UNION CARBIDE INTERNAL CORRESPONDENCE

CHEMICALS AND PLASTICS

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Suspension Vinyls Staff

DATE October 31, 1977

SUBJECT Vinyl Chloride Safety Association Meeting - October 6 & 7, 1977 Valley Forge, Pennsylvania

From: R. L. Frantz

This regular meeting of the Association had a record attendance of eighty-three members from virtually all of the domestic VCM and PVC producers as well as representatives from several foreign countries, including Canada, Mexico, U.K., Germany, Italy and Norway. Union Carbide was represented by Mr. R. N. Wheeler and the writer. A complete attendance list will be mailed to me; if any of you are interested in receiving a copy, let me know.

The first item on the agenda was a discussion of the physiological effects of VCM by Dr. R. W. McBurney, a physician from Diamond Shamrock. Some highlights of his presentation were: VCM is a relatively non-toxic chemical - it can cause narcosis and even death by asphyxiation. It is detoxified in the liver. Its target is the lining of small blood vessels and can cause Reynaud's phenoma by plugging up the blood vessels in the end of the fingers which can lead to AOL (loss of bone structure in the end of the fingers). It can also cause cirrhosis of the liver, enlargement of the spleen and of course angiosarcoma of the liver. Angio is Greek for worms (small blood vessels) and sarcoma is cancer. All of these effects are rare. VCM is a very weak carcinigen - only one in 3400 of those who've had prolonged, extended high exposure to VCM developed angiosarcoma. It is not a risk for workers exposed to from one to twenty-five ppm (his opinion, of course). VCM is picked up in the blood and transferred to the liver and lungs - is expelled through the lungs. A question from Herm Waltemate of B. F. Goodrich to Dr. McBurney was of perhaps more interest than Dr. McBurney's answer. It was "Is it more likely to get angiosarcoma from ingestion than from breathing?" The answer was "No". It was pointed out that there have been sixty-four deaths attributed to angiosarcoma over the last twenty-five years.

A brief discussion of OSHA related problems followed a presentation on medical surveillance and brought forth these items of note:

1) Air Products allows outsiders in the regulated area for forty-five minutes if the monitors show less than 5 ppm VCM.

2) Several companies report only large emergency VCM releases to OSHA. Someone stated that there is an OSHA program directive which says that OSHA should be notified if an employee is exposed to 100 ppm VCM without a respirator. Others said they report only when an employee is exposed to a massive release in an emergency situation. In the absence of exposure, need not report to OSHA.

3) A poll showed that 18 - 20 companies do not allow fertile females to work in regulated area, while ten companies do.

Herm Waltemate of B. F. Goodrich reported on a rash of OSHA inspections at nearly all of their VCM - PVC plants early in August of this year. There were several non-serious citations most of which did not relate to VCM. B. F. Goodrich has a serious problem at their Louisville location - the employees do not believe the monitoring data; they believe the VCM levels are higher than indicated. The OSHA inspection at Louisville was the result of a union complaint and lasted twelve days. B. F. Goodrich said 80% of their OSHA inspections resulted from employee complaints.

In the last two years, nineteen companies reported OSHA inspections; thirteen times OSHA sampled for VCM; three citations because 1 ppm was exceeded. Air Products got a citation for re-entering the area after an accident without monitoring. Firestone was cited for using a MSA mask with a Scott canister.

Both Dow and B. F. Goodrich are testing badge monitor devices.

Four companies use area monitors only for compiling personnel exposures; seven use area monitors plus carbon tubes and the rest carbon tubes only. Only Pantasote who uses the Eicom monitoring system felt that there was good correlation between area monitors and carbon tubes. The rest felt that area monitors generally gave slightly higher results.

A poll on average VCM concentrations in the reactor area showed:

< 0.5 ppm	- 2	
0.5 - 1.0 ppm	- 6	
1.0 - 2.0 ppm	- 8	(I voted here)
2.0 - 5.0 ppm	- 8	
> 5 ppm	- 0	

There was a 50 - 50 division between having VCM unloading facilities regulated all the time and only when unloading VCM tank cars.

B. F. Goodrich reported that 75 - 90% of their area monitoring points were below 1 ppm.

The range of area monitors was from 0 to 10 ppm up to 0 - 3600 ppm. Most use VFA's; three or four use IR. Nine have more than one sample point per reactor.

Alarming at 1 ppm	- 9	
Alarming at 5 ppm	- 14	(UCC)
Alarming at 10 ppm	- 1	
Alarming at 25 ppm	- 1	
Zone Alarms	- 11	
Only control room alarms	- 7	
Alarms @ each point	- 9	(UCC)
Lights & audible alarms	- 19	(UCC)

David Kuhn of Conoco gave an update of EPA activities since October 21, 1976. Nothing much was presented that we have not already received from Nick Wheeler.

There seemed to be general agreement that by law all VCM relief device openings and blown rupture discs should be reported to EPA; however, I had the impression that it was pretty common not to do this. I described briefly the problem we had with RB-90 discs not opening fully and that we were going to the S-90 type (without knife blades). There was considerable interest in this and I went into greater detail with several people who inquired about it after the meeting.

Some discussion ensued on testing and inspecting VCM storage tanks. Most have T & I schedules of five years or more - some of twenty-five years. One case of checking inside VCM storage tanks after seventeen

years and finding no corrosion.

Bob Wilson of Stauffer presented a list of information on changes in DOT regulations for VCM tank cars - head protection, thermal protection, new type labels, etc. From what I've seen of UCC's new VCM tank cars, I believe that our Distribution Department must be tuned in to all of the new requirements.

Next was "True Confessions".

Leading off was a very complete slide presentation, including some excellent photography of an explosion and fire at the Primex 80 MM pounds per year PVC Plant in Pueblo, Mexico. On June 19, 1977 all six of their VCM storage tanks were destroyed by fire. They had six (4 - 90,000 lb, 2 - 60,000 lb) above ground horizontal VCM storage tanks located ten feet apart. Cause of the accident was human error and described as follows:

> An experienced (ten years in this department) employee was assigned to remove a malfunctioning actuator from a remotely operated, spring loaded Tufline valve on the bottom of one of the VCM storage tanks (33 meters long, 3.3 meters diameter). He had done this job many times before since this seemed to be a recurring problem. Instead of removing the actuator from the valve, he started removing the bolts that held the valve onto the tank. All the bolts came out and a three-inch stream of liquid VCM started spilling out the bottom of the tank. A large vapor cloud just drifted back and forth. People inside and outside the plant were told to shut off sources of ignition. Water was sprayed on the vapor cloud. Yet, one hour and twenty minutes after the incident started, there was a visible cloud 1100 feet long, 800 feet wide and five feet high. One hour and twenty-five minutes into the incident the cloud ignited 400 feet south of the spill from outside the plant.
>
> Four people were injured, one who was outside the plant using a fire hose died eight days later. Damage was three million dollars. Black smoke towered 1000 meters high. The fire caused a chain reaction ultimately catching all six of the VCM storage tanks on fire. One tank was still burning the next day. Pictures of one tank which was aluminum (just a melted blob) and one tank which was completely flattened were impressive.

Interesting to compare with our C-1 accident are some figures which were quoted. The steel storage tanks were 5/16" carbon steel rated for vacuum to 150 psig service. One tank traveled through the air 540 meters ($\sim$ 1780 feet) after it over-pressured. Other large sections went 300 meters and 200 meters .

Safety valves on the storage tanks were sized by the ASME code, not the NFPA code which calls for larger capacities.

Primex plans to install a big sphere for VCM storage designed for vacuum to 90 psig, put a big pond of water under it, insulate the bottom half and size the safety valves per NFPA Section 56 for LP Gas.

The next "True Confession" was a brief description of Carbide's Labor Day Explosion of Non-Solvent C-1 Autoclave at Texas City presented by the writer. Since the investigation team had not yet issued its report, I could not give the cause of the accident or very many of the details. I did promise the group a more complete report at a later date. In answer to a direct question, I did state that equipment failure was not a factor.

Next, Esso in Sarnia, Ontario reported they had noted chloride stress cracking in two 304 S.S. pressure vessels adjacent to welds. Vessels had been in VCM service since 1966 under a range of temperatures from 50°C to 85°C (probably resin stripping tanks). They did not find such cracking in 316 S.S. NOTE: I discussed this with Bill Ashbaugh and he indicated that there should be no difference between 304 S.S. and 316 S.S. in this respect.

Following a presentation by Amos Dixon of Goodyear on Safe Methods For Handling Peroxide Catalysts (all of which we follow with the exception that we do not have a back up diesel generator) there was one final "True Confession" show stopper by Pete Bogart of Tenneco. At one of their New Jersey PVC Plants they had the first incident in history where a water sprinkler system caused a fire. They have a water deluge system inside their catalyst storage freezer. Due to a hydraulic shock caused by suddenly shutting water off the system, a water line broke flooding the walk-in freezer with three feet of 75°F water (catalyst was supposed to be kept below 28°F). Several hours later the catalyst started to decompose. No one was hurt, but they lost $4,000 worth of catalyst. A poll showed that of eighteen companies that have walk-in cat storage freezers, nine have water deluge systems inside. Carbide does not.

One final note of interest. During a discussion of methods of VCM Emission Control from vents a poll was taken which showed twenty-five locations are using or plan to use incinerators (most with scrubbers in conjunction) - seventeen of these will have duplicate incinerators, since on stream time is only 50 - 90%; six locations have opted for absorption in solvent and five locations for carbon adsorption.

As usual, this meeting was very worthwhile with many mutual items of safety discussed in an open and frank manner.

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February 13, 1978

TO: MEMBERS OF THE VINYL CHLORIDE SAFETY ASSOCIATION

Attached is a report of the explosion at Union Carbide's Non-Solvent (Carbide bulk process) PVC Plant at Texas City, Texas on September 5, 1977. Distribution of this report to the permanent representative of each member company of the Vinyl Chloride Safety Association is one way Union Carbide is notifying other members of industry of the causes and details of this incident. Please route this report to others in your organization who may be interested.

I believe you will find the report of considerable interest and direct your special attention to the Appendix which describes the nature of a phenomenon called "homogeneous nucleation". As stated in the report itself, this phenomenon apparently played an important part in the highly destructive detonation following the overpressure of the autoclave.

Any constructive comments about the reported incident will be welcome.

Sincerely,

Robert L. Frantz

Robert L. Frantz

RLF/st
Attachment

REPORT OF INVESTIGATION OF EXPLOSION OF VINYL RESINS AUTOCLAVE

AT UCC, TEXAS CITY

At 2:36 a.m. on September 5, 1977, the C-1 Non-Solvent Unit autoclave at Building 119 overpressured and exploded during a routine startup of a vinyl chloride polymerization reaction. The resultant fireball was approximately 300 feet in diameter and debris was hurled over a large area. One two-ton piece of the autoclave shell was blown 1600 feet, indicating the force of the explosion.

Two operators sustained serious burns: Mr. P. R. McCrory, Chief Operator, who died at 12:51 p.m. on September 8, and Mr. J. L. Ingram, who was released from the John Sealy Burn Center in Galveston on November 23, 1977 after 80 days of treatment. Six months convalescence is expected.

Most damage to facilities was in the Non-Solvent Area.

The start-up phase of this type of polymerization normally consists of batch charging chilled monomer to the reactor with agitators running and metering in the desired amount of catalyst through an orifice run. At this time steam is introduced to the reactants through a bottom nozzle to raise the temperature and pressure to the desired operating levels. It was not uncommon to have to reintroduce steam to maintain operating conditions in the early reaction period. In the 29-year history of this operation at Texas City, there have been over 10,000 previous start-ups without serious incident.

This incident was caused by an overcharge of Isopropyl Peroxy Dicarbonate (IPP) catalyst. Approximately 30 to 40 times the normal charge of catalyst was introduced, we believe inadvertently, through a tubing by-pass triggering a runaway reaction. The runaway reaction was subsequently confirmed by laboratory tests to occur at startup operating temperature if 20 times or more than the normal IPP catalyst charge is present.

The runaway reaction experienced was of such extreme intensity that it could not be contained by our standard design and operating practices, which are equivalent to or exceed industry standards. Once it was initiated, it could not be detected early enough by normal operating actions to be brought under control by emergency procedures.

No mechanical defects were found in the design or condition of the equipment and eyewitnesses confirmed all safety devices functioned as designed.

Metallurgical examination of recovered pieces of the autoclave indicates the initial vessel failure was in the head and was caused by simple overpressure. Subsequently the vessel failed catastrophically in a brittle fracture mode, with failure originating in at least twelve sites in the lower shell of the autoclave. This second failure occurred in milliseconds causing high speed cracking with chevrons in the clad-steel portions, followed by non-ductile shear failure in the upper third of the vessel, which was constructed of solid stainless steel. An eyewitness confirmed the vessel failed first in the head.

There appear to have been at least two deviations from the standard operating procedure: (1) the water blowback feed to the catalyst feed line was not set up properly using a double valve and vent system to isolate it from the catalyst header, and (2) the agitators were not turned on! The first deviation allowed the huge excess of catalyst to be fed, initiating the runaway reaction. The second deviation escalated the event from a limited overpressure failure and fire to an overpressure with subsequent highly destructive detonation caused by homogeneous nucleation (see Appendix).

The emergency response by the plant fire squad and operators in adjacent units was truly outstanding. Their prompt and effective actions undoubtedly prevented subsequent secondary problems. Close adherence to established vinyl chloride protection procedures prevented exposure of emergency and rescue personnel and others in adjacent areas to vinyl chloride. Vinyl chloride fueled fires were not extinguished until the source was secured. Even though no exposures to vinyl chloride were known to have occurred, all personnel involved were offered medical consultation.

To prevent recurrence, the following key recommendations have been offered:

A. Catalyst should be batch charged for startup of autoclaves.

B. Cross-ties to the catalyst system should be eliminated.

C. Agitators and steam (the heat source) should be interlocked to prevent heating up without agitation.

D. UCC should initiate a survey to identify systems within the Corporation with potential for homogeneous nucleation and to notify other members of industry of the attendant hazards of this phenomenon.

R. J. Taylor

F. S. Provenzano

January 18, 1978

APPENDIX

Nature of Homogeneous Nucleation Phenomenon

Homogeneous nucleation can be the ultimate result when a volatile liquid is heated in the absence of nucleative surfaces where bubbles can form. (Boiling chips are used in laboratory glassware to provide nucleative surface.) In the complete absence of such surface, the liquid can be superheated substantially above its boiling point. However, ultimately a superheat heat level is reached where the liquid nucleates homogeneously -- that is without external nucleation sites. This can occur with detonative speed, with the superheat being released and transformed into vapor in a period of one millisecond or less.

One requirement for the occurrence of homogeneous nucleation is that liquid is superheated to a temperature at least 90% of its critical temperature, on an absolute basis. The other requirement is an absence of sites for heterogeneous nucleation.

Detonations have been demonstrated to occur when liquified natural gas and water were suddenly contacted. The research is still in its infancy but has proceeded far enough to demonstrate the detonative forces that can be developed. Some work has also been done to define the regions in the pressure-temperature relationships where homogeneous nucleation is possible.

Most of the work to date has been limited to the investigation of situations where two immiscible liquids are suddenly contacted (e.g. liquified natural gas and water). However, the phenomenon can also apply to appropriate situations in a single liquid phase.

In mid-November, a consultation was held at the UCC Charleston, West Virginia Engineering Center with Dr. R. C. Reid of MIT, one of the principal researchers in this field. After a detailed discussion of the C-1 incident, Dr. Reid concurred that homogeneous nucleation would explain the detonation mechanism.

He placed special emphasis on the importance of a sudden pressure letdown (or heat up) in triggering this type of event, pointing out that superheat is quite difficult to maintain if the pressure letdown (or heat up) is gradual. Mechanisms for slow heterogeneous nucleation are virtually always present to some degree. Hence, he felt that the drastic venting associated with the head rupture was a key triggering element. He agreed, however, that homogeneous nucleation can occur without a sudden pressure release.

He also emphasized that even a small superheated region in the body of the liquid is sufficient to initiate a detonation in which the rest of the fluid becomes almost instantaneously involved.