

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

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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.

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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 retorquing 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.

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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.

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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.

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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.

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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.

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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 companies 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.

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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

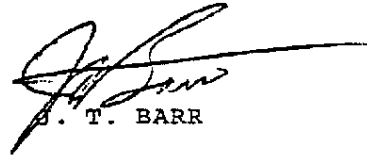
Isoprene and either styrene or α -methyl styrene are the most popular short-stops, but all agree that these are of little value in power loss. Venting gives some cooling and agitation, but offers the problem of low-velocity vapors.

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

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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 VCI plant, and thus subject to long hold times. They add ammonia to a pH of 8 and avoid trouble.



J. T. BARR

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AIRCO CHEMICALS & PLASTICS DIVISION

Air Reduction Company, Inc.

Calvert City, Kentucky

PROCESS ENGINEERING DEPARTMENT

TRIP REPORT

VINYL CHLORIDE SAFETY ASSOCIATION

J. T. Barr

June 10, 1970

Place: Point Pleasant, West Virginia

Date: May 26-27, 1970

Personnel: J. T. Barr

Report By: J. T. Barr

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C. C. West
9 - R. C. Burnham
10 - J. P. Parker

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The attached list of 35 persons from 22 companies producing or polymerizing vinyl chloride were present at the first full scale discussion of safety by a group which hopes to formalize into a group which meets regularly. The meeting was very successful from the standpoint of free and open participation and should be very useful in promoting safety in the industry.

A copy of the proposed program is also attached. We only managed to get through the first eleven items because of the extent of the discussion. Some notes on the more interesting discussions are given below, following the same numbering system.

1. Peroxides

Well over one-half of the companies represented stated that they used Nash Pumps either alone or in combination with reciprocating compressors, and that they had some sort of pH control on the seal water fluid, often including the addition of phenol. Almost none of these people reported that they had experienced serious difficulty with peroxide build-up in the recovery system. Those people who used only reciprocating compressors reported a constant problem with peroxides, and many of them did not seem to be aware of the relationship of these peroxides to air leaks. Union Carbide reported that they had a routine steam-out procedure which seemed to be satisfactory for removal of the peroxides and prevention of a dangerous accumulation.

Almost every representative there indicated that they had had some unfortunate experience with sensitive initiators such as IPP or Lupersol-11, and most of them have fairly elaborate temperature alarms and remote storage facilities despite which they still have experienced difficulty. I did not get any feel for a number of people who were working with Vazo or in-situ systems, and one would expect that they would not have mentioned this subject, but there did seem to be a general feeling that there must be a better way than using IPP and most people spoke disparagingly of it.

2. Emergency Agitation

About one-third of the representatives indicated that they had emergency power available at their installation. Most of these were people who were hooked into private power grids where prolonged interruptions were frequent. Hooker stated that they had 100% emergency coverage for their 60 million lb./yr. bulk plant because there is no water present in the system to act as a moderator and they average four severe interruptions a year. Stauffer reported an average of six interruptions a year and thus had adequate economic justification for their installation. Conoco

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stated that they had a common vent header to a 70-foot stack through which steam was being continuously sparged to dissipate the vinyl vapors from emergency venting. A few other companies reported similar common vent systems with and without knockout tanks in order to remove some of the liquids and solids. This brought on a lively discussion as to the merit of such a system, and most people seem to feel that dumping the contents of several reactors into an unagitated and uncooled knockout tank invited more trouble than blowing it directly out.

New Jersey now has before its legislature a law requiring emergency power in PVC plants, and FIA is being very insistent with its clients that they install this equipment.

The industry appears to be about equally divided between those who have a permanent system for installing shortstop, those who have no system and those who have a temporary system such as a portable charge bomb. It is surprising that there are any portable charge bombs left, and there will probably be fewer after this meeting in which two members described serious explosions from the use of these portable units in trying to charge IPP into their reactors.

Styrene and isoprene were the two shortstop materials that seemed to be in most general use. None of these actually gave permanent termination of the reaction and none are particularly useful in the absence of agitation, although one person mentioned that they had had some success in sparging nitrogen in the bottom valve and venting monomer out the top in order to get a small degree of agitation during the power outage. The degree to which it stops the process depends on the stage in the polymerization cycle, with one gallon of styrene giving about one hour delay. The general reaction appeared to be that when agitation is lost, one should begin to vent the reactors later in their cycle because they probably can be saved without excessive material loss. Reactors earlier in their cycle probably cannot survive a power outage of more than a few minutes.

3. Automatic Spill Detectors

About one-half of the members utilized some type of automatic explosive vapor detection. This is now being required by FIA on all new installations. MSA was first in this business with several installations being made in 1965 and 66, with which people had very poor experience. This probably explains why we were unable to buy such a system from them in 1967 when we tried. Their equipment is now reported to be much improved and is almost on a par with Johnson and Williams who seem to have the best reputation. Davis Emergency also sells a system, but no one there felt it was adequate.

There are two general types of systems in use. One is a multi-point sensor which samples various areas of the building sequentially, and which is usually arranged to hold on a point where it senses an appreciable vapor concentration and remains there until the concentration falls back to a pre-determined level. The other type system is a multi-point diffusion system in which all points are being monitored continuously. The majority favor this latter type because of the delay in the stepping system. Tenneco points out that their explosion occurred less than four minutes after the initial spill, and that most stepping systems have at least a five-minute cycle.

The usual arrangement for an automatic detector system is to have it set so that at 25% of the LEL for vinyl chloride an alarm is sounded and emergency fans are turned on. If the concentration continues to rise to 50% of the LEL, an automatic deluge system is activated. The users reported that seldom did the concentration exceed 25% that it did not go on and pass the 50% point, and that operators soon learned that when the alarm went off they were going to get wet pretty quickly.

The control consoles should be away from the operating area and should not have manual selector switches so that they can be fixed on a single point. They should be behind some sort of blast wall such as is recommended for operators protection, and there should be several manual deluge switches in areas remote from the building.

There was considerable discussion about what constituted adequate ventilation - whether it should be from top to bottom or bottom to top, or even whether there should be an attempt to dissipate a spill outside the building or keep it confined inside. As might be expected, the proponents of these various beliefs based their arguments upon the physical arrangement of their plants, and those who had adequate separation between areas were in favor of maximum venting and dissipation, while those in congested areas favored confining it. Thompson's new plant will have a maximum air change rate of one per minute, and they are maintaining 300-foot spacing between major areas.

The cost of a totally engineered package from Johnson and Williams, including instrumentation for the deluge system, was reported at about \$30,000. MSA is presently charging about \$5,000 for their console only, and one person stated that a reasonable installed estimate was about \$2,000 per sensing point.

4. Inadvertent Opening of Valves

It was generally agreed that despite all that could be done in the way of operator training, interlocks, and check lists,

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that it was impossible to be completely assured that there should be no accidental dumping of monomer. Nevertheless, a number of companies have gone to extreme lengths to minimize the probability of such an occurrence. Dow uses a common key lock on the bottom dump valve and monomer charge valve so that neither of these can be opened unless the other is shut. Hooker has an electro-mechanical interlock between these two same valves. Several companies have interlocks between the manway and the monomer valve. Most companies use elaborate check lists with double sign off procedures. The tendency in the industry is to go to slow opening valves as opposed to ball valves. New Jersey is now considering a law that all terminal valves on hazardous service must be blinded, and there presently is a law that requires blinding of all valves to reactors before men may enter. Monsanto has a policy that all terminal valves are wheel operated. Most people reported that if they used diaphragm valves, they had a back-up plug or gate valve. Several companies including Escambia use Yarway or Strahman rising plug valves in the bottom of their reactors. To avoid operator strain, a portable air driven hand gun is used for opening and closing by several plants. These are the same type that many people use to assist in rapid opening and closing of the manways. Several persons reported they had had unfortunate experiences with air positioners on critical valves which had not been arranged in a fail-safe position on air loss.

The general feeling seemed to be that most plants were getting more and more complex in their instrumentation in an effort to avoid mechanical or operator failure, and that this complexity was reaching the point that it reduced the efficiency of the plant. Several expressed the opinion that the next logical step was to completely automate the plant and thus remove as far as possible the chance of human error.

About one-third of the companies indicated they use some sort of a quick opening manway and that these generally were considered safer than the standard Pfaudler manway. Also, one or two had experienced a partial opening of the manway or a gasket blow-out when an attempt had been made by an operator to open the manway while pressure was still on the vessel. One company had arranged an instrument so that if it sensed more than 1 psig inside the reactor it applied 60 psig to an air cylinder which opposed the operator's attempt to turn the opening lever.

5. Reactor Cleaning

My report on the MCA study on AOL indicated that they had strong statistical probability that this resulted from prolonged exposure to reactor cleaning work. There was some

further discussion of this problem at the meeting, but most of the participants in the MCA study objected to full disclosure of the results of that study due to the non-participants. It was stated by Goodrich that the incubation period appeared to be at least 12 months, that the incident of development among reactor cleaners was below 3%, and that if the degeneration was caught before it proceeded too far there was a good chance of a full recovery upon removal from exposure. They and several others, therefore, check all applicants and workers in the polymerization area once a year by what is called the "cold insult" test which indicates the onset of the disease by identifying the sensitivity to cold of the skin and hand. One representative said he knew of more extensive work which was being carried on in France by a private company. In connection with this, authorities there indicated a more wide spread incidence of the disease there than in this country. He had no further details that he could disclose. A copy of an article from the Journal of the American Medical Association has been circulated.

Because of this problem, and also because of the large number of persons who have been injured in one way or another in working inside reactors, it is the tendency in the industry to avoid entering reactors whenever possible. There is a very wide-spread use of the high pressure lance, although this has its own dangers and is not completely adequate, but it does prolong the interval between hand cleaning. Other companies open and rinse down with relatively low pressure water between each batch, and a number of companies use solvent cleaning. The latter method seems to be primarily in use with stainless reactors, although at least one company does use it with glass.

There has been at least one fatality with the high pressure lance, and several persons have been injured. It is difficult to get all portions of the dome clean, although a T-nozzle on the end to counter-balance the thrust makes it easier to get into out-of-the-way places. It is a line-of-sight cleaning system and will leave shadows, and it requires special care to avoid puncturing the rupture discs and the envelope gaskets.

Goodrich showed a short film of a device which they have developed and are willing to license, which they call the HRC (for hydraulic reactor cleaning). It consists of a rotating spindle on the end of a rotating adjustable arm which fits through a flange which is seated on the manway. This can be moved up and down while the high pressure water squirts from the two ends of the spindle as the whole system rotates and, therefore, presumably covers most of the interior of the vessel. It is said to take a man with a portable lifting unit about 20 minutes to clean a reactor after it has

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been opened and purged, and that with longer use the performance becomes more satisfactory. It is still necessary to enter the vessel about every 9-14 cycles to get to the dead spots and check the glass and do other necessary work. The rupture disc is checked after each cleaning with a mirror, and it has been found that many vessels required the installation of a deflector plate to prevent the high pressure spray from damaging the disc.

Most companies who use the high pressure lance from an external position, use a combination of dead man grip and time delay to avoid injury to the operators and find that they must take special precautions for preventing abrasions and excessive flexing of the high pressure hose where it makes connections with the high pressure header or the hand gun.

6. Remote Cut-Offs

Ray Asti of Stauffer described a very elaborate storage sphere protection system which they have in their plant. They have on each sphere a manual plug valve, an excess flow valve which is made up of a fixed orifice sized to give a flow no greater than twice the normal pump rate, a thermal cut-off valve which is a Fisher air loaded valve and Fenwall thermoelement combination and an automatic downstream shut-off valve which can be operated remotely or by a high signal from the pressure drop across the fixed orifice excess flow valve. These are also interlocked with the normal charging valve and the pump motor. If any of these systems operate in the emergency mode, the deluge system automatically operates. This deluge system consists of HAD heads which are tested once a month and all the valves are soft-seat valves good to 500° F. and are supposed to be well covered by the deluge system. There are in addition hand plug valves outside the firewall. Very few other persons indicated that they had any such elaborate system as this, although most seemed to have some parts or combination of the one described above. Great American has an air operated ball valve on the bottom of all tanks inside their building which can be closed from either of two remote locations. Several have similar systems on their day tanks and weigh tanks. Fusible-link valves are also in use.

A discussion arose over the use of teflon seals and seats since these will fail under severe fire conditions and allow a continuing leak. Ethyl reported that they used A-20 construction in their first plug valves for fire protection but this, of course, assumes that one can reach this valve to operate it.

There was also considerable discussion about whether storage tanks should be diked, if so, whether the dikes should retain

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liquid under the tanks or drain it to a safe area away from the tank storage area or what should be done with major spills. Again as in the earlier discussion on releases within the reactor area, the answers were varied as the physical arrangements of the plants. All persons agreed that one of the major problems with dikes was keeping a dike drain valve shut, and several expressed the hope that some bright engineer would invent an automatic system for draining water from within a diked area that would not let vinyl chloride escape.

7. Emergency Procedures

George Speed of Escambia described a method by which they have recently developed a new emergency procedure manual for their plant. The supervisors made a list of all probable emergency conditions which they could foresee and assigned an equal share of these to each of the foremen for a write-up of the proper procedure for that particular emergency. These were reviewed with the operators, discussed in the weekly safety meetings which are held between the supervisors and the operators, rewritten several times and finally issued in the form of a booklet. Major features of this booklet include a map which shows the location of all the remote deluge and emergency fan trips and indicates the area to which the persons directly involved in that operating area and the people in adjacent threatened areas are to report. It also includes a list of types of fires to be expected and how each type of fire should be combatted. A third section concentrates on how to handle major leaks, spills and emergency venting. There is a special section on handling of runaway reactors. The final section concentrates on actions to be taken in case of loss of utilities or natural disasters. Each section and each example was quite specific on who, what, when and how. It particularly emphasized who was in charge of each group and what area of responsibility he had.

All new operators were thoroughly trained in these procedures, given a copy of the manual, and the completed manual was reviewed further at each weekly safety meeting. All persons are given fire training at least two times a year and are put through dry runs for various emergencies using a tag-out system in which the person attaches a tag with his initials at the proper valve or switch to indicate that he has completed his assigned responsibility at that point. The shift foremen have the primary responsibility for training with the supervisors checking on the progress of the program. The men participate directly in the training by such methods as having one man demonstrate to the others how a Scott air pack is used or some other similar emergency step.

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A general discussion arose over who should have the authority for initiating an emergency procedure. Those persons who had experienced disasters in their plant were particularly emphatic that any person who saw an emergency develop should have the authority to sound the emergency alarm and start the evacuation and disaster control procedure. They agreed that there was no time to go look up a supervisor and request permission for this step. Most plants appear to have an emergency system which concentrates primarily on removing the personnel in the area from danger and initiating emergency ventilation and/or deluge systems. After the persons have retreated to a safe area and evaluated the problem, a responsible person then initiates any action which may be taken inside the danger zone. The first step is always get the personnel out to a safe point.

Providing a safe point to which people may go which is within reach in a reasonable time seems to be a source of difficulty of many plants. The desirability of blast walls and reinforced control rooms was widely acknowledged as was the fact that most plants don't have them. Several persons commented on the fact that they met with a number of surprises when they attempted to check out safe and speedy methods of egress finding such things as doors which opened inward, areas which could soon become impassable because of smoke or heat and other unforeseen safety traps. Several persons pointed out that in the case of a major spill or fire, it was only a matter of a few seconds until visibility was too limited for a person to orient himself, and that this offered particular danger to men who may have been working within reactors or vessels and who suddenly emerged into a smoke filled room.

A point of emphasis was that air packs, masks, tools, control valves, etc., should be located in a safe place outside the probable danger area.

There was complete agreement among those who had been faced with an emergency that the most efficient tool which they had at their command was a well-written and previously well-rehearsed emergency procedure.

8. Rupture Discs and Relief Valves

About one-half of the companies indicated that they use the same combination of rupture discs and relief valves which we have here. About one-third seemed to use relief valves only and the others used rupture discs only. Two companies used two rupture discs in series and one of these was quite surprised to learn that the reason that his had not been working successfully was probably because of pinholes in the lower discs allowing pressure to build up between the two. Not all of the companies were aware of the ball check valve of the type we use here. Some used pressure gauges only or

test valves. Mr. Boyle of Monsanto, who lead this discussion, published an article in Chemical Engineering Progress, August 1967, on the sizing of relief areas for polymerization reactors. This article is available in our library. Some of the general points of design which he brought out were as follows:

One should use the lowest possible setting to gain the maximum efficiency.

Discs should not be used above 80-90% of their rating because of slow tensile failure.

Reduction of the pressure drop in the piping after the relief device is most important because of the two or three phase flow which occurs and that swaging up to a larger size either before or after the relief device is necessary for adequate protection on many vessels, particularly the older Pfaudler glass-lined reactors which provide only minimum size nozzles.

Any vent system should have a drain on it at the lowest point to assure freedom from rain water and other condensate.

The use of plastic bags over the vent pipes to prevent rain or foreign matter from entering is not advisable because these can generate static sparks when they are removed suddenly. One company reported that they used an over-sized sleeve welded away from and above the vent pipe, and that this was successful in diverting most rain away from entering the vent simply because most rain does not fall vertically.

Conoco reported that they felt a safe design criteria was that complete venting of a freshly charged batch within 30 minutes should provide sufficient autorefrigeration to control that batch. This, of course, is not true for a batch that has been allowed to overheat so that polymerization rate is greater than normal.

Design should be based on exotherm conditions existing at the time of relief, and the most viscous probable mixture (slurry) should be used for sizing.

Monsanto and Firestone continued the discussion which had begun earlier on the use of knockout and separation lines to a common vent or flare, and persons who had used this system reported that it took extraordinary maintenance and inspection to assure that the lines remained free and open and that in many cases, it was impractical to design one that would handle an entire plant.

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9. Dryer Fires

I described briefly our experiences with the two occurrences within the past year, and several other companies indicated that they had had similar experiences. All concurred that our diagnosis here that the event was not actually a fire caused by ignition but rather from oxidation of the charred remains of PVC which had lodged in the dryer throat was probably the proper explanation. Several companies indicated that they inspected their dryers as often as once a day. Several companies never experienced this, and others have seen it sporadically. In once case, the burning apparently continued long enough that exit air became hot enough to fuse the product collector bags.

At this point, the program was interrupted for a break, and upon reconvening a member asked for comments from the floor on the use of copper bearing materials in areas which might have occasional exposure to small amounts of vinyl chloride. It was a general consensus of opinion that since vinyl chloride no longer contains substantial amounts of acetylene that the use of copper bearing materials in such areas as bearing races, instrument bellows, and air line connections outside of the process and similar areas where there is not a constant contact with vinyl chloride should offer no hazard.

10. Vessel Entry Procedures

Included at the end of this report is a copy of the vessel entry form which is used by Tenneco when having a reactor cleaned. They have separate forms for every regular operation which is performed in their plant plus a special form for non-routine jobs. Every item on every sheet must be checked by at least two persons, and in many cases a third person, normally the supervisor, must also check on critical steps. The forms are usually kept one month after completion of the job and then discarded.

In this particular operation, the cleaner and his buddy, who remains outside the vessel, are responsible for checking all of the steps of the entry and close out procedures, and the supervisor or foreman makes the final inspection. They are required by law to provide an oxygen reading before a man can enter a closed vessel, and they also check for explosive vapors. The man entering the reactor wears horsehide wristlets without a line being attached. There is available at the reactor a cart which contains an air cylinder and two face masks with 50 ft. hose, a safety line, an alarm and a lift winch. If the buddy has reason to believe that the cleaner is in difficulty, he sounds the alarm, puts on one of the face masks and carries the other face mask and the safety line into the vessel and places them on the cleaner.

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By the time this is done, the alarm should have summoned other persons on the reactor floor who operate the winch and remove the cleaner.

The reactor cleaner is provided with a tool bag similar to a carpenter's apron for carrying the tools. This avoids injury in many cases when a person slips. An exhaustor must always be in the manway when the man is working inside the vessel, and many people indicated that they took the air from outside the building so that in the event of a spill the person in the reactor was protected. Some companies blow air in the bottom opening, but most blow in the manhole, as we do. The MCA currently lists 50 ppm as a maximum concentration of vinyl chloride vapor to which a person should be exposed. This is far below what is generally accepted as a safe concentration, but nevertheless, is currently being enforced in several areas.

A few companies are using the safety carts of the type which we have, but others have run into difficulty from both unions and state authorities on their use. Many persons have gone to low voltage lights inside the reactor to minimize the danger of electrocution in case the bulb is shattered. Some people preferred nylon loops to wristlets, but others who do use wristlets use horsehide because it remains more flexible when wet than does other leather.

Tenneco pointed out that their various safety procedures and job sheets have been arrived at after thorough discussion and review with the men who actually perform the work and that safety analysis and instruction always started with the why and the how and the how not using as much feed back as it was possible to obtain. They felt that this paid off in obtaining better morale and cooperation than would have been possible with ready made procedures handed down from above. Several persons pointed out that management should participate in the tests, surveys, plannings, dry runs and other steps that are necessary to arrive at safe and useful procedures and systems. The operators gain confidence when they see their supervisors participating in the drills and training.

11. Deluge Systems

The deluge system in use at Allied consists of an open system which is designed to provide 125 psig from a balanced header to give a coverage of 0.35 gpm per ft.². This magic number of 0.35 is a hold over from old Rubber Reserve days and while it has not been demonstrated theoretically, it has been shown by experience to be a satisfactory rate of coverage in most cases. Their system is activated by either a rate of rise detector or by a vapor detector. There are also manual trip switches at several exterior locations. All of their major valves and risers are behind a blast wall.

The principles in favor of a deluge system are that they are supposed to reduce the equipment below the automatic ignition temperature and thus prevent start of a fire. They cool vessels and prevent release of material into the area. They are reputed to knock down vapor clouds, although this is a somewhat questionable point, and they require less water and equipment than do high pressure fog systems. There were those there who favored high pressure fog, but admitted that the equipment and water costs were considerably higher than that of deluge systems and that a person caught in a fog could be endangered by lack of oxygen if the fog were really doing the job for which it was designed.

One point which was repeatedly emphasized by all those in the discussion was the necessity for protecting the electrical supply and the main valves and risers from damage by explosions and the desirability of a method for shutting off unneeded sections of a system so that water could be conserved for use in the areas where it was most necessary.

In response to my question concerning the effectiveness of the heat rise shields on fusible sprinkler heads, a statement was made that only 12 square inches of reflector plate was required by the code and that a properly installed plate of this size should not interfere with the water reaching the point where it was desired. It was stated that there was no difference in the speed of response between pilot head and HAD systems, but that fusible link heads often were much slower in responding. Grinnel has installed several pneumatic or sealed tube systems which operate on a pressurized principle. These are reported to be quite satisfactory.

There is a test program currently being undertaken by Arthur D. Little and the MCA to make large scale field tests to see if deluge and/or fog systems actually can reduce large areas below the LEL in the case of a major spill of a plannable vapor. Companies interested in participating in this study are invited to contact the MCA.

I expect this is one of the areas, along with having specified emergency procedures for our plant, where we probably fall short of having an adequate system. One reason is that our entire plant is without any fire protection system at all on the average of once a week for periods of six hours while the fire pond is being refilled, and also when catalyst change is being made in the vinyl plant we have no siren alarm. Another area of potential trouble is that I doubt that we have had adequate testing and maintenance on our present system either in the reactor areas or in the tank farm area and, therefore, do not know if it is reliable or will give adequate coverage.

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The dinner speaker on the 26th was Joe Culotta of Pfaudler who talked on large size PVC reactors. Pfaudler has a weight limit of 55,000 lb. on their firing furnace, and therefore cannot make a 200 lb.-rated vessel larger than about 12,000 gal., but have sold several of this size. Their German operation uses a high-titanium steel that allows thinner walls and has gone to 16,000 gal. This could be done here, but has not. These reactors are 12 ft. i.d. because of shipping restrictions. With 5 D-baffles (cooling tubes inside) a 12,000 gal. reactor has the same area/volume ratio as a standard 4,000 gal. reactor. Bottom entering drives and baffles are becoming standard. Pfaudler continues to maintain that useful heat transfer is better in glass than stainless because of less fouling. The process-side film coefficient is usually controlling. Some of the slides and figures presented in the talk are to be made available to attendees.

In general, I would judge our safety situation in PVC about average for the industry. We can do nothing about spacing and building design. We can improve training and procedures, and should. A number of the other points made above should suggest possible improvements to others.



J. T. Barr

JTB:sl

AP00050779

REPRESENTATIVES ATTENDING THE
VINYL CHLORIDE SAFETY ASSOCIATION MEETING
MAY 26 & 27
at
PLEASANT POINT RESORT

<u>COMPANY NAME</u>	<u>REPRESENTATIVES</u>
Allied Chemical Company	Sandy Schreiber and Austin Eisman
American Chemical Corporation	Harold E. Kling
Air Reduction Company (Airco)	J. T. Barr
Borden Chemical	Sherwood Hall and George Bevis
Conoco Plastics	Bob Allen and Marcus Smith
Dow Chemical Company	K. H. Olfke and S. H. Englund
Escambia Chemical Corporation	George B. Speed
Ethyl Corporation	M. H. Koenecke
Firestone Plastics Company	W. W. Hadden
General Tire & Rubber Company	Robert W. Landrie and M. G. Glenn
B. F. Goodrich	Glen D. Schaaf and Mr. Dennis Dowell
Goodyear Tire & Rubber Company	M. Trowbridge
Great American Chemical Corporation	John Floros
Gulf Oil Canada, Limited	J. A. Fehrenbach
Hooker Chemical	William Wetzel and J. R. Mehall
Monsanto Company	William J. Boyle, Sr. and Paul E. Bureau
Olin Corporation, Thompson Plastics	W. J. Bradford and Robert E. Lander
Pantasote Company	E. T. Biehl, J. C. Smith
Stauffer Chemical Company	Ray Asti and A. H. Hopkins
Tenneco Plastics	P. Bogart and Clay Thompson
Union Carbide Corporation	C. E. Bowman and R. H. Wheeler
Uniroyl Chemical	W. H. Iliff

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PROGRAM

1. Peroxides - J. T. Barr, Airco
2. Emergency Agitation and Termination - S. Schreiber, Allied
3. Automatic Alarms for Spill Determination and Emergency Ventilation - M. Smith, Conoco
4. Prevention of Inadvertent Opening of Valves - G. Rozand, Tenneco
5. Reactor Cleaning - G. Schaaf, B. F. Goodrich
6. Flow Valves and Remote Cut Offs - R. Asti, Stauffer
7. Writing and Implementation of Emergency Procedures - G. Speed, Escambia
8. Rupture Discs and Relief Valves - W. Boyle, Monsanto
9. Dryer Fires - J. T. Barr, Airco
10. Vessel Entry Procedures, Safety Procedures and Job Sheets - G. Rozand, Tenneco
11. Deluge Systems - S. Schreiber, Allied
12. Quick Connect Couplings - M. Glenn, General Tire
13. Spark Sources - J. Smith, Pantasote

AP00050781

Reactor Cleaner

Buddy

FOR YOUR SAFETY, EACH ITEM MUST BE INITIALED AT TIME IT IS COMPLETED.

Verify with the appropriate operator the reactor to be cleaned

Is the agitator locked out and key in your pocket and safety sign in place?

*Is the dump line isolation valve closed and safety sign on valve handle?

*Is the reactor clean-out valve open?

Is the reactor dump valve open or removed?

NOTE: If not open, check with Reactor Operator. Reactor Operator will open dump valve if reactor is ready to clean and make sure it is the correct reactor.

Close the dump line hamer line blind.

*Is the main charge valve closed and safety sign hung on it?

*Are all valves on reactor header closed?

*Is the charge line hamer blind in the closed position?

Verify with the operator that the reactor has been aired out for at least 15 minutes.

*Have you tried the agitator switch at reactor on both high and low?

*Enter oxygen reading. Vapor reading.

Are safety signs posted on agitator push button at reactor?

Are you wearing wristlets?

Is the lift winch in position and fully operable?

Is your hard hat off?

Is the safety light in good condition?

Are the ladders in good condition and in the reactor?

Are there two sets of air bottles and air masks available for immediate use with cylinder valves open at reactor? Cylinder pressure

Does buddy know location and purpose of emergency horn valve?

Is the reactor operator aware that you are in the reactor?

Are you aware of the safety rules, "Keep scraper out of pockets, wear gloves, air mover hose in man-hole while man is in reactor, and that proper eye protection must be worn at all times while cleaning reactor - both cleaner and buddy."

Signature that all above have been checked.

Cleaner

* FOREMAN ALSO INITIALS STAGED ITEMS

Buddy

AP00050782

Reactor Operator's signature and the started items have been completed.

Are both relief ports clean and rupture discs visible and not inverted?
If NO, what action was taken? _____

Were the baffle build-ups removed? _____

Were the reactor drain and dump valves closed and hammer line blind returned to open position? _____ (NOTE: If dump valve is missing, notify appropriate operator.)

Have all reactor cleaning accessories been removed to their proper storage area? _____

Was first floor under reactor washed down? _____

Cleaner's signature _____
Cleaner

Supervisor's signature that he had inspected cleaned reactor.

Supervisor

Reactor Operator

Reactor Operator's signature and the started items have been completed.

Reactor Operator's signature and the started items have been completed.

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