varnish batches. This cleanup was started shortly after lunch on the day of the injury. A class A cleanup involves filling the kettle 2/3 full (approximately 2000 gal.) of cold water, introducing 600-1000 pounds of 50 per c nt caustic by applying vacuum to the kettle, venting the kettle to atmospheric pressure, application of steam to the kettle jacket and holding the kettl contents at 100°C for an hour. Normally the caustic solution is then cooled to 80°C, pumped to the hold tanks and then discharged to the sewer. In this case, however, supervision had instructed operating personnel to backflush the condenser prior to transferring the wash caustic to the hold tanks. Condenser backflushing is not a routine operation and is performed only when supervision determines that it is necessary. Backflushing is accomplished by circulating the hot caustic solution through a portion of the varnish transfer line and pump, then through a temporary rubber hose section which joins the varnish transfer piping and the kettle vent line (on discharge side of condenser), then back through the condenser into the kettle. The temporary connection to the vent line leads to a closed system when the necessary steam jet and transfer line valves are blocked.

At the time of the accident, one hose section had been attached to vent line and another to the varnish packout line. The two hose sections were not as yet connected. The injured had backflushed a condenser once before and was depending on his past experience plus verbal comments passed on by other operators on how best to proceed.

He recalled a conversation with another operator who had noted that before starting the circulating pump it was necessary to open the manhole to avoid a pressure build-up during the backflushing. He recalls performing the following sequential steps immediately prior to the accident.

1. Steam to jacket turned off but jacket not vented. Instrument charts shows 30 psig steam.

2. Within 30 seconds he loosened manhole and started to swing open.

3. As soon as manhole was lifted, hot (100°C) caustic solution boiled out, striking the employe at knee level.

4. At this point, the injured dropped the manhole cover and dashed for the nearest shower.

After flushing with considerable water, the employee reported to the infirmary and was immediately taken to the company physician and treated for second degree burns on both legs.

Cause:

The investigating committee discussed the accident with the injured employee, and other operating personnel. In addition, the various temperature-pressure instrument sheets were analyzed.

The committee has concluded that the kettle was under a slight positive pressure (1-2 psig) at the time the kettle manhole was loosened. In addition, since steam pressure was still on the jacket, the wash-solution was slightly superheated. Upon opening the manhole cover, the wash solution boiled vigorously and splashed out of the open manhole.

The committee is of the opinion that three factors led to the accident. These are as follows:

1. The fouled condenser led to the pressure build-up in the kettle.

2. Lack of a specific procedure to cover this type of operation.

3. Vent facilities are not provided which are independent of condenser and thereby are subject to plugging.

Recommendations:

1. Clean condenser.

2. Install kettle vent line off inlet condenser head.

3. Prepare detailed procedure covering backflushing operation.

4. Discontinue use of temporary rubber hoses for handling hot caustic solution. Install a permanent line.