AIR PRODUCTS & CHEMICALS INC.

CHEMICALS GROUP

CALVERT CITY, KENTUCKY

TECHNICAL DEPARTMENT

TRIP REPORT

VINYL CHLORIDE SAFETY ASSOCIATION

JOHN T. BARR

FEBRUARY 17, 1971

Place:	Memphis, Tennessee
Date:	February 10-11, 1971
Personnel:	John T. Barr
Report By:	John T. Barr
Distribution:	Copy No. 1 - R. C. Burnham 2 - W. D. Draffen 3 - R. R. Harvey 4 - W. T. Langston 5 - T. G. McClary 6 - J. P. Parker 7 - F. C. Rehberg 8 - H. L. Watson 9 - Circulation 10 - File

The second formal meeting of representatives to the Vinyl Chloride Safety Association was held at Memphis, Tennessee on February 10, 11, 1971. Thirty-five people attended, representing all but two of the domestic producers of monomer or polymer, plus Gulf of Canada and ICI. Two minor changes in wording of the By-Laws were approved. It was reported that the SPI was agreeable to accept the group as a sub-committee, and the officers were instructed to proceed with further investigation. This would require that all member companies also become members of the SPI, if they do not already belong. A motion to fix limits on financial obligations of members was tabled until the outcome of the SPI affiliation is known.

The general tenor of the meeting continued as a frank and open discussion of various incidents which had occurred in plants, their cause, and means of prevention or minimizing damage from the release of vinyl chloride vapor. Many of the hazards and solutions are common to our PVA and Emulsion plants, as well as the PVC area.

I. Major Accidents

Mr. E. A. Rose of Diamond discussed their accident. The primary cause was release of vapor from a freshly-charged reactor upon failure of about 11 inches of CRT gasket on the large cover needed in older reactors for removal of the fixed-blade agitator. This had accidentally been damaged in cleaning and the non-corrugated metal filler was blown out. It had possibly been weakened by corrosion, for it had been in service several years. Three potential sources of ignition were listed:

a. Static generated when the material foamed out and liquid spray evolved.

b. Vapors reaching a gas-fired drier in an adjacent area. A fire door was found open and there was a "secondary" explosion in the drying tower, but no soot was seen.

c. A start-stop station hanging from a conduit box near the gasket was found blown off after the fire. This could have been severed by the vapor stream, or knocked off later by the explosion.

Damage was generally confined to the siding and services. No major structural damage occurred. One man died in the drying area from a combination of burns and injury when a pallet of bags fell on him.

They have taken the following preventive steps:

1. Ground off the glass from the faces and welded up the 36" opening. (The insurance company described this step as "precipitous".)

2. Forbidden the wearing of any short-sleeved clothing and any synthetic materials. Several other companies indicated that they had similar rules, both for static prevention and personnel protection.

3. Blocked up the fire door openings.

4. Added more escape ladders.

5. Removed all remaining glass-lined pipe and minimized use of CRT gaskets generally. An inspection program, including retorqueing of gaskets was instituted.

6. Installed an automatic vapor detection and deluge system.

7. Welded stainless collar on manways and installed quick-opening heads, with Buna-N O-rings.

8. Revised and checked the electrical system. Another company reported that they had found that vinyl chloride is a good solvent for the cement used in seal-offs, with the result that a pin-hole in a dP diaphragm or thermowell resulted in monomer in the MCCs.

9. Instituted a Loss Prevention study comprised of seven groups to make a continuing study of operating practices and safety conditions.

Mr. E. T. Biehl described the 1968 fire at Atlantic Tubing. This resulted when an operator failed to position properly a soft asbestos manway gasket, and it blew out on reaching operating pressure. Static is given as the probable source of ignition. The greatest damage was caused by the fall of the reinforced concrete roof, which raised some 20 feet.

An old-type MSA detector was in operation, but was stepping on a point remote from the leak, and neither it or the rate-of-rise deluge system activated automatically.

The plant has not been rebuilt, and is in litigation with the insurance company who feels it can be rebuilt as is. The company disagrees, principally because many reactor nozzles were displaced up to 10° from normal by the falling concrete.

The plant was insured by FIA and rated the safest plant in the state in 1965. Since that time, over $250,000 was spent in additional safety devices, principally on demand of the town.

Mr. C. Thompson of Tenneco reported on safety steps taken in rebuilding their plant in New Jersey. This fire was described in a previous trip report, but occurred when a man slipped and broke the handle off a ball-type bottom valve with it in an open position.

Their new plant is 350 feet away from other installations, 150 feet from their property line. An elaborate bottom valve system is shown in the attached sketch. This was pointed out as not giving them the alternate of dumping a reactor when the detector system is showing vapor present.

The new plant has a deluge system that is activated by the vapor detector at 40% LEL or manually. An emergency control board for critical activities is located in a remote bunker. The deluge system gives 0.35 gpm/ft.^{2} on floor and tanks. Water supply is 1500 gpm @ 100 lb. backed by 2-2500 gpm emergency pumps. The ventilation system runs at 15 changes per hour in winter and 30 in summer, taking air in from roof level and discharging laterally across each floor, and the emergency system adds another 30 cph. It is activated manually or at 20% LEL by a 24 point J&W sensor with the heads 9-18" from the floor. This is one head for every 600 ft.^{2}.

They appear to have overreacted to their particular prior problem and ignored others.

They emphasized the following points which they had learned:

1. Do not move injured persons further than necessary for their immediate safety until trained personnel can take over. A burned man was hauled around in a pick-up to his detriment. Diamond confirmed this point.

2. Do not put out fires from storage tanks until authorized. They had considerable trouble with the local fire departments wanting to extinguish the small storage tank that burned 6 days, but considered it safer to let it burn than release monomer.

3. Be prepared to face the great amounts of water to be disposed of and the HCl fumes generated.

4. Emergency plans should be tested and retested under plant conditions as well as on paper. Particular emphasis should be given to long-time situations (manpower, water and food, etc.).

Goodrich described an occurrence in Mexico in which an operator realized that he had an overcharged reactor and let some of the mixture into an overhead foam trap (they strip in the reactor). Here it polymerized without agitation or cooling, blocked the entrances and reliefs and detonated, throwing the tank head over 650 feet.

The Lake Charles monomer plant fire occurred when mechanics removed a check valve for cleaning in a coked-up line from a DCE cracking furnace. While they were at the shop, another plug in the upstream line blew out because a gear-operated valve had its position indicator installed wrong at the factory. This dumped several thousand gallons of DCE-VCl mix which was ignited by the furnace. Most of the damage was in electrical and instrumentation.

Mr. Bill Boyle of FIA delivered the dinner address. He highlighted the fact that in the 6 1/2 years ending June 1970, FIA had losses from 14 vapor cloud explosions totaling $17 MM. Three of these were in PVC and cost $8 MM. (There have been five major losses in PVC since 1955, four since 1965, with total losses of $10-12 MM and ten deaths.) Their actuarial loss is about $1 MM/yr., and they will, of course, attempt to recoup this.

He stated that FIA was in favor of using open head deluge systems with Grinnell T-2 or T-4 heads at 0.35 gpm/ft.^{2}.

He complimented the group on its formation, and expressed the hope that the PVC industry would see the same sharp drop in accidents that the Rubber Association did after its formation. Prevention of spills from operator and mechanical failures and prevention of ignition after release are most important, in his opinion.

He expressed concern about possible static problems in solvent cleaning, and hydrogen peroxide handling problems in the Goodyear catalyst system.

FIA feels that prevention of ignition can best be achieved by installing a high-turbulence deluge system for mixing, diluting, and cooling, and by proper dissipation of the cloud by good ventilation.

II. Fire-Water Systems

A considerable portion of the discussion was devoted to deluge systems. Dick Schwab of Allied described the installation at their Painsville Plant. It consists of an open head system activated by either fusible heads or a J&W detector set to alarm at 20% and trip at 40% after a 15-second delay for confirmation. It covers at 0.35 gpm/ft.^{2}, and is fed by two 2000 gpm @ 125 lb. pumps, one electric, one diesel-driven. Air flow is in at the roof, through the grating floor and out at ground level. Detectors are at every other exhaust fan. Normal rate is 10 changes/hr., increasing automatically to 20 at 20% LEL. There is battery power on the J&W system, and valves are air activated so it is not affected by power dips. It has tripped several times in four years of service, on leaks and cleaning procedures. There have been no fires.

Danny Dowell of Goodrich stated that they found a open-head system to cost about twice a standard closed head. They also experienced tripping with a 15° HAD system on kettle heat-up cycles, so while deluge is quick and thorough, it is expensive and requires too much water. They installed a fog system on the premise that a humidity of over 85% was adequate to prevent static ignition. Reference was made to National Fire Protection Bulletin 77, 1955. They use Spray Systems nozzles 1/8 G643W that deliver 1.3 gpm in 10-foot circles. Trouble was experienced with carbon steel lines, so they now use PVC or galvanized, with a Vokes filter with 20 mil clearances. On a summer day, they raised the relative humidity from 53% to 85% in 1 minute, and to 90% in 1.5 minutes. The idea is to dissipate potential static, and the system is backed up by a standard closed head system.

I asked the question if anyone had considered the possibility that activating a fog or deluge system in an explosive atmosphere could cause a static discharge before the desired wetting down had occurred. There was no answer.

Bob Allen of Conoco described the installation in their new Oklahoma plant. They asked FM for permission to install a dam on the reactor head that would be flooded and cascade water down the vessels. This was denied because FM had data that indicated that excess heat would direct the flow away from the affected area. This was believed to have come from some Automatic Sprinkler films concerning flammable liquids, and may have been the result of deposition of hydrophobic soot on the walls. They thus installed individual vessel protection heads on each vessel.

They were also refused approval for fog only because of lack of data, but added a system to the required deluge. They chose to add a low pressure steam header to the intake system to get humidity control.

They have a J&W multiple point system that alarms and speeds up ventilation at 25% LEL, and activates deluge and fog at 50%. This costs them about $1,000 per head installed. This cost could double if the control panel was also explosion-proof. There are three other companies other than J&W and MSA now active in vapor detector instruments, but none have installations in PVC.

Conoco obtained permission to split the deluge headers into 8 sections with outside lines and shutoff valves (100 feet from the building) to conserve water in case of a header breakage or localized fire. They expect to be required to lock the valves open. It was commented that various FM offices often issued conflicting requirements.

Other features of the Oklahoma plant include outdoor reactors, a normal 10 change/hr. for air in the enclosed area, increasing to 20 at 25% LEL, manual activation buttons by doors and at remote points, life lines leading to exit points (several companies emphasize this because of smoke, fog, and disorientation of men in an emergency), remote control on all operating valves, and optional evacuation instructions dependent on wind direction, point of release, and other conditions.

Four present PVC installations have the old MSA stepping-type vapor detector, five have the new continuous samplers, and seven are planning installations, all J&W.

The magic number of 0.35 gpm/ft.^{2} is believed to have arisen in the forties from work done by the Rubber Reserve that demonstrated that a water flow of 0.35 would protect a vessel containing flammable liquid such as naptha in a fire situation so that the then accepted relief valve criteria would be adequate. It has no bearing on structure protection or jacketed polykettles, especially ones with a live charge. Every incident involving power loss has resulted in reactor venting, deluge or not. Fortunately, all of these had adequate velocity to throw the plume above the fire and did not result in further explosions. Six installations have auxiliary power, and several others have dual sources, such as we have. Most explosions and fires have resulted in such extensive damage to electrical systems that auxiliary power would have been of no use after the fact.

III. Vapor Disposal

The disposal of vented vapors, air from the work area, etc. is still in much dispute. A few companies have common headers and knock-out pots leading to remote areas, but report high maintenance. Some keep steam sparges going to assure good velocity. Codes require the next larger vent valve or disk size because of back pressure. Those who use only rupture disks are not sure how to detect pin-holes. One has put a J&W head in the line.

Vertical vent stacks from rupture disks or relief valves are required by some insurers to have weep holes or drain valves to prevent water buildup. These are a source of trouble from plugging. Some people try to keep out rain by the use of extension pieces such as we have for our stacks, but have not installed yet; others put plastic or rubber buckets over the open ends. These are difficult to install. Almost everyone who had tail pipes cut at 45° report serious damage to piping or nozzles from the side reaction, and now use a square-cut pipe and adequate anchors.

IV. Reactor Cleaning

Nine companies, including Escambia, now have some sort of high pressure reactor cleaning. The reported license fee for the Goodrich procedure is $50,000, and no one reported having taken the license. Glenn of General Tire described theirs. It was built using a surplus Moulton-Gaulin homogenizer and delivers 26 gpm @ 3000 psig. They have other surplus pumps available. It is located away from the reactor area for use in exchanger cleaning, etc., and has remote start-stop on the reactor floor, as well as micro switches on the drop header connections. Some people have put shields around the quick-disconnects to guard against hose or coupling failure. Their driving force for installation was the AOL problem, as well as to shorten cleaning time.

No system was reported to be completely adequate, and still required some periodic hand cleaning. This is why Escambia is going to solvent. However, General Tire reports that addition of 2.5 ppm talc, detergent, etc. greatly improves performance. Mill or untreated water is required. Deionized water has generated static. Those who have a system use steam, water, or short bursts from the high pressure gun to humidify the reactor, even after testing for vapor, to eliminate static.

Details on mechanical construction are available if needed, both on the General Tire and Escambia systems.

V. Gaskets

Numerous gasketing problems were revealed. Use of CRT (envelope) types is decreasing because of poor quality control, high costs, damaged faces on glassed nozzles, and the rapid rate of polymer buildup on exposed surfaces. These should have corrugated liners rather than plain, and should be retorqued, especially around agitator entrances, on a regular schedule to allow for compression of the asbestos. The same precaution goes for lead envelopes.

Asbestos appears to be a satisfactory pipe flange gasket. Buna-N or Viton-E seem most popular for O-rings and soft gaskets.

Several companies report trouble with poor quality control on both dimensions and cure. They test one of an incoming lot before placing in stock, and report much better service after returning a few shipments. The importance of continual retraining of operators and mechanics on proper placement and installation was emphasized. (viz, the Thompson and Atlantic Tubing fires.)

VI. Ignition Sources

Static electricity is often blamed for ignition when nothing else can be found, and so is falling into disrepute as a catch-all, yet its dangers are very real. Much of the efforts in fog and deluge systems is to prevent its occurrence. It is nevertheless always present in air transfer lines and even in apparently well-grounded pipes that transport non-conductive liquid. Some companies have grounding programs similar to that in our vinyl plant. Several report static discharges from handles of sleeve-lined valves. Some types of these have an internal grounding spring, but these often are left out by the factory or on repair. Bottom filling tanks are standard, and a few forbid synthetic clothing.

Few comapnies have had the Bureau of Mines demonstration that we witnessed. It is reported that Ethyl Corporation has a training film, and that Carmody Trainer has a demonstration kit.

In an effort to eliminate other ignition sources, the required distance between buildings is being increased, up to the 350 feet reported by Tenneco, and such auxiliaries as motor control centers and control rooms are located 60-100 feet away from vapor sources. A few fires have been caused by moving equipment, similar to our recent compressor incident.

About half of the companies have some sort of control room as opposed to all instrumentation in the reactor area. Most of these are of standard electrical construction, are pressurized at 0.1-0.2 inches H_2O/in.^{2}, and generally do not have windows. They are for operator and equipment protection, and require the men to move out to the floor for normal work activity. Only Conoco and the new Goodrich plant seem to be very far along toward remote operation.

VII. Explosion Suppression

Mr. M. Charney of Fenwal gave the Thursday luncheon talk and described their explosion suppression devices. These detect the pressure wave that travels in front of an explosion, or the ultraviolet radiation of the source of the fire, and snuffs the fire by explosively releasing Halon 1301 in sufficient quantity to reduce the flammability. They have 450 installations, and average 50 activations per year, with no explosion to date. The largest area that they have been able to protect is 50,000 ft.^{3}, and they are not yet ready to try the system on reactor areas.

In response to my question, Mr. Charney stated that they had tested PVC dust, and found it "extremely difficult" to ignite.

VIII. FIA Test Program

The purpose of the proposed FIA program which was circulated earlier is to test the suppression of ignition of VCl vapor clouds by deluge, fog, and water curtains under conditions similar to most present operating installations. They hope to have the program designed by March, and bids back in May. The present cost is estimated at $50,000. FIA will pay $5,000 and the cost of publication. They think some other outside money will be available, but hope that the industry will provide primary support. Escambia has offered the use of its land area for the tests.

IX. Miscellaneous Items

Isoprene and either styrene or α-methyl styrene are the most popular short-stops, but all agree that these are of little value in power loss. Venting gives some cooling and agitation, but offers the problem of low-velocity vapors.

Several companies have experienced bomb threats. They have generally tied their procedure for this to their standard emergency procedures, head counts at mobilization points, shut down drills (or tag-out dry runs). Searches are by

volunteer groups, with Police and outside Fire Departments on stand-by only. Those involved attempt to minimize external appearances of such occurrences, on the grounds that this is what the caller desires. It is reported that Army Ordnance groups will assist. There have been seven threats, one case of fire bombs thrown over the fence. Three companies have procedures, seven are preparing them. All companies which have had occasion to use them comment on the value of continuing drills for emergency procedures.

Only one company has reported any problem with uninhibited monomer, and this was thought to be due to a car containing oxygen. Diamond has a plant much like ours with the recovery system a part of an old VCl plant, and thus subject to long hold times. They add ammonia to a pH of 8 and avoid trouble.

J. T. BARR

JTB:sl