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3. BFG Vinyl Chloride Storage Tank Safety Standard
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OLD CASE HISTORIES

1. Thompson Chemical Explosion, 1964 -- John Barr, Air Products

The evening January 12, 1964, a reactor was taken out of service and a new sight glass installed. The reactor sight glass was a Pfaudler type using tempered glass, an envelope CRT type gasket, and flange fastened. When the reactor was returned to service and charged, the sight glass leaked. Someone tightened the flange bolts to stop the leak causing the glass to break. The VCM cloud that was released ignited and burned several hours. The reactor building and all the reactors were destroyed. Seven people were killed and 22 injured. The plant was shut down permanently after the fire.

The problems were:

- a. The reactor was not hydrotested after the new glass was installed.
- b. An old type sight glass was used.
- c. They attempted to tighten the sight glass bolts under pressure.
- d. Plant facilities were inadequately separated. Process equipment was closely packed. There was a school across the street.
- e. Poor crowd control. Some of the public entered the plant during the fire.
- f. The building construction was not adequate to withstand a fire.

The accident, coupled with a Tenneco plant explosion several years later, led the industry to form the Vinyl Chloride Safety Association. The following audience survey questions were asked.

- a. Does everyone hydrotest after service (excluding quick opening manheads)? Yes.
- b. How many use in-line blank flanges? 3
They said it saves about half the blinding time. They are used on vapor lines and some slurry lines (to avoid cross contamination of resin). The reactor is hydrotested after swinging the blinds.
- c. How many do not use sight glasses on PVC reactors? 20
- d. How many do use sight glasses on PVC reactors? 9
All of these use a "pressure products" type sight glass which uses laminated glass compressed from the side. Air Products finds the sight glasses useful for preventing overfilling the reactors and for other purposes, too.
- e. Any problems with sight glasses? No response.
Barr mentioned that heat from a light can increase risk of chloride stress cracking if no heat circulation is provided.

2. Hooker Burlington Plant Fire, 1968 -- Joe King, Occidental

The fire occurred during the initial start-up of the first bulk (mass, no water used) polymerization plant in the U.S. The process (Pechiney) goes to 10 percent conversion in a prepolymerization reaction (prepo) and then is completed in a post polymerization reactor (popo). The prepo reaction pressure is 180 to 190 psig. The prepo is rinsed with VCM to the popo. The transfer from the prepo to the popo is controlled by a hydraulic operated valve.

The plant was in the third week of start-up. Several French engineers were assisting with the start-up but the day of the fire they were sightseeing in New York City.

Fire water was supplied from one 400 M gallon tank. The Delaware River was near the plant. There was a calendaring unit next to the PVC plant. Also there was a gypsum plant nearby.

At 11:00 p.m. on a day in March, 1968, operations was getting ready to transfer the second prepo batch. The remotely operated transfer valve was opened. An operator saw a flash in the reactor area. He immediately started the deluge system. Power was lost briefly and then restored. The fire water pumps, one diesel and one electric, were started.

At first the operators were not sure there was a fire, but after seeing smoke for several minutes, they called for outside help. A fireman went in the process area and found the lower flange of the transfer valve (4") leaking.

It became apparent that they would run out of water after two hours. The fire water tank was only 1/3 full at that point. Water was added to the fire water tank at 1,000 GPM by two wells but the fire water pumps pumped 6,000 GPM. A procedure of running the fire water pumps for 15 minutes, then shutting them down for 15 minutes was started.

Nine fire departments were called involving a total of 100 men and 16 pumpers. The fire water runoff ditch was dammed. Two pumps were used to circulate water back to the tank. Two pumpers in series were used to transfer water from the river to the tank. Two other pumpers were used to transfer water from the gypsum plant.

Foam was tried to the point foam was three feet deep in the reactor area. Then they decided it was better to let the VCM burn.

For some reason the plant could not stop the leak. Both the prepo and popo reactors continued to depressure through the leak. Probably 20,000 pounds of VCM were burned in total.

The plant called the New York police to ask for help finding the French engineers. The police found them and returned them to the plant at 12 noon the next day. The engineers found the nitrogen system intact and only 7 psig of VCM pressure on the reactors. With a combination of nitrogen and CO₂, they were able to kill the fire and stop the leak.

Damage was estimated at \$200 M, mainly to I beams, piping, instrumentation, and HCl corrosion. Downtime after the fire was estimated at four to six weeks. There were no injuries.

The leak was caused by faulty maintenance. After the first prepo batch was transferred, the transfer valve was found to have a damaged seal. The valve was removed, repaired, and replaced. Its flanges were of a tongue and groove design with a hard asbestos gasket. The downstream flange was not properly refitted. Operations hydrotested only the upstream side of the valve.

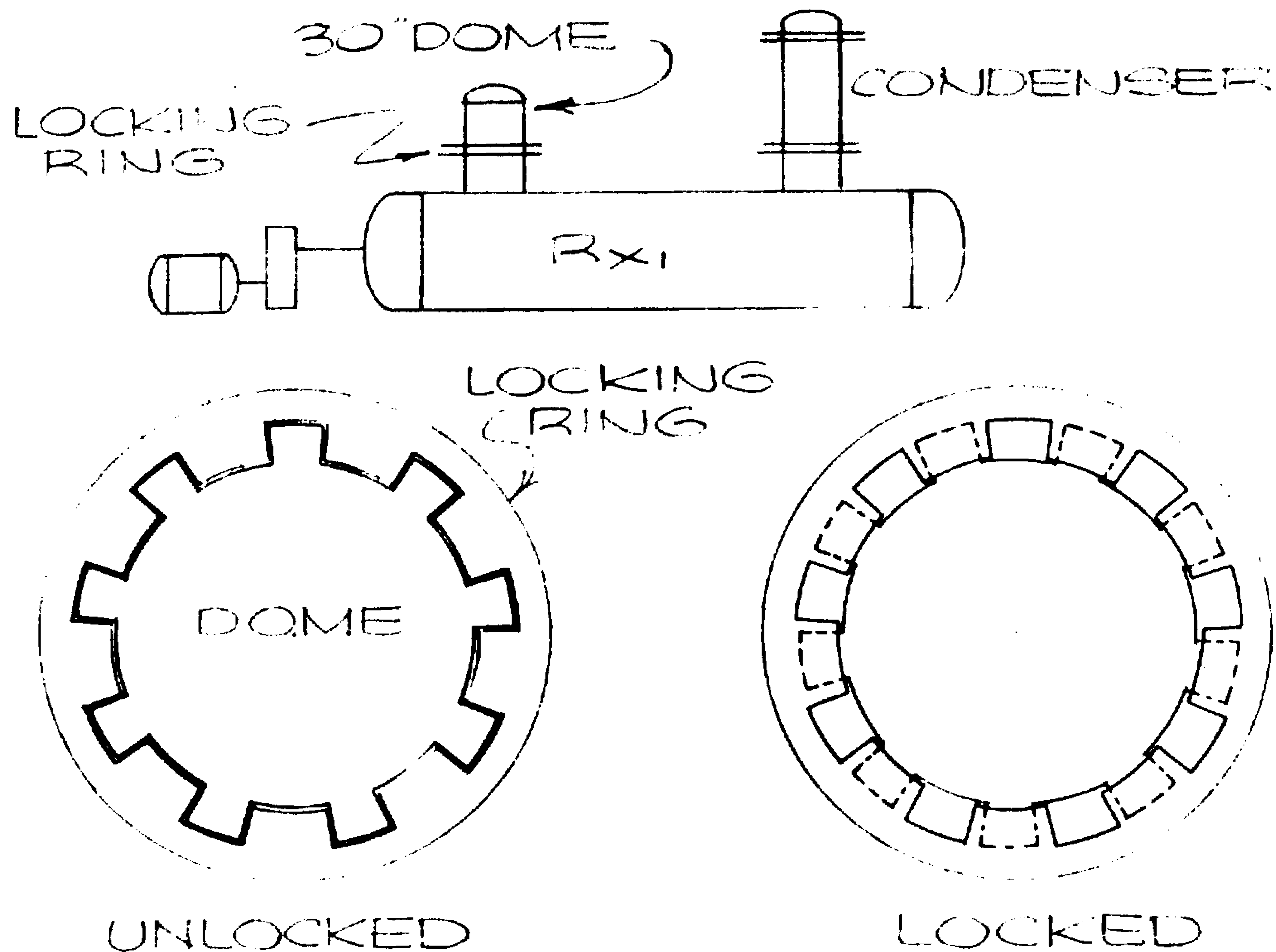
They were not sure what ignited the VCM. Their insurance company required them to:

- a. Install a second 400 M gallon fire water tank.
- b. Overhaul their pressure testing procedures.
- c. Prepare contingency plans.
- d. Plan for fighting fires like this in the future (use methods of the French engineers).

Apparently there were no isolation valves around the transfer valve at the time of the fire. Isolation valves were installed afterwards.

3. Goodyear Plaquemine Fire, 1972 -- Dan Langlois, BFG (formerly of Goodyear)

This fire occurred on the popo of Goodyear's bulk PVC plant. The reactor was charged and the pressure brought to 128 psig. Three minutes later the dome blew off releasing 19,000 pounds of VCM. The VCM cloud ignited, perhaps from a spark caused by the dome hitting a pipe. Three people were seriously burned but there were no fatalities. The fire burned for three hours.



The dome slipped out of the locking ring and broke a three-inch nozzle on the dome (or maybe vice versa). Perhaps the dome had not been tightened completely. Or the broken nozzle could have caused the dome to twist out of the locking ring. They don't know which happened first.

A steel wedge was made to insert in the locked dome flange to prevent it opening accidentally. A proximity switch was installed to confirm that the wedge was in place before charge would start. Alarms sound if the wedge is removed during operation. This has worked well.

A Dow engineer in the audience reported that a similar thing happened in a Union Carbide licensed PVC plant in Japan he was helping to start-up. He requested a second hydrotest on the plant reactors because they used the same type of twist locking manway flange. One manhead twisted off during the hydro and blew through the roof. They decided to replace the manheads with Lenape manheads.

4. PPG Oxychlorination Explosion -- Ben Reynolds, PPG

The explosion occurred in early 1977. PPG has used oxygen based oxychlorination since the late 60's.

The oxychlorination reaction area was started up around noon. Operation was normal. At 6:00 p.m. an ethylene flow adjustment was made. At 10:00 p.m. there was an explosion in the vent scrubber. Five minutes later there was a second explosion. A fire started and burned for 25 to 30 minutes. The deluge started after the first explosion. Mutual Aid responded. State police helped control traffic. No one was injured.

The scrubber was destroyed and 13 other vessels were damaged. Losses were \$1 MM of repair costs plus business interruption. The No. 1 reactor was down 10 weeks and the 2 adjacent reactors were down 6 weeks.

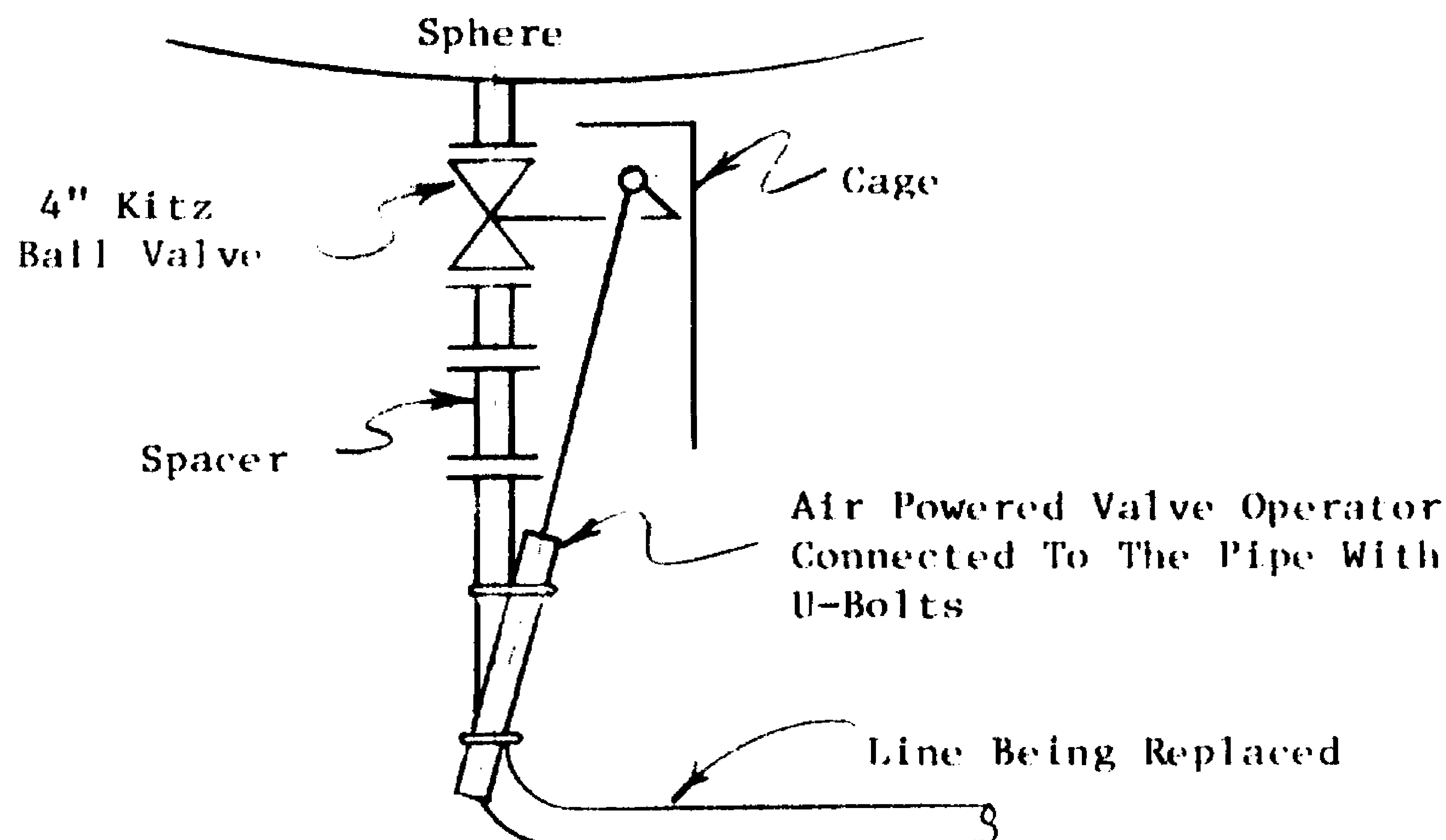
The explosions were caused by a feed imbalance in the ethylene and oxygen streams. Normally the oxygen concentration (in the vent scrubber I assume) is about 3 percent. At the time of the explosions it was 30 percent, well within the flammable region. They had ethylene and oxygen analyzers at the time but they were not working.

The process was modified as follows:

- a. Dual Modicons were used to monitor feed streams and oxygen concentration.
- b. They have sequenced the start-up with programmable controllers. Start-up can be advanced only if the prior condition is satisfied.
- c. Shut down is done under automatic control.
- d. Instrument voting (redundancy) was used.
- e. Shutdowns and other safety instrumentation are checked every six months.

5. BFG Altona, Australia, VCM Sphere Release -- Herm Waltemate, BFG

A four-inch liquid line off the bottom of a large VCM sphere was being replaced due to corrosion. There were seven other smaller lines connected to the bottom of the sphere. Only the four-inch line had a remote operated valve at the tank. None of the lines had excess flow check valves.



The valve was closed. The pipe fitter was not allowed to remove the expanded mesh cage around the valve or the operator. However, he did remove the operator's U-bolts, freeing it from the pipe. In the process of trying to move the unbolted line the line flange hooked the valve operator, partially opening the valve. Liquid VCM began to blow out. Operations could not close the valve with air pressure because the operator was only connected to the valve stem; it did not have anything to push against. They tried to use a long 2x4 to pry the valve operator and close the valve. However, the 2x4 snapped. Apparently the recoil caused the valve to go wide open. One and one half million pounds of VCM (the entire contents of the tank were lost over a six-hour period. There was no fire or explosion.

This incident was investigated thoroughly by BFG. They concluded that the accident was caused by a breakdown of their maintenance work order procedure. A new companywide maintenance work order standard was prepared (attached) which requires that the release by operations of hazardous equipment must be done at the job site in the presence of the craftsman, among other things. The release is valid for that shift only and must be repeated for the next shift. This helps to insure that both operations and maintenance understand the status and hazards of the work.

Also a companywide VCM storage tank standard was prepared which is also attached. It requires:

- a. Liquid valves must be:
 - 1) Quick opening and closing, fail closed.
 - 2) Remote operated, from two local points outside the dike and one remote (usually the control room).
 - 3) Valve must pass fire testing.
 - 4) Valve must not be top entering. This eliminates plug valves.
- b. Relieving system must be sized correctly. Some of theirs were found to be undersized due to inlet block valve losses.
- c. Automatic deluge sprinkler system is required. Some of their tanks were protected with fire water monitors only.
- d. Continuous LEL monitors are required. When 50 percent of the LEL is reached, all liquid valves on the storage tank are closed.

They found some BFG plants like excess flow valves, others did not. They decided to make excess flow valves optional. Air operated valves are required even if excess flow valves are used.

NEW CASE HISTORIES

6. Formosa Plastics, Baton Rouge Plant -- Jim Fields, Formosa Plastics

Explosion and Fire at VCM Railcar Loading Rack

On July 30, 1983, an explosion and fire occurred at Formosa Plastics' Baton Rouge VCM plant railcar loading rack. The loader was severely burned and is still hospitalized. They have not been able to talk to him to find out what he knows about the cause of the fire.

Five railcars were being loaded. Two cars were loaded before midnight. The three remaining cars were loaded next. After loading, the lines are blown with nitrogen. The plant nitrogen pressure was "up and down" and not high enough to blow the lines. While waiting for the nitrogen pressure to increase, the loader sampled the cars. The second loader (the one burned) came on duty at 3:00 a.m. The first loader explained the situation, then took the samples to the lab. The second loader apparently disconnected one car that was partially loaded, disconnected the second car, and started to disconnect the third card. There was an explosion and fire. They don't know what the source of ignition was.

The relief valve on a second car started releasing due to the fire. The relief discharge caught fire 45 minutes later. The fires burned four or five days. They hot tapped a car to drain its VCM to a pit to burn it to end the fire quickly.

The found all three angle valves open on the car involved in the initial release. The loading hoses were burned off but the hose/tank car connections were still connected on one liquid hose and one vapor hose. The second liquid hose was not connected. Either the loader opened the hose with the valve open on the car or the hose connection failed when he tried to blow the hoses with nitrogen.

The railcar excess flow valves never did work.

Formosa has made the following changes since the fire.

- a. All the Kam-Loc couplings were replaced with Hammerlock couplings.
- b. Check valves are screwed into each (liquid only?) railcar valve before the loading hoses are connected.
- c. A remote operated valve has been installed in the loading line. It can be closed locally or in the control room.
- d. Railcar loading hoses are tested every six months at 260 psig. They used to be tested to 150 psig annually.

- e. A loading check list has been prepared. Each loader must show the loading status correctly on the check off sheet at shift change.
- f. Loading procedures were updated.
- g. Loading placards are displayed on the cars being loaded.

7. High Pressure Water Fatality -- Joe King, Occidental

A hydroblast system of German design was used to clean PVC fouled exchanger tubes. The hydroblast system used a special nozzle having six forward and one backward facing holes. It was designed to pull itself through the tube. The water pressure used was 4,200 psig. The nozzle was attached to an 18-foot 1/4-inch stainless steel rod. However, the nozzle was directly connected to a hose; there was no flow through lance.

The mechanic using the hydroblaster controlled the water flow by stepping on a foot valve at the exchanger. A second mechanic was positioned at a pump motor shutdown switch six feet away.

Both mechanics were experienced and had operated the hydroblast equipment many times before.

The mechanic using the nozzle signaled to the second mechanic to start the pump. He then cleaned seven tubes. The hose bucked quite a bit during the cleaning which indicated the exchanger tubes were badly fouled.

Just after the mechanic started to clean the eighth tube, his helper saw him jump, then slowly turn and fall. The helper immediately stopped the pump. The nozzle had broken free of the rod, jumped out of the tube and struck the mechanic in the neck. It then entered his chest. He was killed from lacerated lungs and a lacerated esophagus.

They have taken the following steps to avoid a recurrence.

- a. Exchanger tubes are drilled out some predetermined distance before the water lance is used. The eighth tube had only been cleaned for two inches of its length.
- b. They are considering using a short section of rigid pipe between the hose and nozzle.
- c. Outside contractors are now used for hydroblasting.

Someone in the audience said that Haliburton can hydroblast exchangers under remote control.

Goodyear, BFG, and Conoco all use a rigid lance.

BFG has had people cut their hands with the blast water when they pull the lance out of the tube. They now mark the lance near its nozzle end so the operator knows when it's about to come out.

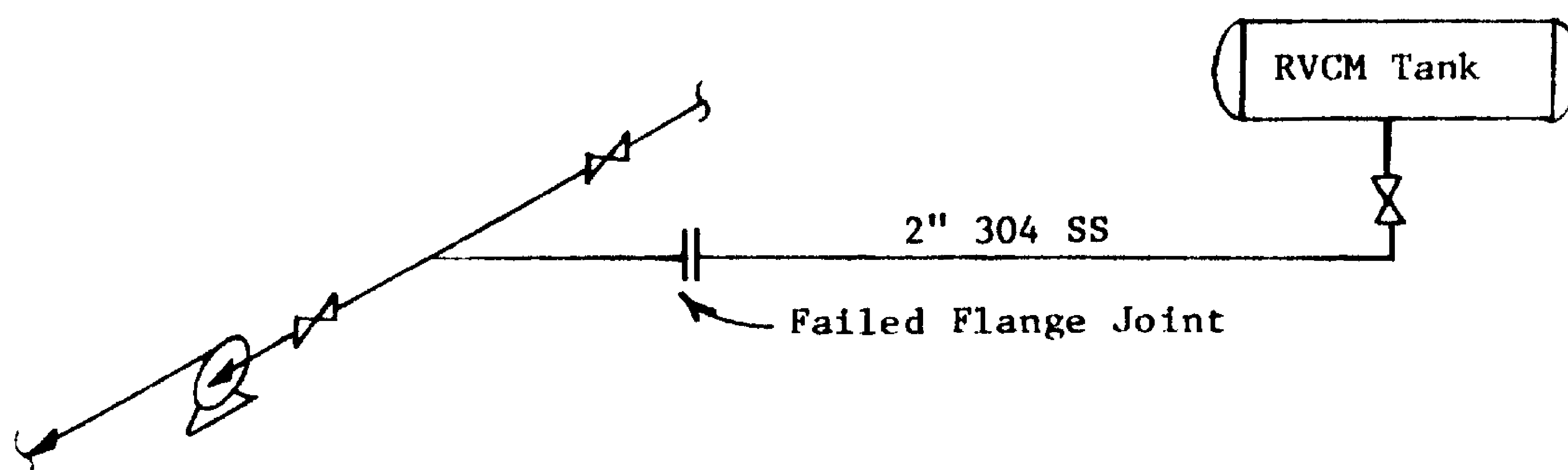
8. Resin Transport Trailer Rupture -- Jim Wallace, Exxon Canada

On June 28, 1982, a rented 1,800 cubic foot PVC transport trailer blew up while being unloaded. No one was hurt. However, the trailer failure was quite violent. A large section of the trailer opened up and peeled back. Resin was blown over a 300 foot area.

The unloading line had plugged twice during the unloading but the pressure only reached 14 psig. The trailer was tested when new at 25 psig. It had two relief valves set at 15 psig but they did not relieve.

Subsequent investigation showed that the trailer had been rolled over and damaged three months after it was made in 1977. The trailer was straightened and repaired. However, the welding was not done correctly. The weld had a lot of porosity and poor penetration. The rupture occurred at that weld. They are not sure if the car was pressure tested after the repair or if the relief valves were checked.

9. Failure of a VCM Line -- Jim Wallace, Exxon Canada



The fixed point monitors indicated a leak. They found the flange to pipe weld was leaking. They blocked in the leaking section of the line quickly. There was no fire or major release.

Afterwards someone kicked the line and the leaking flange to pipe weld completely failed. The flange was monel. The 304 stainless steel line had suffered galvanic corrosion at the weld.

Cross Section of the Weld



The flange had been installed by a contractor. He did not have a two-inch flange so he used a monel flange figuring that it would be even better than stainless steel.

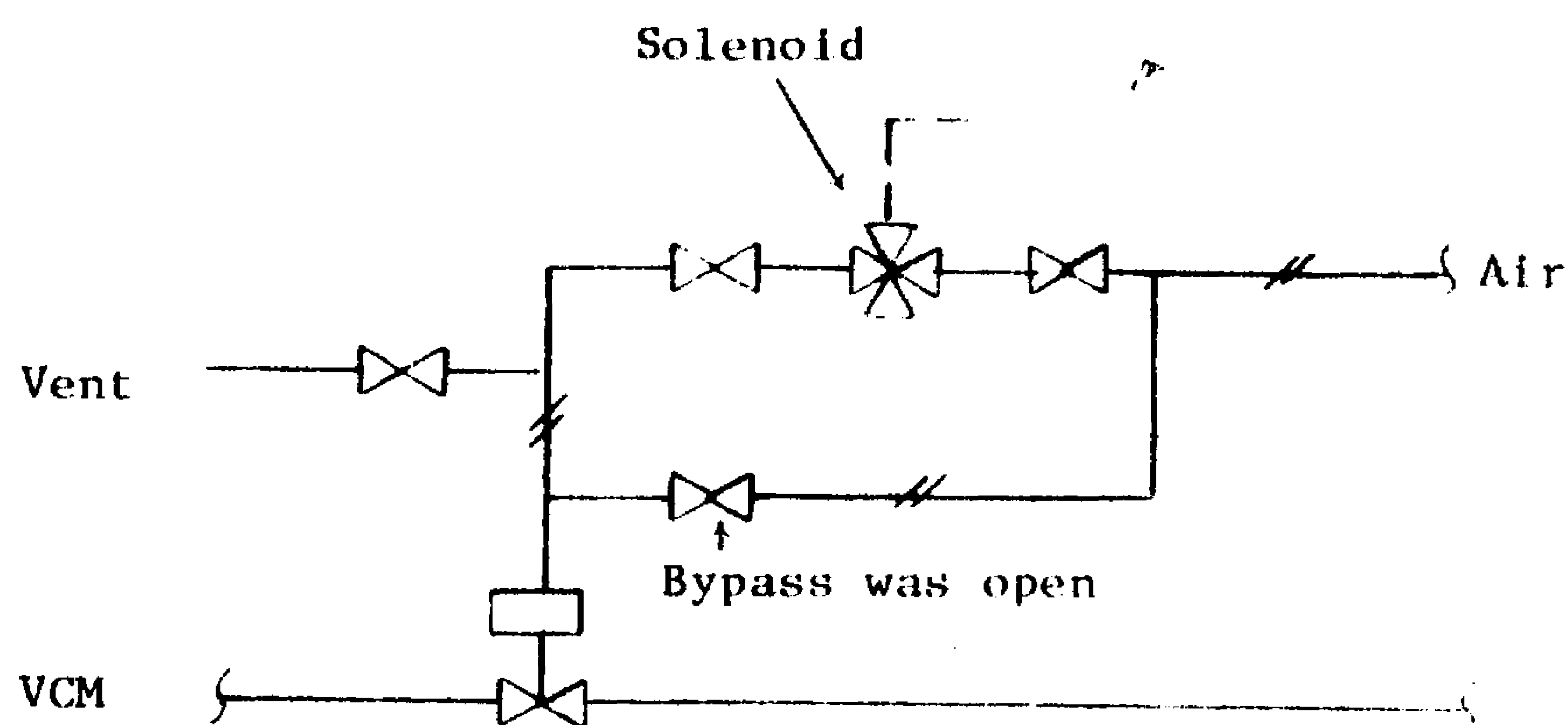
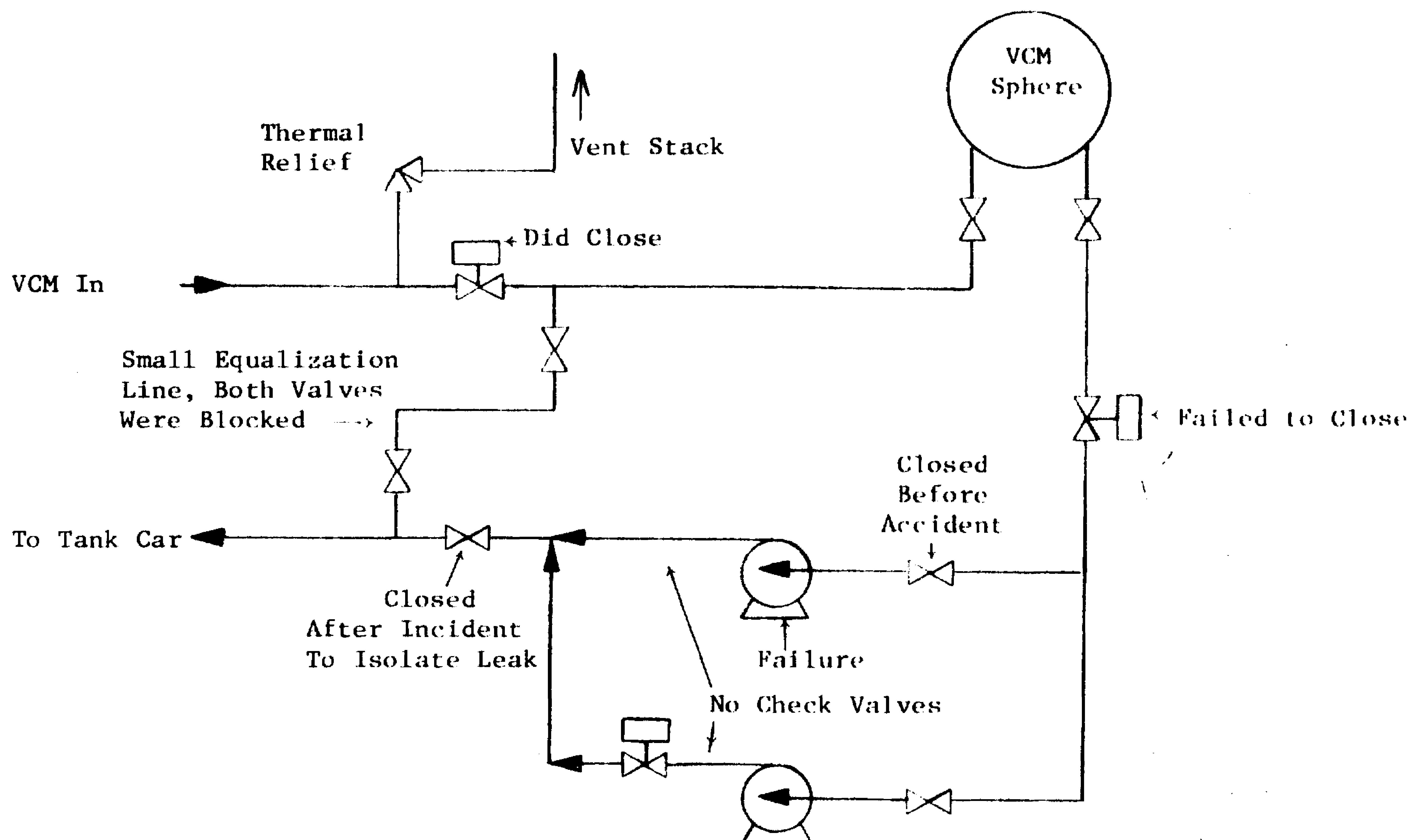
Esso is now using more stringent inspection procedures to make sure the right metallurgy is used.

Wallace said Esso has always used stainless steel for wet RVCM. In an audience survey eight companies (including Conoco) said they do not use stainless steel in this service. Eight companies do use stainless steel. One company reported they had had failure of stainless steel hoses on an RVCM tank mounted on load cells.

10. VCM Loading Pump Housing Failure -- Ben Reynolds, PPG

A blocked in loading pump in their VCM tank farm failed due to overpressure from thermal expansion of the VCM. The pump's parts in contact with VCM were steel, but the back of the pump was steel clad cast iron. The back failed 360° around its circumference. The force of the failure sheared the pump base and motor mounting bolts and bent the pump shaft. The pump seal did not blow out.

The pump is located in a VCM storage area that contains two 2,500 ton spheres and 8 bullets. See the sketch below.



The pump was not running at the time. Normally the pump and lines are left liquid full but the valves to the sphere are left open. However, the pump suction valve was closed this time.

A shipping loader heard a loud bang and saw VCM spraying 30 to 40 feet around the pump. The 40 percent LEL tripped deluge started automatically. The shift supervisor arrived within three to five minutes. The leak was isolated within 11 minutes. The all-clear was sounded within 25 minutes.

Approximately 4,000 pounds of VCM were released from the pump. When the sphere liquid inlet isolation valve was closed, it created a hydraulic shock that popped the thermal relief valve. It stuck open and released 1,200 pounds before being isolated. Five minutes after the release started a fixed point monitor 1,000 feet away registered 44 ppm VCM.

The sphere isolation valves are tested routinely. However, the pump suction isolation valve did not close because its solenoid had been bypassed.

PPG is checking the tank farm piping to make certain that it is protected against thermal expansion. All solenoid bypasses have been removed. They are reconsidering the use of cast iron in VCM pumps.

11. VCM Railcar Derailment -- Steve Ashby, Conoco

On April 22, 1982, Conoco was notified by Chemtrec of a derailment at Pittsburg, Texas involving Conoco VCM railcars. At the Railroad's request, Steve Ashby and Sid Pitts left immediately. Upon arrival they found the railroad (KCS) had 75 people at the site. The Conoco safety representatives provided information on exposure limits, potential health effects, and flammability. The superintendent asked them to approach the wreck and appraise the situation. They found one car had been punctured and emptied. One car was leaking below the creek water level. Another car was slowly leaking.

A dairy herd one mile downstream was drinking creek water. The railroad was concerned about the herd.

The VCM from the car leaking below creek level could not be salvaged. The Railroad decided to vent it. It was vented from 3:00 p.m. to the next morning. There was a strong wind the second morning which dispersed the vapors in the area. Venting was stopped.

Three cars were transferred with a contractor's compressor. The two empty cars were purged. They were able to save 500,000 pounds but 500,000 pounds was lost.

The railcar coupling shields did work. The car that was punctured was holed from the side.

The first day an EPA contractor arrived. He was interested in creek water contamination primarily. The second day the Regional Administrator arrived. He took two drager tube samples. He was concerned about hydroquinone in the VCM. He left when he was convinced there was no hydroquinone in the VCM.

The VCM concentration in the creek was 3 percent 50 feet downstream and 10-20 ppm 150 feet downstream.

No injuries occurred.

12. Solvay VCM Tank Car Explosion

In April of 1983 VCM railcars were loaded at a German VCM plant for shipment across Italy to a PVC plant in Austria. One of the railcars was rejected by Italian customs officers. German officials decided the car should be unloaded at the PVC plant rather than returned to the VCM plant. Both groups of officials thought the car had a brake problem.

The car was left on the PVC plant's main track approximately 300 meters from the reactors and over 100 meters from steam boilers and electrical generator.

Several days later the car exploded. A plant technician saw a cloud around the car, smelled the VCM gas in the air, then ran to the main entrance to sound an alarm. He then came back into the plant to shutdown the steam boilers and turbine. Two PVC reactor workers heard the explosion and saw a 1 1/2 meter thick cloud around the car and a 10 meter high liquid stream jetting from the car. The plant area was isolated and everything was shut down. There were no PVC reactors in polymerization.

A few minutes after the explosion the VCM "leak" had stopped, apparently due to autorefrigeration. There was still VCM in the car but there was no pressure on the car. They found a 150 mm slit that was 20 mm wide in the top of the car. The VCM concentration in the air near the split was 1,200 ppm. The air outside the plant area never exceeded 10 ppm. There was no fire.

The railcar was pushed to the VCM unloading station manually. Approximately 10 cubic meters of liquid VCM was recovered from the car which contained 50 cubic meters filled. One worker fainted due to VCM inhalation but was recovered. He was hospitalized for two days and was found to be all right.

Pat Cavanaugh



To Distribution

Date 4/2/84

This page was accidentally left out of the 1983 Vinyl Chloride Safety Association Meeting Report issued by John H. McCulley, Jr. on March 16, 1984. Please insert it in the appropriate place.

Thank you.

A handwritten signature in cursive script, appearing to read "Pat".

Pat Cavanaugh

Investigation determined that the car had been overloaded and probably ruptured due to thermal expansion. German VCM railcars do not have pressure relief valves.

There was quite a sequence of errors involved. They were:

- a. The man filling the car originally made a mistake in calculating the weight of the car. He had calculated the other 14 cars loaded at that time correctly.
- b. The second loader did not check the railcar weights and calculations.
- c. The VCM plant was supposed to weigh all cars twice before shipment but their second scale had been out of service since 1977.
- d. The German railcar inspectors did not check the weight.
- e. The same thing happened at Italian and Austrian customs.
- f. An Italian finally discovered that the car was overloaded. He notified the German authorities but it was Friday before Easter. Apparently due to the holidays, the Germans did not notify the Austrian plant before the car exploded.

13. Angio Update -- John Barr, Air Products

The latest count on angiosarcoma cases worldwide was reviewed. Every occurrence in PVC plants involved some reactor cleaning. The average latency period is 22 years. Germany has a shorter latency period than the U.S. There have been around 100 cases of AOL reported. These people had all cleaned reactors, too. Only one person has developed both angiosarcoma and AOL. Additional information is attached.

The angiosarcoma cases tend to be clustered with one plant having several cases and another not having any. This lead to the next topic.

14. Similarities of Plants with Multiple Cases of Angiosarcoma -- John Barr

Barr's analysis, plus comments from the floor, pointed toward the following similarities or factors.

- a. Often (always?) the small reactors were located in buildings. Therefore building ventilation differences could be a factor.
- b. Plant requirements for breathing air protection varied. Some plants required workers entering vessels to use breathing air equipment many years ago whereas others did not.

- c. In some plants reactor cleaning was an entry level job which often resulted in relatively short-term exposures. In other plants reactor cleaning was a permanent job.
- 1) Air Products, Pensacola - Reactor cleaning was an entry level job.
 - 2) Firestone - Service and utility groups did the cleaning in all Firestone plants.
 - 3) BFG, Niagra - The reactor operator did not clean the reactor. The dryer operator rotated regularly through a reactor cleaning assignment.
 - 4) Union Carbide, Texas City - A labor pool did the cleaning. The bulk resin reactors were cleaned every 140 hours. They had two workers that cleaned reactors every week of their work life (about 20 years) without breathing protection, and apparently they did not get angiosarcoma or AOL. The VCM concentration in the reactors during cleaning was around 200 ppm.
 - 5) Animal studies have shown a synergism with alcohol consumption. A person from Air Products said they had some operators at their Pensacola plant that would leave after a hoot owl shift, drink beer all day, get a little sleep, and then go back to work. Then they would purposely sniff VCM to cure their hangovers.

15. PVC Dust Inhalation Studies -- John Vaughan, ICI

ICI's first PVC dust inhalation study was done around four years ago. They surveyed 818 of their people who had worked with PVC. The workers were checked for lung function and with chest x-rays. The survey concluded that exposure to PVC dust was associated with respiratory disfunction. The effect on the lungs was on the same order as the effect of smoking and about 1/7 that of the changes brought about by old age. Increased breathing protection control was recommended.

A second ICI survey was made two years later with 229 workers from the original group re-examined along with 127 others from another plant. That survey reached the same conclusion.

ICI has now prepared internal guidelines on exposure to respirable dusts. Dust masks are mandatory in dusty areas. Respirable dusts are those 5 μ or smaller in size.

In their dust monitoring they have found respirable dust to be invisible to the naked eye. John described a PVC paste resin bag and box filling area that had a high respirable dust concentration yet the air did not appear dusty. However, when a beam of high intensity light was shone through the work area, the air looked like cigarette smoke. They used the light to determine that the dust was coming from pinholes in bags and from emptied bag flattening. They now are more careful about inspecting bags and have installed a special wedge shaped bag flattener to slowly force air from empty bags.

Their monitoring has shown virtually no respirable dust problems associated with handling suspension PVC.

John Barr of Air Products said their dust monitoring sometimes shows high total dust levels but never respirable dust problems.

16. Area Monitoring System, Leak Detectors, etc. -- Mike Nevill, VCM Plant Superintendent, Dow Chemical

Dow uses Beckman 6700 or 6710 flame ionization detectors to monitor VCM concentration. Their system can be summarized as follows.

- a. Four 10 stream analyzers are used with there being some overlap.
- b. Samples are pulled continuously with water jets.
- c. They calibrate the detectors at 5 ppm. The measured span is 0-25 ppm.
- d. Cycle time is 50 minutes depending on the number of things monitored.
- e. The monitoring data is managed by a computer.
- f. Their action level is 5 ppm. They wear Scott Air Paks above that.
- g. The detector span is checked daily.
- h. Full calibration is done weekly.
- i. Once a year they field calibrate each sample point.

Likewise for leak detection they:

- a. Use HNU's to respond to high VCM concentration alarms and for leak patrol.
- b. Calibrate the HNU's before each use with a calibration gas mixture of VCM in N₂.

- c. Survey one-fourth of the plant each week on leak patrol. Their response level (definition of a leak) is a concentration of 10 ppm six inches away from the leak source. They check every valve packing, pump seal, etc.

Personnel monitoring is done with a Du Pont portable air sample pump using charcoal adsorption.

Medical exams are offered to contractor employees as well as plant employees.

The need to save area monitoring results for 30 years was discussed. Air Products is debating whether to save them or not. DOW, BFC, and Conoco do not save them.

Eleven companies use badge monitors and 19 use air pumps.

When questioned about the definition of a leak used, two companies said 5 ppm at 6 inches, one 10 ppm at 12 inches, and one 25 ppm at 6 inches.

17. Plant Evacuation -- Planning and Training -- T. M. Jones, BFC Convent Chlor-Alkali Plant

Jones said it was important to explain to the plant workers how to report a problem and when to do it. Recognize that it takes guts to pull a switch that shuts down a plant and causes an evacuation.

They try to drill twice a year. There was a suggestion from the floor that plants include press handling training in the emergency drill. Several people who can be obnoxious should be chosen to play the part of the press.

18. Safety Performance Assessment -- John Vaughan, ICI

ICI became concerned about their workers getting a blase attitude toward safety. They decided to let floor people from one plant review the safety program of another plant. Their objective was to cross fertilize safety ideas and increase safety awareness.

They do this by forming a team consisting of a manager, engineer, supervisor, safety representative, shop steward, and tradesmen. The team is limited to a maximum of 12 people. People are selected that have no technological experience with the area being inspected. A plant is inspected once a year. The inspection takes one full day. The team functions in an advisory mode only.

A form was prepared to evaluate and rank safety systems such as lone worker situations, general chemical hazards and toxicity, and safety manuals. Where changes are needed, the team works to get plant commitment, then reviews whether the changes were made in the next annual inspection.

They have found this to be a good program. Employees look forward to the annual harangue they go through in their plant and their participation in reviewing other plants.

Ten or 12 companies use or have used a similar program developed by Du Pont called STOP. Their experiences are outlined below.

a. Georgia Pacific

They use contract maintenance people. They had the contract maintenance employees use STOP. They found the workers enjoyed it for around three months, then safety awareness dropped. Georgia Pacific concluded it was not successful because it did not get the attention it needed.

b. BFG

They have used STOP in some plants, in particular when plant supervision is set in their ways. They use it for 12 to 24 months only to increase safety awareness. They think it loses effectiveness if used continually. They do think it is an excellent program however.

c. Tenneco

They started using STOP five or six months ago. They have had to require each person submit X safety idea cards per month. They do intend to keep it going.

d. Union Carbide

They have used it but found its usefulness declined quickly. The initial training results were good. The formality of filling out cards was a problem and the number of cards submitted fell off quickly.

e. Another company uses STOP when an employee is relocated or transferred.

In response to a question, 15 companies said they have safety incentive schemes such as gifts (jacket, knives, etc.) for good safety ideas. Ten of those companies felt they were effective.

19. Controlling Runaway Reactions and Emergency Power -- Adolf Peterson, Georgia Pacific and Jim Wallace, Esso Canada (Results of Questionnaire)

Peterson started by reviewing Georgia Pacific's procedure. He defined a runaway reaction as any reaction that requires abnormal action to control.

a. Preventive Measures

- 1) Use proper initiator and the correct quantities.
- 2) Check the jacket profile of the last batch -- heat transfer, instrument problems. Operators are given guidelines to help decide when a reactor needs cleaning or instruments need repair.
- 3) Check type and quality of other ingredients -- VCM, water, and colloid. Check variation from set charge level.
- 4) Confirm agitator and jacket circulation pumps are operational and alarms are working.
- 5) Check other things -- colloid system, etc.

b. Guidelines for Action to be Taken

- 1) Agitator shut down and cannot restart in 1-5 minutes.
 - a) Kill batch with large quantity of short stop. The short stop is water soluble, but it does not completely kill the reactor. If reaction continues and better killing is needed, an oil soluble inhibitor is added.
 - b) Vent to recovery.
 - c) Maximize cooling on jacket. Flood the jacket with chilled water.
 - d) Check for available empty reactors or an empty blow down tank.
- 2) Jacket circulation pump fails.
 - a) Maximize cooling from chilled water pump.
 - b) Add water soluble short stop.
 - c) Vent to recovery.

- 3) Gradual temperature rise above high alarm point.
 - a) They have a small amount of ingredient injection into their reactors (implied that it was continuous). They stop that.
 - b) Stun the batch with several gallons of water soluble short stop.
 - c) Follow with the oil soluble inhibitor.
- 4) Gradual pressure and temperature rise above the first high alarm point. The first high pressure alarm point is set 5 psig above normal operating pressure.
 - a) Check jacket cooling, block in steam valve if it is open.
 - b) Maximize cooling.
 - c) If it occurs at the end of a batch, cooling is not very effective so they would stun the batch.
 - d) Vent to recovery.
 - e) Kill with oil soluble inhibitor if in the first half of poly.
- 5) Second pressure or temperature high high alarm--10 psi above normal pressure.
 - a) Stun with the water soluble inhibitor.
 - b) Follow with the oil soluble inhibitor.
 - c) Maximize cooling.
 - d) Vent to recovery.
 - e) Equalize to empty available vessel.

c. Equipment Available

- 1) Take chilled water supply pumps to maximum cooling.
- 2) Recovery system has excess capacity.
- 3) Kill pots with high pressure water and nitrogen flush are loaded and available at all times. Can remotely input.

- 4) Backup generators for power to agitators and jacket circulation pumps. The generators start automatically after a specified time delay. The generators "save them" once or twice a year.
- 5) Normally there is an empty reactor or blowdown tank available.
- 6) Have a vessel in their recovery system (a foam trap) that is always under full vacuum and available for venting.

The following surveys were made. There was one vote per company.

- a. How many plants manually charge initiator? 25
- b. How many automatically charge initiator? 7
(Tenneco, Kema Nord)
- c. How many have back-up generators? 15
- d. How many do not have back-up generators? 14
- e. Agitator alarm -- Is it monitoring shaft rotation? Yes, 15
(Borden, Tenneco)
- f. Agitator alarm -- Does it monitor the motor drive? Yes, 12

Georgia Pacific does not encourage the operator to transfer a complete batch to a blowdown tank. They are supposed to transfer only enough to control the batch. They are concerned about a resin chunk being caught in the transfer valve preventing the valve from closing and overpressuring the blowdown tank. Most companies have several remotely operated valves in the dump line.

Are short stops effective without agitation? Georgia Pacific said they have not lost a batch rupture disc due to failure of the short stop system for three years. They said BFG uses a gas (NO?) to kill the reactor when agitation fails.

Georgia Pacific reactors have a manual vent valve in addition to the relief valves. However, they do not manually vent in an emergency. The last VCSA relief area survey indicated that they had plenty of relief capacity in comparison to others so they do not think manual venting should be required. John Barr said that the EPA VCM standard does permit manual venting but it must be reported. In response to his question seven companies said they have written procedures that allow manual venting as a last resort. Two PVC companies have flare systems that can handle a venting reactor.

RESULTS OF QUESTIONNAIRE

Twenty-seven companies completed the questionnaire. Survey results will be sent to all companies that participated.

1. When is the initial action taken on controlling a runaway, when the normal controls are not controlling?

	<u>Mean</u>	<u>Range</u>
a. Temperature	4.5 °C	1-8 °C
b. Pressure	10.7 psi	3-25 psi
c. Auto Response	5 yes, 22 no	

2. What causes runaways?

	<u>Selected</u>		
	<u>1st</u>	<u>2nd</u>	<u>3rd</u>
Charge Error	8	5	1
Mechanical Failure	1	3	5
Instrument Failure	2	4	3
Agitator Failure	4	1	7
Cooling Loss	2	6	2
Formulation	4	2	3
Condenser Plugged	2	1	1
and Other Causes			

3. What control technique is used first, second, and then third?

	<u>Selected</u>		
	<u>1st</u>	<u>2nd</u>	<u>3rd</u>
Increase Cooling	19	-	-
Liquid Phase Inhibitor	1	5	9
Vapor Phase Inhibitor	1	1	-
Dump	1	2	3
Vent to Recovery	2	11	6
Vent to Atmosphere	-	-	2
Vent to Flare	-	2	-
Vent to Blowdown Tank	-	-	-

4. Are inhibitor systems used to control or kill reaction?

Control - 3 Kill - 17

Results of Questionnaire (Continued)

5. Number of back-up inhibitor systems.

One - 11 Two - 4 Three - 4 Six - 1

6. Where is improvement needed? Reliability

7. Backup Power

Frequency of power supply interruptions ranged from negligible to six per year. Is back-up power available? Yes, 12 No, 15

8. Do you burp a reactor after injecting inhibitor?

Five do if power has been lost. BFG is one of the five. None of the five have had bad results. They do it by venting for just a few seconds. Ethyl vents through a ball valve for 5 seconds, waits 20 seconds, then repeats. The ball valve is four-inch and it is opened wide.

9. What is the frequency of runaway batches per year? Answers ranged from 0 to 250.

10. What percent of the runaways result in emissions? Answers ranged from 0 to 62 percent.

20. Update on EPA Court Action -- W. C. Holbrook, BFG

a. Air Products -- John Barr

Their compliance plan for the Calvert City plant was to essentially build a new plant. For a \$25,000 payment to the EPA they were able to extend the compliance period for two years. The plant start-up was in March, 1979. They had 20 releases after start-up. They received a show cause order in 1980. The EPA filed a civil suit against Air Products in 1981. Management decided to settle out of court. The EPA agreed to a payment of \$120,000 which essentially bought forgiveness for everything up to the time of the settlement. The EPA accepted Air Products' defense on about one-third of the releases. They reached an informal agreement not to contest emissions below 100 pounds. The settlement was based on \$12,500 per release.

In the settlement Air Products agreed to a compliance program that includes more training, an annual review of past releases, and lots of "nit picking" record keeping. Operators and mechanics have to be trained for 90 hours before being assigned to the vinyl area. Also every vinyl worker must receive 24 hours of annual

training. The consent period is three years calendar time or two years total operating time. There is provision for automatic payment for violations of the consent agreement during that period. However, they still have the opportunity to argue that a release was not preventable.

b. Ethyl -- Herb Olsen

Ethyl was brought to court by the EPA for 98 releases. The EPA filed suit for \$2.45 MM. A Judge Parker dismissed the suit based on an interpretation of the regulation as a work practice standard.

c. Borden

Three suits have been filed by the EPA against Borden plants.

1) Leominster, Massachusetts PVC Plant

The plant had four emergency releases in 1982. They used the Judge Parker decision to argue for dismissal. Their judge disagreed with that however. He said the standards "no relief valve discharge" meant zero emissions, which makes the standard an emission standard. He also argues that the regulation says it cannot be contested after it has been in effect for 60 days. Their case is still being litigated. They have not gotten to the point of deciding whether the releases were preventable.

2) Mono-Chem Acetylene-Based VCM Plant in Louisiana

The Mono-Chem plant is now wholly owned by Borden. In 1979 and 1981 the plant had two releases. Since Borden has acquired it, they have had three releases. Some were not discovered or reported. The EPA argues that they were preventable. The EPA also alleges that the plant's VCM incinerator exhaust exceeded 10 ppm at times and was not monitored continuously. A hearing was scheduled for early November. They planned to use the Parker decision as the argument for the releases. Their judge is not Judge Parker.

3) An Ethylene-Based VCM Plant Across from the Mono-Chem Plant

That plant had 34 relief valve discharges from 1979 through 1983. Eighteen were not reported within 10 days. The EPA is asking for \$25,000 per release plus injunctive relief. Borden will file a motion to dismiss the EPA suit using the Parker logic.

d. Oxy -- Joe King

- 1) Their Louisiana large reactor PVC plant received a Section 114 letter followed by an EPA suit in July. As best I can interpret my notes, the EPA asked for \$1 MM for violations during the period when Firestone owned the plant and \$100 M for violations that occurred since Oxy acquired it. Half of the \$1 MM was a penalty for failure to report releases within 10 days.

On October 11 Judge Parker dismissed the suit. The EPA has appealed that decision.

- 2) Burlington, New Jersey PVC Plant

This plant received a Section 114 letter in April, 1981. However, the EPA has not done anything further. Since then, the state has gotten enforcement authority.

The plant had a bad record of releases for a number of years, then its performance got much better. However, in 1983 they had five releases in two months. The plant uses rupture discs without relief valves. Their management became nervous about their situation and decided to approach the state and the EPA. The EPA elected not to participate and are not involved in the insuing negotiations. The state contracted a review of the plant records to a law firm which subsequently concluded that the releases were not preventable and recommended they be forgiven. The plant then received a cease and desist order which forgave the past releases but questioned the plant's authority to operate the vent incinerator. Apparently the state thinks a separate permit is required for the incinerator and that the permit must cover anything (even reactors) that are connected to the incinerator. The plant has asked for a formal hearing.

- 3) Pottsdam PVC Plant

Up to August of 1982 that plant had 22 stripped resin excursions. They settled with the state and paid a fee of \$1,500. Their next semi-annual report listed 17 stripped resin excursions. In the interim the state had developed guidelines, based on a formula plus a judgement allowance, that were much more costly. The fine per excursion would range from \$9,000 to \$30,000. Oxy is trying to get information on the guidelines through the Freedom of Information Act. They planned to meet with the state in November.

The state is also investigating releases at that plant. There were none until four occurred this year. One release involved less than 100 pounds of VCM and the state is not interested in pursuing it.

e. BFG -- W. C. Holbrook

1) Calvert City VCM Plant

The EPA filed suit against the plant in August, 1982, following four Section 114 letters. They had a show cause hearing and plant inspections. They had not heard anything from the EPA for two years before the suit was filed.

The suit alleges harm to public health. BFG challenged that. In BFG's opinion the EPA has no facts to support that. Total VCM emissions from the plant are 53 percent below what the standard would allow.

Eighteen releases are involved. Sixteen are partial bypasses of the incinerator and 14 involve releases below 100 pounds.

Since the suit, there have been three EPA plant visits and two conferences. EPA attorneys and engineers participated in the plant visits. A trial date was set for mid-December. BFG filed a motion to dismiss the suit, referencing the Parker decision. The EPA filed an amendment saying that the releases also violated the 10 ppm emission requirement.

2) Louisville Plant

A suit was filed in April, 1983 after several Section 114 letters were issued. Again the EPA alleged harm to public health. The plant's emissions were 74 percent below what the standard allowed. There were 17 releases of which 12 were below 100 pounds. One was a manual vent. The plant has not had a significant release in two years. BFG plans to file a motion for dismissal.

- 3) Their California plant has to comply with a 10 ppb standard that is enforced by the local district. They have been sued three times. Any time they report exceeding the 10 ppb limit in a semi-annual report, they get a suit. Two suites have been settled for \$3,500 or less. The one pending involves 11 issues. These include one relief valve discharge, one small leak found by an inspector, a couple of reactor opening losses, and one ambient air high concentration (above 10 ppb). The local district is asking for \$10,000.

4) Plaquemine Plant (ex Goodyear)

The plant has received several Section 114 letters. They have had 19 releases with about one-half being manual vents. Total emissions are 55 percent below what the standard would require. They expect to be sued.

BFG is arguing that releases from rupture discs are not covered and where possible are using the statute of limitations defense.

f. Conoco -- Reviewed by Joe Ledvina

g. Georgia Pacific

They received a Section 114 letter in the Summer of 1982 but haven't heard anything else from the EPA. They had 70 releases including manual vents, relief discharges, and significant leaks.

h. PPG

Their Lake Charles VCM plant received a Section 114 letter in May, 1982. Since then, they have had one phone call from an EPA hired consultant. They have had around 30 releases with most of them being relief valve discharges.

i. Shell

Their Norco, Louisiana VCM plant received a Section 114 letter last Spring. The plant was shut down in June. The EPA was concerned that their enforcement action may have been a factor in the shut down.

Their Deer Park, Texas VCM plant has had releases but had not been contacted by the Texas Air Control Board (TACB) yet.

j. Tenneco

The EPA has required the TACB to notify their Pasadena, Texas PVC plant of an emission violation any time a VCM relief valve is vented to the flare.

21. Handling VCM Waste from Small Pilot Reactors -- Jim Wallace, Esso Canada

Jim reported on the results of a survey of pilot reactor operators. Eighteen companies participated in the survey. Probably most of these were U.S. companies since the survey was mailed only six or so weeks before the meeting.

Fifteen of the companies had small R&D pilot reactors. Three companies had the pilot reactor located in the PVC plant and directly connected to the plant VCM recovery system. Several (about three) companies had pilot reactors in a PVC plant that were not connected to the plant recovery system.

Seven companies had pilot facilities remote from the plant. Only one of those (Conoco) had a recovery system. Four of the seven said they did not recover unreacted VCM because their pilot reactors are small (1 liter to 10 gallons).

Nine companies vent RVCM to the atmosphere. Some use vent stacks. The average stack height is 40 feet with the maximum being 85 feet. One company vented VCM at ground level but used steam to help disperse the VCM.

Two companies incinerated vented RVCM and scrub the incinerator exhaust.

There was some confusion about whether local regulations governed pilot reactor RVCM venting. Companies with pilot facilities in New York, Oklahoma, and the United Kingdom reported that local regulations did control venting.

22. Valve Position Indicator Switches -- J. H. McCulley, Conoco

Results of a questionnaire on plant experience with valve position indicator switches were reviewed. Most plants have found valve position switch reliability to be low. It was disturbing to see some of the plants with high failure rates rank the reliability as acceptable. Most of the failures were caused by water penetrating the switch or by mechanical damage from plant personnel (during maintenance, etc.). Reliability did not seem to depend on frequency of use.

The survey results are summarized below.

a. Survey Participation

Total Number of Companies Responding	15
Total Number of Plants Responding	14+
Total Number of Forms Returned	42

b. Types of Switches Used

Capacitance Proximity	-	1/44	2%
Electromechanical	-	28/44	65%
Inductive Proximity	-	9/44	20%
Hall Effect Proximity	-	5/44	11%
Other (Pneumatic)	-	1/44	2%

c. Mean Time Between Failures (Months)

<u>Type Switch</u>	<u>Min</u>	<u>Avg</u>	<u>Max</u>
Electromechanical	1	18	60
Inductive Proximity	1	10	24
Hall Effect Proximity	2	7	10

d. Cause of Failure

	<u>Electro- mechanical</u>	<u>Inductive Proximity</u>	<u>Hall Effect Proximity</u>
Shifting	4	1	3
Mechanical Failure	3	-	-
Water	15	-	2
Damage by Personnel	10	6	3
Vibration	2	1	1
Bent Indicator Arm	2	1	1
Electrical Failure	-	-	2
Total	36	9	12

e. Maintenance Performed

Realign or Replace.

A listing of the survey results, based on questionnaires returned before the meeting, is attached.

23. Miscellaneous Comments

a. EIF, Israel

Earlier in the year EIF approached Conoco to ask if we would license them reactor condenser technology. At the VCSA meeting we were told that they found a way to greatly shorten their reactor turnaround time and no longer have a need for additional suspension resin production. They are using reflux condensers on paste reactors with success. They said BASF, Shin-Etsu and others use external condensers. Some producers use reflux condensers. They said BASF and Shin-Etsu are removing 50 percent of the heat of reaction via condensers. They also said that they knew that we removed less heat than that!

They have problems with static on the dried resin. They have tried steam and ammonia injection without much success. Steam worked but they got wet resin. Ammonia water worked also but it was difficult to control. A foreman discovered that placing a bucket of ammonia water next to the inlet to the transfer air compressor would help control static. They have not been able to correlate resin static with humidity. They have measured the resin static charge and find it positive sometimes and negative at other times. John Barr suggested that they move their transfer air intake to just downwind of the cooling towers. EIF had already tried that but it did not work.

They had an incident with their fluid bed dryer. The double lock valves on the dryer outlet developed problems so they shut off slurry feed. They left resin in the dryer and kept the air blowers on but shut off steam to the heating coils. Just prior to this the speed of the air blowers had been reduced to save energy but that had dropped air flow to the point where they were not getting good fluidization. The steam valve leaked enough steam to start the resin degrading. They were not aware of this until the dryer walls became so hot the insulation on the outside of the dryer caught fire. They estimate the temperature reached several hundred degrees Centigrade. The resin in the dryer did not fuse but did turn dark gray.

b. Exxon Canada

Jim Wallace said their PVC plant expansion had just started operation. It included large reactors of their own design and a NIRO fluid bed. The reactors have performed well. However, they are having problems controlling the fluid bed.

c. Shintech

Shintech has found a way to increase their reactor productivity and plan to install an additional fluid bed dryer. The Texas Air Control Board had not issued them a permit for the dryer because with the increased capacity, air emission modeling of the plant showed some fence line concentrations of VCM to be greater than ten parts per billion, the California Standard. Texas does not have this standard, but still did not want to issue the permit.