

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 -- 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 $\frac{5}{16}$ -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.

CMA 015555A

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) of 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 while 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 charge 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