TELEPHONE HUDSON 3-6126

Manufacturing Chemists' Association, Inc.

(FOUNDED 1872)

1825 Connecticut Avenue, N. W.

WASHINGTON 9, D. C.

August 1965 Issue

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.

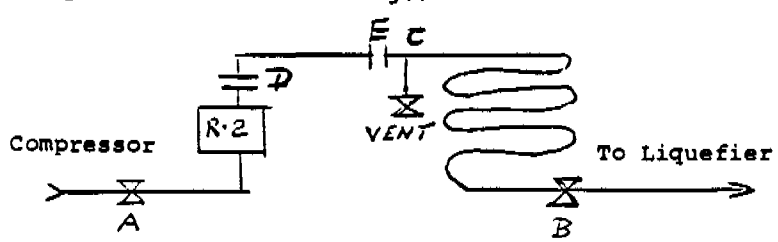
Reader's Comment on Case History No. 1111
"Oxygen Incident"

Preventive Measure A refers to installation on each cylinder of a two-stage regulator. This is one way to lick the problem and perhaps it is economically feasible on a manifold that accommodates only four cylinders. Most industrial and hospital oxygen manifolds however are made for a much larger number of cylinders and a regulator on each cylinder would get pretty expensive. There are oxygen manifolds available from a number of reputable suppliers which have been tested and listed or approved by Underwriters' Laboratories and by Factory Mutual and I believe that the use of such an approved manifold would generally be a better way to solve such a situation.

CASE HISTORY NO. 1112

Operator Burned When Block Valve Fails

Description: A rugged converter had been shut down, block valved from the system, and depressurized in order that the catalyst could be replaced. As the operator loosened one bolt on flanged spool "E", a small flow of gas was heard. He then tightened valve "B" further and the gas flow stopped. Two operators then removed all bolts and disconnected flanged spool "E". They then began disconnecting flanged spool "D". When all but one bolt had been removed, one operator walked away. At that time gas suddenly surged and ignited, severely burning the other operator on arms and legs.



Cause: Failure of valve seat due to thread on seat being tapered.

Preventive Measures:

1. Entire plant to be shut down and system depressurized before start of maintenance work.
2. Installation of double block valves, with bleeder valve between.

CASE HISTORY NO. 1113

Vinyl Chloride Fire

Description: In a vinyl chloride production plant, a caustic scrubber vessel was isolated from the system and was being prepared for a periodic recharging. The scrubber lid was opened and by a visual check, it was established that the inlet valve to the scrubber was partially plugged and not completely closed.

The engineer on duty was consulted as to what might be the way to proceed to get the valve freed of the plug and also the valve closed.

It was decided that heat (steam) be applied to the valve and by alternately opening and closing the valve, the problem might be overcome.

Since the vessels, columns and furnaces in this area are out of doors (not confined to any building), the wind direction is important in precautionary measures to be taken when a vessel is opened. In this particular instance the engineer mentioned that the wind direction was from the north so that in the unlikely chance any vinyl chloride vapors were freed, they would be blown in a direction that would not sweep them to the furnaces (approximately 150 feet away). The lid was swiveled into position but was not bolted. The valve was heated and on the third opening and closing of the valve, the plug was suddenly released.

This pressure pushed the swiveled lid

to one side and a geyser of caustic solution and vinyl chloride went up into the air, raining down on the four men below. Two of the men ran away from the area in a direction away from the furnaces but the other two ran in a general direction towards the furnaces.

One of these two stepped under a shower and wet himself down. The other employee apparently had gotten no caustic on him and decided to go back to the scrubber to check the valve. He was caught in a wave of flame as he approached the scrubber. Apparently he ran to the shower and doused the flames but the burns he received resulted in his death five days later.

Cause: The fire was caused by the ignition of large quantities of vinyl chloride vapors by the furnaces. The large volume of vinyl chloride came from the caustic scrubber and was released by the unsafe operating method in an attempt to remedy an abnormal situation. Three attempts were made to seat the valve with the top manhead closed but not bolted. This method of reseating had been used in the past except in this case the top head was not bolted down.

Preventive Measures:

1. Change in procedure for recharging scrubber.
2. A detailed procedure for preparation of scrubber for maintenance will be written using a safety check list.
3. Automatic steam snuffing will be incorporated into the emergency gas cut-off switch. This could prevent flammable vapors from being sucked into a furnace and ignited by the hot brick even though the gas to the burners was off.
4. The use of a closed vent system for all low level relief valves in the units will be re-evaluated.
5. A high vent system is being studied.
6. Relocation of the caustic scrubbers is under consideration.

CASE HISTORY NO. 1114

Anhydrous-Ammonia Handling

Description: About half-way through the unloading of a 40,000 lb. anhydrous ammonia tank truck, a stream of ammonia was noticed leaking out of the bonnet of the stop valve on the liquid unloading line at the tank. The truck was immediately taken off the line and the storage tank vented to the AN neutralizing pit to relieve its pressure.

In the meantime, the acid mechanic investigated the leak and determined that the bonnet on the valve was cracked and nothing could be done short of replacing the complete valve.

Considerable time and difficulty were encountered in reducing the pressure on the tank sufficiently to stop the flow of liquid ammonia as there is no shut-off between this valve and the tank. However, by using the Frick compressor and exhausting it to the atmosphere, the pressure on the tank dropped sufficiently to install a new valve with the aid of a Scott Air-Pak mask.

Investigation: This storage tank is part of a typical anhydrous ammonia system containing 4 storage tanks in all. Two of these tanks are used for the AN neutralizer through a separate piping system except for the liquid unloading line which is common to all. The tank in question plus the fourth tank are heated and segregated for AOP use.

Ammonia is received by tank truck and unloaded through a combination of the truck's liquid pump supplemented by the plant's Frick compressor. The pressure on the line at the time of the incident was estimated at 140 psi.

Valving on both tank systems are similar employing Vogt 120 series Ammonia Valves (300 lb) and all valves are at ground level except emergency shut-off valves in the older AN neutralizer tanks which would have helped considerably in this situation had they been available on the tank involved.

Examination of the valve afterwards revealed a 2½" crack following the transition line between the rounded body and flatten bonnet flange with a bonnet stud in the center. For a closer examination of the 'break' metal, the cracked section was broken loose from the body requiring only a light hammer tap. The thin white sections were bright metal and were all that held the valve together. The remaining area of the 'break' had been dulled somewhat but the absence of rust leads us to believe it was a 'fresh' break.

Conclusion: The incident was a result of a flaw in the valve coupled with an induced strain from excessive pressure on one of the stud bolts. The strain probably occurred when the valve was overhauled two months ago although the mechanic who did the job does not recall any difficulty. He has done the same job many times in the past.

Action Taken:

1. Publicize this incident as an illustration of the dangers in handling anhydrous ammonia and the need for careful cleaning of gasketed surfaces and uniform take-up on holding nuts.
2. Install emergency shut-off valves on the liquid ammonia lines as close to the tanks as possible and set-up a schedule to test periodically to insure ease of operation during emergencies. These valves will also assist in the periodic renewal of the lead seats of the regular stop valves.

3. Replace all 300 lb valves in the liquid lines on the AOP (heated) storage system with 600 lb valves to provide a greater margin of safety. This is recommended in the engineering standards. Such valves are now in service on all ammonia lines in the AOP but were not originally specified on the storage tanks.

Armed Services Explosives Safety Board
Case History

CASE HISTORY NO. 1115

Caustic in Aluminum Tank Trailer

Description: In the course of trying to recover some monochlorobenzene (MCB), we almost had a very serious accident.

The MCB has been stored in a tank for about two years. There was a trace of phosgene in the MCB when it was put in the tank, and it had slowly hydrolyzed. We used 25% caustic to neutralize the acid values, but ran into an emulsion. To break the emulsion, it was pumped through a filter into a mild steel tank trailer, starting on a Thursday.

On Saturday the trailer sprang one leak which was patched. Again on Sunday, it started to leak.

On Monday we called the tank trailer manufacturer and told them what the problem was and that we needed another mild steel trailer to replace the one we had. Later the same day the second trailer arrived. We then started to pump from the leaking trailer into the new one through a filter. After about ten gallons had been transferred, the filter started to leak.

It took about half an hour to repair the filter. As they were getting ready to start the filter pump back up, a supervisor climbed on top of the trailer to check the flow. He looked in the hatch cover and saw that the material in the trailer was boiling or effervescing. A closer inspection of the trailer showed that it was aluminum and the caustic was reacting to form hydrogen.

The contents of the trailer were dumped and nitrogen hose was used to purge the tank. Simultaneously, the trailer was washed with water.

CASE HISTORY NO. 1116

Platform Truck -- Operator Walked Backward

Description: Employee was leading a loaded power platform truck out of a storage area perpendicular to the aisle. He was walking backward in order to guide his load past other loaded skids in storage without damaging the material. As he turned his truck into the aisle he backed against another platform truck which was parked, perpendicular to the aisle, in another storage area across the aisle from where his load had been stored, pinning his lower right leg between the two power trucks.

Cause:

1. The employee was walking backward while leading a truck and did not see the obstacle behind him.
2. The parked platform truck was too long for the storage area and was parked partially in the aisle.
3. The employee did not exercise precaution required to safely move equipment and load along the aisle.

Preventive Measures:

1. Employees have been re-instructed to look in the direction of travel.
2. Arrangements are being made to provide more working and storage space in this area.

Also see Case History No. 1101

CASE HISTORY NO. 1117

Maintenance

Description: Two men were removing a 6 inch flanged gate valve from a horizontal pipe. The valve was near the floor and was very rusty. They removed all the nuts and bolts from the flanges except the ones on the bottom of each flange and then attempted to rotate the valve on these bolts to break the joint. Being unsuccessful, they attempted to spread the joints with an hydraulic jack In order to steady the jack while pressure was being exerted, one man held the jack in place with his hands next to the valve. As soon as the pressure was exerted, the joints between the flanges released. Due to the high center of gravity, the valve rotated on the two bottom bolts and pinched the tip of the man's finger between the valve and the jack. This resulted in an amputation of the tip of the finger.

Preventive Measures: A third bolt inserted in an upper hole would have prevented the valve from falling.

CASE HISTORY NO. 1118

Laboratory Incident

Description: A solvent in contact with an open gas flame caught fire. Property damage was slight; however, a supervisor received an arm laceration requiring 12 sutures. The

supervisor elected to us a gas burner rather than a heating mantle to prepare two liters of a flammable solution in a stainless beak r in a hood. While turning off the gas he inadvertently tipped over the beaker and the contents ignited as the solution ran to the floor. He left the laboratory to obtain water, shutting the door behind him. Upon his return, he had to break the glass to unlock the door and lacerated his forearm. Other employees quickly quenched the fire by using various types of fire extinguishers.

Cause:

1. Not securing equipment
2. Use of improper means of heating

Preventive Measure: Use mantles

CASE HISTORY NO. 1119

Hydrochloric Acid

Description: Employee was filling small bottles with product which contained a small amount of hydrochloric acid. Some of the product spilled over onto his apron, ran down the legs of his trousers and into his safety boots. The employee did not flush his feet off with water immediately and he sustained chemical burns of both feet.

Cause:

1. The bottle filling station was a temporary set-up and awkward to work around.
2. Employee failed to comply with previous instructions and did not water flush the product off immediately, nor did he report to First Aid until the following day.

Preventive Measures:

1. The equipment has been realigned to provide for easier handling.
2. Additional protective equipment, such as personal protective equipment,is being provided.
3. Proper handling of hydrochloric acid is being reviewed with all concerned personnel.

CASE HISTORY NO. 1120

Dryer Explosion

Description: Trays of a granulated product wet with alcohol were placed directly in a recirculating electrically heated dryer. A short time later the flammable vapors reached the explosive range and presumably were ignited by the thermostatic control or the heating elements. The dryer was completely damaged, many windows were broken and considerable glassware in a nearby laboratory was shattered by the shock wave. Damage is estimated at $17,000 but fortunately no one was injured as the explosion occurred during a rest period.

Cause: Operating instructions called for placing the wet material in a humidity controlled, air-conditioned room overnight in order to evaporate most of the solvent prior to placing the product in the dryer. The air in this room is not recycled. This incident clearly illustrates, however, that it is hazardous to use any equipment with ignition sources in processing flammable material. It should be noted that even single pass air-conditioned rooms can be unsafe for handling flammables.

CASE HISTORY NO. 1121

Peroxide Detonation

Description: Fifty ml of mother liquors from a hydrogen peroxide oxidation reaction was being concentrated in a rotary vacuum evaporator. Approximately five minutes later there was a typical severe peroxide type detonation which destroyed the 100 ml glass flask and shattered powdered and broken glass throughout the laboratory.

Cause: Although it has not been determined why the aqueous ethanolic mother liquors detonated, it is believed that the peroxides in the solution were concentrated to the critical point. All vacuum operations should be shielded to protect laboratory personnel from flying glass in the event there is a detonation or the glassware breaks or implodes while under vacuum.

FGS:cm
10/11/65

TELEPHONE HUDSON 3-6126

Manufacturing Chemists' Association, Inc.

(FOUNDED 1872)

1825 Connecticut Avenue, N. W.

WASHINGTON 9, D. C.

October 1965 Issue

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.

CASE HISTORY NO. 1132

Accidental Release of Vinyl Chloride - Three Fatalities

Description: Release and ignition of a large volume of vinyl chloride monomer resulted in three fatalities.

The immediate cause of the vinyl chloride release was the removal of the manhole cover on a reactor which was in service. The maintenance rigger was removing the manhole covers from an adjacent reactor which was ready for cleaning w' he apparently became confused and removed th.. cover from the reactor in service, under pressure. The large volume of vinyl chloride thus released ignited, probably due to a static spark, and the ensuing flash fire resulted in the death of the rigger and two laborers who were standing by for cleaning. Although human loss was severe, equipment loss was nominal and the fire was quickly brought under control.

The man performing this work was experienced and familiar with the job and the equipment involved. Very careful check-off procedures to prevent just such an occurrence did not protect the men from this one lapse of consciousness of which reactor was in service and which one was to be cleaned.

Cause: Mental lapse - process equipment opened under pressure.

Preventive Measures: Work permit and tagging procedures as well as steps essential to insure adequate communications between operating and service personnel have been carefully reviewed. The real lesson is the danger of complacency which can result from long-term repetitious conduct of hazardous work. Frequent reminding by supervisors and constant alertness by the men performing the work is the on'.. real protection from such occurrences. F ..er measures have been taken to prevent recurrence, specifically: (1) Padlocking the manheads and controlling the issue of keys, and (2) installing a running light at the manhold location.

CASE HISTORY NO. 1133

Operator Knocked Off Trailer

Description: An equipment operator was reversing acid out of a well back into an acid trailer tank. One tank was full, so the operator picked up the 2" (steel) transfer line to move it two to three feet to the opening of an adjacent tank. When he picked up the line, a pocket of gas in the line caused it to whip, knocking him off the trailer. He fell approximately five to eight feet to the ground, suffering a dislocated left shoulder and fractured right wrist.

Cause: An operator (employed 6 months) had not been properly instructed in the job procedure for this operation.

Preventive Measures: Supervision will be held responsible for the instruction of new employees on proper job procedures.

CASE HISTORY NO. 1134

Foot Caught in Shear Point

Description: An employee was operating a scrap bailer in the raw materials department. The hopper that lifts the scrap from the floor level into the bailer compressing chamber was in a raised position. The operator was standing at the control panel. When he switched the lever to lower the hopper, he walked toward the pit where the hopper recesses into the floor. As he neared the pit he apparently slipped on the floor plate, and his foot was caught between a flange that had been welded to the h pper and the edge of the pit. The hopper came down on his left foot behind the steel cap of his safety shoe. His injury consisted of a severe laceration, contusion and fracture of the left little toe.

Cause: The cause is attributed to unnecessary exposure. The employee allowed himself to become exposed to a known hazardous condition.

Preventive Measures: The control lever used

to raise and lower the hopper shall be changed t make it necessary for the operator to remain at the panel control out of the hazard area until the hopper has completed its cycle and comes to rest in the recessed pit. This will be accomplished by installing spring loaded buttons for the raising and lowering of the hopper. Any time the operator takes his finger off the control button the hopper will stop, regardless of position. This type of control will serve two safety functions:

1. Prevent operator from exposing himself to a shear point.
2. Provide an emergency stop.

CASE HISTORY NO. 1135

Acid Spray from "Empty Line"

Description: Two maintenance men were assigned the job of removing the bonnets from two 6" acid valves. The circulation pump had been shut down to allow the acid to drain back into the pump tank. A 4" valve on the pump discharge is throttled at this point to between two and three turns open to control the rate of drain-back and to prevent reversal of the impeller. It is necessary that the 4" valve on the top of the tower be open to permit the acid to drain back. The drain-back described usually is accomplished in about 25 minutes. Approximately 2 hours after the drain-back it was necessary to close the 4" valve at the top of the tower. With the valve at the pump highly throttled, it is believed all of the acid in the coils of the cooling tower had not finished draining when the valve at the top of the tower was closed. With this valve closed, the acid piping was no longer vented and residual acid would cease draining. It is believed this was the condition that existed when the mechanics started to remove the bonnets. Before starting the job they put on the required personal protective equipment, namely; rubber pants and jackets, plastic gloves, hard hat, face shield, and eye protection.

There are two identical systems, north and south, and each contains a 6" valve from which the bonnet was to be removed. The mechanics followed the prescribed procedure for breaking open an acid line by partial loosening of the bolts to control leakage if any should occur. The bonnet was removed from the north valve without event. No acid was present and no leakage occurred. However, when the bonnet on the south tower was loosened, acid sprayed out from between the body and bonnet with force and in considerable quantity. Both mechanics were sprayed with acid. One received minor burns to his arm and both feet. The acid got up his sleeve, onto his arm and ran off his pants onto his feet. The spraying acid hit the other mechanic in the face shield and neck area causing second degree burns t left ear, left side of face, neck and upper chest. It should be noted that these burns would have been more severe if he had not been wearing a face shield.

Cause:

1. The 4" valve above the pump was not opened after the normal drain-back. This would have overcome the effect of the valve being throttled more than the operator realized--causing acid to remain in the piping.
2. Not knowing the acid was present in the piping system.
3. The fact that the joint between the body and bonnet is of a spigot design made it difficult for the mechanic to provide enough looseness for a leak to show if there was acid present and still be able to retighten the bolts to stop the leak. With a spigot design, a fairly good seal could well be maintained while the bonnet was being raised, and this would continue until the spigot cleared the top of the well. At this point the area through which the acid flows would increase rapidly and little control could be maintained by tightening the bolts.

Preventive Measures:

1. Review the findings of this investigation with all personnel.
2. Make it a part of shut down procedure to open the throttled valve to a wide open position at the conclusion of a drain-back.
3. A study will be made to determine where vent and drain valves should be installed in these circulating systems so that a test can be made that will tell if the pipe system is drained or not.

CASE HISTORY NO. 1136

Corrosion in Sodium Cell

Description: An operator was burned by molten inorganic salts unexpectedly discharged from a sodium cell. Investigation disclosed that corrosion had occurred to the steel cell base adjacent to graphite anodes creating two holes through the base into the principal water cooling system. The 600°C. molten salt rapidly converted the cooling water to steam which forced the bath out of the top of the cell.

Cause: The corrosion is believed to have be caused by cracks in the electrodes at the upper surface of the base plate.