MINUTES OF VCL SAFETY ASSOCIATION MEETING AT CLEVELAND

OCTOBER 24-26, 1973

A. General

The agenda of the meeting is covered in Attachment 1.

Each item covered will be discussed in the text of these minutes.

A list of the attendees is covered in Attachment 2. An updated list of the member companies and their official representatives is covered in Attachment 3.

If further information is desired on any of the items covered in these minutes, please contact me as I may have further details.

B. Blend Tank Safety Guidelines - P. Bogart

Mr. Bogart compiled a list of safety guidelines on blend tanks based on data that he received from various sources within the PVC industry. He wrote these up and they appear as Attachment 4 of this report. He asked that we read these and then submit comments back to him. I will perform this function.

C. Monomer Loading and Storage Safety Guidelines - D. Miller

Mr. Miller presented Shell's design criteria for VCM storage. These criteria are really the Shell International guidelines for LPG based on an LPG fire they had sometime ago. They include:

1. No liquid must be allowed to stand underneath the vessels. It must all drain away.

2. All spheres must be at least a diameter apart.

3. There must be fire walls around all pumps and safety valves.

4. Only essential nozzles are allowed below the maximum liquid level in the vessel.

5. No valves are allowed beneath the drip line of the vessel. Instead they place spring loaded ball valves outside of the dikes.

6. All piping of VCM is above ground.

7. Varex style level gauges are used.

8. Fire coverage is provided by hydrant mounted fog nozzles and a deluge ring with buried headers.

He will have these guidelines typed and distributed to all members.

D. Reactor Entry - J. Palinski

Mr. Palinski presented the procedures currently in use at Universal PVC Resins Inc. This is a subsidary of Robin-Tech. They were formerly owned by Allied Chemical. I will note just the pertinent points or deviations from current Dow procedures that were discussed during the course of this presentation.

1. A vessel entry permit is required when entering any vessel, hole, etc. that is greater than 4 feet in depth.

2. The permit is valid for only one shift after which it must be renewed. The permit must be displayed at the site at all times, and is removed at the end of the shift and the job. The permits are then filed by the safety supervisor and retained for ninety days. They have found that they are very useful for insurance purposes.

3. The safety watch must always be at the manhole and can cover only one vessel. This point brought up some additional discussion with the following information being obtained:

   a. Ten companies require a constant watch as was described here and as used by Dow.

   b. Fourteen companies will allow a watch to cover more than one vessel or for the watch to go away from the manhole for short periods of time.

   c. Three companies rely on a personnel protection alarm system. This system revolves around the utilization of an electrical device, which requires acknowledgement by the man in the vessel every three minutes or outside personnel are notified of a potential problem automatically.

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4. The man in the vessel wears a safety belt or shoulder harness or wristlets but has no line attached to them. In the event of a problem the safety watch at the manhole sounds an alert and when help arrives he then goes down into the vessel and attaches a safety line to the man's harness. This brought out considerable discussion on the merits of this type of system and the dangers involved in sending a man into a vessel with an unknown problem possibly existing.

5. They use an explosion proof drop cord light at 110 volts. A show of hands revealed that 22 companies used portable cord lights with 12 of them being 110 volt and the remainder being lower voltage.

6. They blank or remove all lines. A show of hands revealed that 12 companies are now using block and bleed systems instead of blanking where repetitive reactor entry is required.

7. The foreman takes oxygen and L.E.L. reading at three different points in the reactor prior to entry. This is rechecked whenever a man reenters a vessel after a break or at shift change.

8. All electrical circuits are locked by as many as 3 or 4 different people with different locks at the breaker. These include locks by the foreman, the maintenance man involved (if there is one), the man in the vessel, and the safety watch at the vessel manhole.

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E. Safety Valve Testing - R. Frantz

Mr. Frantz reviewed the general safety valve testing procedures utilized by Union Carbide at their Texas City Plant. Operating people decide on the type and frequency of testing based on the following criteria:

1. Testing is carried out at least once per year on Class 1 valves, which include those in corrosive service, those that might be subject to plugging, or those new valves in unknown services.

2. Testing is carried out between one and two years on Class 2 valves, which include those on fired pressure vessels, those under extreme pressure and temperature, and those with less severe corrosive service then those in Class 1.

3. Testing is carried out between two and five years on Class 3 valves, which include all other safety valves.

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Their testing is scheduled by computer, but in addition they paint each valve a distinctive color for the particular year it was tested so that anyone can tell at a glance the last year the valve was tested.

Union Carbide does not use safety valves on reactors. Rather they only use frangibles due to the fact that they have had previous problems with valves plugging up. They currently use one 3" and one 4" disc on a 5700 gallon vessel. These discs are in separate parallel lines venting directly to the atmosphere.

Additional discussion at this point revealed that 6 companies use only a disc with no safety valve (similar to that described by Union Carbide), while 12 use a frangible under a relief valve similar to what we at Dow use. This previous data applies to reactors only.

In the case of VCM storage, 19 companies use only valves while 12 use discs below safety valves. Union Carbide uses reverse buckling safety discs. Discussion revealed that nine companies had at one time used reverse buckling discs but only 3 are currently using them. Some companies have had trouble with reverse buckling discs in that sometimes the disc can flip up without being cut by the knife edge. It was pointed out that installation is extremely important. Other companies have backed away from reverse buckling discs because if you happen to hydrostatically fill a vessel, the disc won't break at the proper pressure. Also, the vendors do not recommend reverse buckling discs if a possibility exists of hydrostatically filling the vessel. I inquired as to whether the people using reverse buckling discs were utilizing this disc to test the safety relief valves in place. Several people indicated they had seen a demonstration of testing valves in place but none were currently using that system. All people removed their valves for testing as indicated by a show of hands, and 19 checked their reactor valves at a frequency of 1 year or less.

F. Safety Valve Sizing - F. Frey

Mr. Frey presented 3 considerations from a philosophical point of view.

1. The valves should not be larger than required.

2. Should assure that the vessel will not rupture.

3. Should minimize the amount of material being vented.

He stated the main reason that he had agreed to be the discussion leader was his concern for the divergence of opinion on the size or method of sizing the safety relief valves for reactors. He then illustrated by example. If we assume that we have a 10,000 gallon reactor, the standard formula (which is based on .0012 square inches per gallon) would indicate we need 12 square inches of vent relief area. The Diamond Shamrock revised formula would indicate that we need a vent area of 16 to 21 square inches. The Goodrich technique would indicate we require 13 square inches of vent area. W. Boyle's (Monsanto) formula would indicate 56 square inches and the FIA specification would indicate an area of from 67 to 140 square inches would be required.

Mr. Frey then proposed that the Vinyl Chloride Safety Association fund a research program to investigate the required techniques for sizing relief valves for PVC reactors. No conclusion was reached on this point despite the fact that Frey indicated Boyle thought it would be a rather simple matter and could be carried out for something less than $10,000.

Subsequent discussion referred to Huff's paper (Dow Chemical) at last years AICHE meeting and the question was asked as to whether it could be applied to PVC reactors. I indicated we were doing some work on safety relief sizing for Saran vessels and would check out if this data could be presented at a subsequent meeting. There was then a discussion on the sizes of vents currently being used in the PVC industry on various sized reactors. This data was tabulated as follows:

Reactor Gallons	Relief Size	Vent Area	Comments
4,000	6 x 8	16 $in.^2$)	
10,000	8 x 12	26 $in.^2$)	
16,000	2 - 8 x 12	52 $in.^2$)	at 190 psia at Diamond Shamrock
24,000	3 - 12 x 16	220 $in.^2$)	
16,000	3 - ?	90 $in.^2$	safely relieved a vessel
20,000	2 - 12 x 16	140 $in.^2$	FIA approved this for Georgia Pacific at 200 psia
4,200	3" Disc		bulk polymer
13,400	2 - 4" Disc		bulk polymer
10,000	2 - 10" Disc	160 $in.^2$	ICI at 200 psia (never have had both flow)
2,200	3" Inlet Valves	)	
6,000	4" Inlet Valves	)	have safely relieved

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G. Static Control - W. Bradford

Mr. Bradford attempted to employ the technique of goading us into a discussion as to why we need to ground to control static. He specifically asked why anyone bothers to ground VCM railcars when loading or unloading because he contended that there is not an explosive mixture there anyway. This of course resulted in quite a discussion with the following major points coming out.

1. Most people feel it is just a good standard operating procedure to ground systems handling hydrocarbons.

2. Tennaco had a 3,000 gallon VCM spill which was ignited by a resin conveying line static discharge so it can happen.

3. ICI had a code that required jumper grounds on monomer lines. After extensive testing they proved it wasn't necessary as the bolts in the flanges provided satisfactory ground.

4. API has proven that spark proof tools are not warranted. In fact, you can get a spark from spark proof tools as well as standard tools.

5. Twenty-one companies have Division 1 reactor areas.

H. Catalyst Handling - R. Stack

Mr. Stack presented the PPG movie on catalyst decompositions. This movie has been presented to Dow personnel in the past. He suggested that since catalysts are looked upon by the FDA as being bad (whereas initiators are not nearly as bad because they are consumed) we should be talking of initiators and not catalysts in the PVC industry. He indicated that there is an Organic Producers Safety committee in effect now and PPG is a member. It includes manufacturers in the U.S. as well as the rest of the world. This group has developed a manual on methods of classifying and testing various initiators. A summary of the data from that committee is covered in Attachment 5. Several comments came out during the discussion.

1. No one has ever seen an explosion unless the material has been confined.

2. Sometimes you get ignition on decomposition but other times you do not.

3. PPG prefers that catalyst solutions be added through open manholes, however, they do indicate that in the polyethylene business they are pumped in as solutions to hot reactors.

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4. Seven companies have had problems with decompositions or fires this past year.

5. In a separate discussion with W. Keim of PPG, I learned that several people are (and have been for sometime) using "neat" IPP in PVC reactions. When doing this they weigh out the IPP in ice cream cartons and charge it to a reactor with water in it at a very closely controlled temperature being very careful that the time from addition to heat up is closely controlled. He further indicated that polyethylene producers are actually pumping 10 to 20% solutions of IPP in solvents to their reactors. He also said that several people take the solid IPP immediately upon receipt and make up a solution in up to 10,000 gallon quantities.

I. Pressure Vessel Obsolescence and Inspection - J. Barr

General comments from this discussion were as follows:

1. Eight companies are required by company code to test vessels, but the remainder are not. Approximately 12 companies are utilizing thickness testing of some sort. General input indicated that glass lined reactors from 17 to 23 years old were still in service and that it really depended on the care and treatment of the vessel as to whether they were obsolete or not. One company said their Engineering Department had predicted that after 30 years you should expect to see some fatigue failure in stainless steel vessels. However, Goodrich has vessels 30 years old with no failures thusfar.

2. All people but one have had chloride ion stress crack corrosion on their Bird centrifuges and this one has been in service for over 8 years now. No explanation was given for this seemingly unusual length of service.

3. The general conclusion was that it appears that vessels don't really become obsolete.

J. OSHA Experience - W. Bradford

Mr. Bradford revealed that within Olin there have been many OSHA inspections, but not at the PVC plant. Of these, 16 were to check on compliance, 13 to check on complaints and 3 to check on fatalities. There were a total of 256 violations with fines of $4,000. They are currently contesting a noise complaint violation in a metal working plant. The violation sites that are in this new building they did not engineer the noise out. Guarding signs, walking surfaces, etc., are the most common violation areas. Three

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PVC and one VCM plant have been inspected based on a show of hands. In general, most companies say the inspectors are very capable. However, they do seem to come in and look at specific areas and pass over other areas that might really be more important.

K. Monomer Leak Handling - R. Langer

Mr. Langer of Dow discussed the conductivity type halogen analyzers in use in the Midland Division, how they are checked, the printout available computer systems in use, etc. He stressed 1) the need for time weighted exposure average data for people, 2) the fact that operating personnel make notes on the charts whenever high levels become apparent thus having them intimately involved and 3) this is a good method for early detection of leaks. Goodrich personnel indicated they had a similar type system utilizing a Bendix analyzing unit. Several companies came up to me afterwards and asked for more specific data on this type of analyzer and I have referred them to the AED Company who are now manufacturing these units for Dow.

L. Safe Monomer Venting - M. Trowbridge

Mr. Trowbridge indicated there were 3 primary reasons for venting.

1. Frangible premature failure or fatigue failure.

2. A power failure (which could be offset partially by having auxiliary power).

3. Runaway batches (which in some cases could be offset by short stop addition.

He indicated that at Goodyear their safety piping consists of a frangible in the main line followed by a three-way valve. On one leg of the three-way valve they have a safety relief valve and on the other leg they have another frangible relief. In normal operation they have the three-way valve directed to the safety relief valve but if there is any indication of plugging they swing the three way valve to the second frangible and discharge directly to the atmosphere. In addition to this they usually have a small (2 to 4") manual vent on each reactor. They use a gauge rather than a bubbler to determine pressure between the frangible and the safety relief valve. Several comments came out in the discussion after this talk.

1. Several companies have put bends in their vent lines to direct monomer vapors in a certain direction but when the frangible or safety relief ruptured the line was straightened out due to the

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torque of the exiting gas. One company indicated that it was important to cut the top end of the vent pipe off square rather than at a beveled angle as this also could cause bending due to the torque.

2. All but one or two of the companies have separate manual vents in addition to the safety vents. Three companies have had recovery vent systems ignite due to lightening and as a result they have installed steam snuffers. One company has installed a steam ejector at the top of the vent stock to help disperse the monomers after a vent release.

3. In Germany there was a report that the government in one area required a recovery system on the emergency vent system. There was much concern about this subject and the question came up as to whether it would also be required in the U.S.A. in the future.

4. About half of the people use flame arrestors on their recovery system vents, while the other half do not.

5. It was reported that A. D. Little has a computer program that can predict dispersion of VCM vapor clouds. This work was originally done for the Coast Guard but A. D. Little would be willing to discuss the information with others. It is scheduled to be released in January 1974. The primary concern here is with the detonation of these vapor clouds. The secretary will make a contact on this and report back at a later date.

M. Noise Control - E. Schenke

The important item coming out of this discussion is that you must document all the action that is taken to avoid or eliminate noise problems and further we must keep the pressure on vendors for quieter equipment.

N. VCM Exposure Standard and Environmental Health Problems - P. Bogart

The following points came out in this discussion:

1. The MCA study on animals was initiated on September 1 and preliminary results are expected back by January 1. No one but Bogart knew of this. The European Studies by Viola indicate that at levels of 200 ppm or lower there are no problems on mice.

2. Four companies including Dow have the lower level set at 50 parts per million. Eleven other companies have carried out surveys to determine their actual exposure levels, but have set no level below the 200 part per million government regulation.

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3. The J&W analyzer that reads down to 50 parts per million is considered very inaccurate. However, the Century portable vapor analyzer is considered to be very good.

4. One company said that they were averaging 80 parts per million TWA and that it would be very difficult to get this below 50 ppm.

5. Goodyear has been given a goal by their company that they get the VCM level in their resin down to 50 parts per million.

The group decided not to discuss the subject. The discussion ended with Bogart making a pitch that everyone go back to their environmental control people and ORC representatives and tell them to start providing input to the various governmental agencies. It was felt that if we don't provide input now we may never have another chance.

O. Accident Reviews

1. VCM tank car derailment in Fort Wayne by Goodrich. An excellent presentation was given including a film and still pictures. A detailed write up was also handed out and is included as Attachment 6. I inquired about the availability of the film for use by Dow and they said that it may be available in approximately 6 months. I gave them my name and address and they indicated that they would contact me. Several interesting points came out in this discussion.

   a. The International Association of Fire Chiefs have now established a policy that if you can't get large volumes of water on the exposed steel of the vapor space of a vessel in 5 to 8 minutes you should back off 2,000 feet and wait as the car will explode due to the metal softening in the vapor space area.

   b. They are exploring the railroad's sizing of relief valves and are having some difficulty finding their way through the details.

   c. They feel that the car exploded due to the relief valve either being damaged or that it was not large enough to handle the liquid release.

2. Two catalyst storage problems by General Tire. Both of these incidents involved the storage of diluted material in bottles stored in the original freezer containers as received from the vendor which are kept cold utilizing dry ice. In one of the incidents they felt the problem was due to either poor gasketing or a man putting an overheated sample back in the freezer after he had used a portion of it. The second

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incident was a result of a man not placing the dry ice in the freezer properly. There was no fire in either case just a vapor release. During the course of the discussion it was pointed out that not removing the paper used to cover the dry ice is against the regulations of the FIA, and also it is extremely important to have the grating in the bottom of the freezers in order to get good circulation.

3. Another catalyst problem. This incident involved the loss of 13 trays of neat IPP in an upright freez[illegible]. [illegible]y receive their material in plastic trays and store it in the same freezer as received. They feel the incident was a result of the freezer not being iced properly on their site. There was a decomposition but no fire.

4. A neat IPP problem by Monsanto. Again, in this case, the IPP is received in plastic trays stored in a freezer and they utilize this freezer for their inplant storage. In this case approximately 4 to 5 hours after the freezer had been delivered, it exploded and and burned. They do not know if anything had been taken out of the freezer or not. They suspect the material did not arrive properly iced or the shelves slipped down hindering circulation in the lower portion of the freezer.

5. VCM release while unloading a car by Dow Chemical. I reviewed the incident at our main monomer tank farm wherein a flexible line broke after it had been subjected to vibration as a result of the excess flow check in the car operating improperly. I described the safety system that we had valves that could be closed remotely in order to avoid inexcessive spills should such an incident like this occur. Many people were interested in the system we had installed. Further discussion revealed that there have been many problems with flexible lines utilizing steel braiding. Several companies pointed out that going from steel braiding to stainless steel braiding has resulted in no problems with up to 7 years of service.

6. VCM release while unloading a car by Goodrich. They had a problem very similar to ours where a flexible line parted and 5,000 gallons of material spilled out to the ground. Unfortunately they did not have automatic valves like we did and had to send a man in with a Scott air pack to close the valve on top of the car. Additional discussion at this point revealed that there have been many problems with excess flow check valves. Several companies indicated they have had line breaks and the valves did not operate properly. The conclusion is "don't trust excess flow valves".

7. Flexible line break under a monomer receiver by ICI. Another instance of flexible lines breaking while in service. In this case releasing 1,000 pounds of VCM to the ground. Discussion revealed that almost all people use flexible lines somewhere in their operation. Fourteen companies indicated they use swivel joints for tank car unloading and have only minor problems with leakage if they are greased every time they are used or on a once a week basis.

8. Explosion in a blend tank by BPCI. In this case there were two 30,000 gallon slurry tanks that were interconnected with an air ventilation duct with dampers in each branch of the line as well as in the common line from the fan. It was a push type system. Indications were that the initial explosion occurred in the fan and the second explosion occurred in the tank which had the damper open. The other tank had its damper closed and had no problems. Damage was limited to curving or bulging out the top of the tank and blowing the duct off of the top of the tank. The tank was equipped with a 12" diameter vent and a 24" x 15" rectangular manhole. This vent area was apparently sufficient to relieve the vessel to limit the damage. The tank was three-quarters full at the time of the incident. Discussion revealed that one company uses an inert atmosphere and holds at 2% oxygen maximum while another one use inert atmosphere but does not check the atmospheric composition. Eleven companies use a forced air purge and only check on a spot basis. Eight other companies don't do anything at all with respect to purging or checking..

9. Vent line fire by Tennaco. In this particular case the plant was in the midst of an electrical storm which caused a voltage drop and as a result all the agitators stopped. A continuous vent from the recovered monomer system ignited possibly due to lightening. Upon noticing the problem they set off the deluge system and left the building. Several problems existed at this point.

   a. Once they left the building they didn't have any way of knowing what was going on and therefore what action should be taken to correct the problem. They are installing critical instruments in an outside bunker so they can observe the reactor conditions on a continuous basis even after an evacuation.

   b. They had no way of snuffing out the fire from the recovery system vent line.

   c. The situation was really complicated when after approximately 8 minutes they were able to restart the reactors and then the pressure began to rise and 2 of the reactors ultimately released their contents to the atmosphere and discharged one-half of the vessels contents. Fortunately, the wind was

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blowing these vented gases away from the fire on the recovery vent line and there were no serious problems as a result of the entire incident.

10. Overpressuring of a reactor by Olin. This incident involved a 2,200 gallon kettle that had just been loaded. Since they don't have a continuous pressure recorder they don't know exactly how high the pressure got or exactly what happened. The first indication of a problem was monomer coming from the seal and shortly thereafter they heard the rupture disc (which was set at 160 psig) blow. When the operator got to the 4" manual vent valve the manhole gasket began to leak and the operator immediately set off the deluge system. The foreman then put on a Scott air pack and went back in the building and vented the reactor to the atmosphere. They think the reactor was charged and in the process of being heated up with the agitator off and then the operator started the agitator. Although he claims that he did not. They found 95% of the glass was spalled off of the inside of the vessel due to the over-pressurization. The vessel was safetied with a 4" x 6" pop valve and a 4" frangible disc, but that was apparently not enough to completely relieve the pressure. Corrective action includes placing an automatic valve in the hot water line which will not open unless the agitator is on. They also have established a policy that an agitator cannot be started if it has been overlooked in the original startup procedure. Discussion about this incident revealed that many different types of manhole gaskets are currently in use including lead, teflon, solid lead, and neoprene. In addition 7 companies pressure test the reactors after opening the manway while 9 companies vacuum test after opening the manway. Six to 9 companies have had the "O" ring in the Lenope quick opening manway blow out. One company has switched from the Lenope to a Tube Turn type with much better results.

11. Opening the wrong reactor dump valve by Panasote. An operator went down to the bottom floor and opened the dump valve on the wrong reactor. Half way through the dump he recognized the problem and closed the valve. The J&W monomer detection system set off the deluge water system. They did not have any other warning devices to alert a man of this type of problem. Since that time they have installed a pressure device that prevents the bottom valve from being opened if the reactor is under any positive pressure. Discussion revealed that 9 companies have some type of lock or fool-proof system to prevent this type of incident. Another 5 companies rely on lights and another 10 companies rely on double valves beneath their reactors. No one gave any indication of problems with opening the wrong reactor manhole.

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12. Explosion in a mass PVC plant in Europe. This incident involved a thermocouple well coming out of the bottom of a reactor dumping 12 tons of VCM to the building. The deluge system came on but the vapor cloud exploded resulting in 4 or 5 fatalities. Although no one is certain exactly what caused the incident, it revolves around some maintenance that was to have been done on the thermocouple wells before this run had been initiated. They think that the maintenance man removed the bolts and attempted to remove the thermocouple but it was stuck due to a resin formation. Then, rather than reinsert the bolts it was forgotten. Two different pressure checks of the system before loading the reactor failed to reveal the problem. The ignition is thought to have been provided by the control room or the monomer recovery system, both of which were not far away. The fatalities all occurred as the men were leaving the immediate area. Apparently they were caught in the advancing flame front. The feeling is that the men could have been saved if they had gone behind the blast walls for protection. Instead they just seemed to run away with no apparent plan as to where they were going. The major lessons to be gained from this incident include:

a. Maintenance procedures are extremely important and must be followed to the utmost detail.

b. Evacuation routes should be very well defined and should be carried out on all drills on a frequent enough basis to assure that people will follow them.

c. Since the incident may have been caused by stud bolts holding the thermocouple well in place this type of bolting should be avoided if at all possible.

Further discussion with regard to Item c revealed that there are many problems with the conventional stud bolt in that resin can get into the threads preventing proper installation. It is recommended that in its place we use a bolt that is threaded on both ends and rely on a nut and washer on the outside, which would be removed when removing the thermo well.

13. Explosion in a PVC silo in Europe. This explosion occurred in a large compartmented silo in a PVC compound plant. The silo capacity was several hundred tons. At the time one of the compartments was undergoing maintenance in the form of welding in a nozzle in the top of the vessel while the other compartments were in operation. During the course of the welding operation a flash fire or explosion occurred and flames came out of the top fatally burning a man who was working there. They believe the first flash disturbed some dust (a fine dusty modifier that was being used) in the bag filter and this dust then resulted in a dust explosion and fire. They ruled out a VCM explosion because in the cold temperatures they would think there is not enough VCM present. Discussion at this point revealed that some companies are spot checking with L.E.L.'s in their PVC silos. While they do find VCM present it is not in the

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explosive range. It was pointed out by several companies that stearates can cause dust explosions and they are very sensitive.

14. Explosion in a pipe by ICI. This was a very unusual incident where a man opened a water valve allowing water to rush into a section of contained slurry line. Since there was a sight glass in this line he was able to see an explosion or flash of fire and later inspection found the presence of carbon. The only thing that they can determine is that it was some sort of compression ignition. They have also had two other instances of this type. While they are just local reactions they are of considerable concern. It was suggested that it may have been the result of a water hammer affect or static in a teflon lined ball valve.

15. High pressure water lance fatality. Without revealing the source company I discussed the high pressure lance fatality that had occurred at Wyandotte as the result of a man being struck by a water spray from a high pressure lance. This has been covered in a separate letter.

16. General discussion on vessel entry. Due to the high safety incidence rate involved with vessel entry, the possible exposure of personnel to monomers, and the generally poor economics resulting from vessel entry, it was the general feeling that the industry needs to find some way to avoid having to enter vessels that have contained any type of monomers. There were some people present that felt this may be something that would be legislated while there were others that did not. The general feeling was that until we could come up with some system that would prevent the need to enter vessels we would have to continue to do it but would have to exercise extreme caution whenever this operation was undertaken.

R. L. Dostal
12/12/73

R&S 140778

Vinyl Chloride Safety Association
Cleveland Ohio Meeting
October 24, 25 and 26, 1973

R&S 140779

Agenda

October 24

8:00 A.M.	Registration
9:00 A.M.	Business Meeting - Ray Asti, Chairman
9:30 A.M.	Review of Industrywide Safety Guidelines
	P. Boget - Blend Tanks
	W. C. L. Rogers - Monomer Loading and Storage
	R. Asti - Future Assignments
10:00 A.M.	Coffee
10:15 A.M.	Reacton Entry (J. C. Palinsky - Universal PVC Resins, discussion leader)
11:00 A.M.	Safety Valve Testing - (R. L. Frantz - Union Carbide, discussion leader)
12:00 Noon	Lunch
1:00 P.M.	Safety Valve Sizing - (W. J. Boyle - Monsanto and R. Fry - Diamond Shamrock, discussion leader)
2:00 P.M.	Static Control
2:30 P.M.	Catalyst Handling - (R. Stack - PPG, discussion leader)
3:15 P.M.	Pressure Vessel Obsolesence and Inspection
4:00 P.M.	O.S.H.A. Experience - (W. J. Bradford - Olin, discussion leac

October 25

8:30 A.M.	Handling Monomer Leaks - (R. Dostal-Dotw, discussion leader)
9:15 A.M.	Safe Monomer Venting
10:00 A.M.	Coffee
10:15 A.M.	Noise Control (E. Schenke - Tennaco, discussion leader)
11:15 A.M.	Monomer Exposure Standard - (P. Bogart-Tennaco, discussion l
12:00 Noon	Lunch
1:00 P.M.	Accidents and Near Misses - All

October 26

8:30 A.M.	Accidents and Near Misses, continued
12:00 Noon	Adjourn

Attendees at October 24-26, 1973 Meeting

Cleveland, Ohio

Mr. J. T. Barr	Air Products and Chemicals, Inc.
Mr. Earl Primeau	Air Products and Chemicals, Inc.
Mr. Norm Brock	Air Products and Chemicals, Inc.
Mr. M. M. Garretson	Allied Chemical Corporation
Mr. Harold Kling	American Chemical
Mr. A. Godfried	Borden Chemical
Mr. Don Young	Borden Chemical
Mr. J. A. Gray	B.P.C.I.
Mr. C. Arthur Gellner	Certain-Teed Products Company
Mr. Suchochleb	Conoco Chemicals
Mr. Earl Gremillion	Continental Oil Company
Mr. A. F. Gallagher	Continental Oil Company
Mr. R. E. Frey	Diamond Shamrock Chemical Company
Mr. J. Robert Mehall	Diamond Shamrock Chemical Company
Mr. Eli Zinn	Diamond Shamrock Chemical Company
Mr. Bob Dostal	Dow Chemical Company
Mr. Larry Adcock	Dow Chemical Company
Mr. Henry G. Smith	Ethyl Corporation
Mr. Francis Hoy	Firestone Plastics Company
Mr. Harlan Jewett	General Tire
Mr. Joe Mudd	General Tire
Mr. Claude Acree	Georgia-Pacific
Mr. Harry Lloyd	Georgia-Pacific
Mr. Glen D. Schaef	B. F. Goodrich
Mr. Herman Waltemate	B. F. Goodrich
Mr. Amos Dixon	Goodyear
Mr. Mal Trowbridge	Goodyear
Mr. John C. Floros	Great American Chemical Corporation
Mr. Brian D. Cole	Hooker Chemical Company
Mr. Maryin LeCornu	ICI, Ltd - England
Mr. D. B. Hopkinson	ICI, Ltd - England
Mr. J. R. Sanchez	Industrias Resistol, S. A.
Mr. S. D. Law	Keysor-Century Corporation
Mr. David L. Gendron	Monsanto Chemical Company
Mr. H. L. Donaldson	Olin Corporation
Mr. W. J. Bradford	Olin Corporation
Mr. E. J. Goettman	Olin Corporation (Assonet, Mass.)
Mr. R. H. Carte	Olin Corporation (Assonet, Mass.)
Mr. Roy W. McCune	Pantasote Company
Mr. K. K. Sheth	Pantasote Company
Mr. Henry Rzempoluch	Pantasote Company
Mr. William A. Keim	Pittsburgh Plate Glass
Mr. Roy Stack	Pittsburgh Plate Glass
Mr. Ray Asti	Stauffer Chemical Company
Mr. L. W. Hager	Stauffer Chemical Company
Mr. Don Miller	Shell Chemical Company
Mr. P. Bogart	Tenneco Chemicals
Mr. John T. Sweeney	Tenneco Chemicals
Mr. David A. Ellwood	Union Carbide (So. Charles, W. Va.)
Mr. Jay E. Giffin	Union Carbide (So. Charles, W. Va.)
Mr. R. L. Frantz	Union Carbide
Mr. Walt M. Iliff	Uniroyal, Inc.
Mr. Norman C. Walter	Uniroyal, Inc.
Mr. Jack Palinsky	Universal PVC Resins, Inc.
Mr. Cal Rehfuss	Universal PVC Resins, Inc.

R&S 140780

VINYL CHLORIDE SAFETY ASSOCIATION

Attachment

R&S 140781

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R&S 140782

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R&S 140783

Please add any additions/changes or new members.

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Name: ______________________
Title: ______________________
Address: ______________________
____
____
Phone: ______________________

Mail to: Mr. P. L. Bogart,
Tenneco Chemicals
P. O. Box 129, River Rd.
Flemington, N.J. 08822

Attachment 4

BLEND TANKS

Definition: A "Blend Tank" is defined as a vessel utilized to contain resin slurry prior to drying. Such tanks may also be referred to as "Slurry Tank" or "Holding Tank".

Type: Blend tanks are normally non-pressure vessels equipped with power-driven agitators. (Slurry is retained under agitation.)

Hazard: The primary hazard connected with blend tanks is associated with the unreacted monomer carried within the slurry after stripping. This in turn comprises two areas of concern:

I. Explosibility
II. Toxicity

Suggested methods of control for each catgory include:

I. EXPLOSIBILITY

A. Insure that vapors within the blend tank do not enter the explosive range.

B. Prevent any source of ignition within the tank.

(Note: While either of these steps taken alone should theoretically suffic experience has shown that a combination of both objectives is required.)

A-1. Maintain vapors constantly above the U.E.L. (upper explosive limit). Filling and emptying of the tank, varying monomer contents of the slurry, and varying rates of monomer release under agitation makes this approach impractical.

NOT RECOMMENDED.

A-2. Maintain vapors constantly below the L.E.L. (lower explosive limit). This may be accomplished by controlling the amount of unreacted monomer carryover, or dilution of vapor within the tank.

Preliminary indications are that the percentage of unreacted monomer carried over is greater than has heretofor been recognized. Until more efficient methods of stripping are developed and implemented, control of monomer quantity cannot be depended upon to achieve vapor-air mixtures below L.E.L.

R&S 140784

Dilution with air, introduced at atmospheric and exhausted mechanically; introduced mechanically or by pressure and exhausted at atmospheric; or introduced and exhausted at atmospheric ("open-hatch" method), is the most common current practice and has been thought for many years to be a satisfactory precaution. There is, however, serious question as to whether introducing air into the vapor space may not actually increase the hazard by diluting the vapor below the U.E.L. There is also the problem of insuring that all the vapor space is sufficiently diluted.

RECOMMENDED WITH RESERVATIONS

Should the air-dilution method be chosen, the following precautions are suggested:

- Introduce a sufficient supply of air, at a constant rate, to fully dilute the entire vapor space, regardless of slurry level, to below L.E.L.

- Insure the reliability of air supply, including power supply to blowers or exhausters.

- Design air introduction or exhaust so that sufficient velocity is maintained to insure dilution. Do not rely upon natural draft.

- Monitor the vapor space for monomer content.

- Connect the monitor to an alarm and develop procedures to be followed if monomer content exceeds L.E.L.

A-3. Inert the atmosphere of the vapor space

Maintaining an inert atmosphere in the entire tank vapor space effectively precludes ignition of vapors. This can be accomplished by introduction into the tank of an inert gas in sufficient quantity, at a controlled continuous rate, to preclude the presence of sufficient O_2 to sustain ignition. It should be understood that introduction of inert gas does not preclude the presence of monomer in the vapor space.

RECOMMENDED.

R&S 140785

Where inerting is used, the following suggestions are made:

- Nitrogen is the preferred inerting agent. Use of CO usually involves an inert-gas-generator, which can cause safety problems of its own.

- Insure a sufficient supply of inert gas, introduced at a rate which will suffice to inert the entire vapor space at all times regardless of slurry level.

- Monitor the nitrogen flow by the use of flowmeters or similar devices.

- Check O_2 level in the tanks by means of continuous-reading or frequent intermittant reading monitors. Such monitors should be programmed to give an alarm should the O_2 content approach unacceptable levels, and should preferrably be designed to automatically increase N_2 flow when such a condition occurs.

- It is recommended that the O_2 level in the tank not be permitted to exceed 8%.

B-1. Ignition prevention

In order to prevent ignition of monomer vapors in, and associated with, blend tank operations, the following precautions are suggested:

- The blend tank area should be treated as part of the monomer train and all precautions taken in the reactor area should be applied here as well. These include, but are not limited to:

  Class I, Group D, Div. I electrical equipment;
  No smoking, flames or open lights;
  Hazardous work (hot work) permit required.

- Where tank vents are provided, they should be equipped with flame arrestors, and in the case of inerted tanks, conservation vents.

- Vent discharge, even on inerted tanks should be remoted from ignition sources.

R&S 140786

- Potential friction points, such as agitator shaft bearings, should be evaluated and precautions against static generation and friction heating, under both normal and abnormal conditions, taken.

  Examples: Use of soft metal collars at point of entry of agitator shaft through tank top. Use of mis-alignment sensing switches on shafts, etc.

II. TOXICITY

The second area of hazard which must be considered with blend tanks is exposure to the anesthetic effects of monomer. This consideration is of course not exclusive to blend tanks, but assumes particular significance because of the tendency to regard blend tanks as beyond the monomer area.

Operations:

The primary area of exposure is the roof hatches, or manways. These hatches are opened to check levels in the tank, to check the condition of the tank interior, and to wash out the tank.

Elimination of the necessity to perform these tasks through the hatch in turn eliminates most of the monomer exposure.

It is recommended that:

- Operating procedures be so developed as to obviate the necessity for personnel to go on or across the tops of blend tanks.
- Hatches and manways be closed and sealed with a frangible seal, such as a railcar seal.
- Tank levels be determined by the use of remote-reading level gauges.
- Washout be accomplished by the use of remote-operated fixed or rotating nozzles within the tank.
- Agitator motor switches and any other operating devices be located at ground level.

R&S 140787

Maintenance:

When it is necessary to go on top of a blend tank, to inspect, or perform maintenance, the buddy system should be strictly enforced.

When entering a blend tank, all confined space entry procedures shall be followed.

R&S 140788

SPI

THE SOCIETY OF THE PLASTICS INDUSTRY, INC.

250 PARK AVENUE • NEW YORK, NEW YORK 10017 • 212/687-2675

The Society of the Plastics Industry, Inc.

SUGGESTED RELATIVE HAZARD CLASSIFICATION OF ORGANIC PEROXIDES

BY

ORGANIC PEROXIDE PRODUCERS SAFETY DIVISION

FOR

USERS AND VENDORS OF ORGANIC PEROXIDES

R&S 140789

11/72

THE SOCIETY OF THE PLASTICS INDUSTRY, INC.
SUGGESTED RELATIVE HAZARD CLASSIFICATION
OF
ORGANIC PEROXIDES

The Organic Peroxide Producers Safety Division of SPI classification system is designed to evaluate the effects of a number of factors likely to be encountered in shipping or storing organic peroxides: heating at various rates under partial confinement, long term storage at various ambient temperatures, mechanical shock, explosive shock and direct application of flame.

The following tests have been used to classify organic peroxides by the OPPSD system. Details of each test method are described in separate write-ups.

Pressure Vessel Test (PVT)

The rate and energy of thermal decomposition of peroxygen compositions are measured under conditions of rapid heating and partial confinement.

Rapid Heat Test

The type of decomposition that occurs to peroxygen compositions is determined under conditions of moderately rapid heating in a test tube.

Self-Accelerating Decomposition Temperature Test (SADT Test)

Susceptibility to Decomposition

The lowest ambient oven temperature at which a peroxygen composition in its largest commercial package will undergo self-accelerating decomposition is established.

Damage Potential

The severity of such decomposition is also determined by damage to the container, oven, etc.

Impact Sensitivity

The susceptibility of a peroxygen composition to undergo decomposition upon being struck by a falling weight is measured.

Modified Trauzl Block Test

This test measures the energy released by a peroxygen composition when initiated by an explosive force (blasting cap).

R&S 140790

Burning Test

This test determines the flame height that results by burning a specified quantity of a peroxygen composition.

Results for each test are divided into three hazard ratings:

3 - Maximum Hazard

2 - Intermediate Hazard

1 - Low Hazard

The numerical results from the seven test categories are totaled to arrive at the final classification.

The classes are:

	Code Word	Numerical Range - Total of 7 Tests	Suggested Maximum Gross Wt. Limit
Class I	Danger	15-21	Subject to
Class II	Warning	11-14	Test by
Class III	Caution	8-10	Competent
Class IV	No Code Word Unregulated	7	Authority

Other chemical, physical and physiological characteristics such as flammability, toxicity, corrosivity, and special conditions for refrigerated storage and shipment are not included in this main classification system, but form the basis for additional labeling requirements.

R&S 140791

PROPOSED LIMITS

Test	Numerical Rating	Results
		Vent Diameter (mm)
Pressure Vessel Test (PVT)	3	20-14
	2	<14-1.0
	1	<1.0
		Force of Decomposition
Rapid Heat Test	3	Rapid - equal or greater than t-butyl peracetate in benzene
	2	Moderate
	1	Mild
		Force of Decomposition
Self Accelerating Decomposition Temperature (SADT)	3	Rapid Decomposition (Considerable Damage to test oven)
	2	Moderate Decomposition (Considerable damage to container and possible slight damage to test oven)
	1	Mild Decomposition (No damage to oven and some or no damage to container
		Temperature
SADT	3	<10°C
	2	10°-49°C
	1	>49°C
		Height
Impact Sensitivity[1]	3	<10 cm.
	2	10-25 cm.
	1	>25 cm.

R&S 140792

11/72

Proposed Limits Cont'd

R&S 140793

Test	Numerical Rating	Results
		Expansion (ml.)
Modified Trauzl	3	60-35
	2	<35-15
	1	<15
		Flame Height
Burning Test[2]	3	>152 cm.
	2	152-91 cm.
	1	<91 cm.

[1]Applies to solids and pastes. Liquid peroxides with shock sensitivity of less than 25 cm. are not classified under this system.

[2]If a product burns very vigorously, it is given maximum hazard rating even if the flame height is less than 152 cm.

EXAMPLES OF CLASSIFICATIONS FOR ORGANIC PEROXIDES

Test Result

Product*	PVT	Rapid Heat	SADT (Decomp.)	SADT (Temp.)	Impact	Trauzl	Burning Test (Flame Height)	Total Points	Ha C
Lauroyl Peroxide	2	2	1	1	1	1	1	9	
Decanoyl Peroxide	2	2	1	2	1	1	1	10	
Benzoyl Peroxide (Dry)	3	3	3	1	3	2	3	12	
70% Benzoyl Peroxide (Wet)	2	2	2	1	1	1	1	10	
Di-t-butyl Peroxide	1	1	1	1	1	2	2	9	
t-Butyl Hydroperoxide 70 (with approx. 20% DTB)	2	1	2	1	1	2	1	10	
t-Butyl Hydroperoxide 70 (with approx. 30% water)	1	1	1	1	1	1	1	7	
75% t-Butyl Peracetate in OMS	2	2	3	1	1	2	2	13	
75% t-Butyl Peracetate in Benzene	2	3	3	1	1	3	2	15	
t-Butyl Perbenzoate	2	2	2	1	1	2	2	12	
t-Butyl Peroctoate	2	2	2	2	1	2	2	13	
An 85% Cyclohexanone Peroxide	2	2	2	1	2	2	2	13	
A 60% MEKP	2	1	2	1	1	2	2	11	
IPP	2	2	2	3	2	3	3	17	
A non-regulated 60% MEKP	1	1	1	1	1	1	1	7	
50% BPO in TCP	2	2	1	1	1	1	1	9	
50% BPO Fire Retardant Paste	1	1	1	1	1	1	1	7	
25% Acetyl Peroxide in DMP	2	3	3	2	1	1	2	14	
50% 2,4-Dichlorobenzoyl Peroxide in Silicone Fluid	1	2	1	1	1	1	1	8	
50% Benzoyl Peroxide in Silicone Fluid	1	2	1	1	1	1	1	8	
50% Benzoyl Peroxide in Plasticizer (Paste)	1	2	1	1	1	1	1	8	
55% Benzoyl Peroxide in Plasticizer (Paste)	1	2	1	1	1	1	1	8	

*Peroxides by various manufacturers may have different test results and different classifications.

R&S 140794

R&S 140795

SUMMARY

VINYL CHLORIDE TANK CAR DERAILMENT
Fort Wayne, Indiana - July 20, 1973

For your perusal, we have prepared the following compilation on the vinyl chloride tank car derailment. Data was obtained from newspaper articles appearing in the "The New-Sentinel", July 21, 1973, Fort Wayne, Indiana; "The Journal-Gazette", July 21, 1973, Fort Wayne, Indiana; and from a report issued by O. C. Johnston, July 25, 1973.

At 3:40 p.m. on Friday, July 20, 1973, 13 railroad cars of a 123-car Penn Central train derailed one-half mile from the west city limits of Fort Wayne, Indiana. Four of the derailed cars contained vinyl chloride being shipped from the Calvert City, Kentucky plant to Hooker Chemical Company in Stevens, New Jersey.

According to authorities at the scene, one of the vinyl chloride tank cars was punctured and caught fire in the initial impact. A box car of wood shingles also derailed and ignited in the initial derailment. A second tank car derailed and imbedded itself in the burning box car. The other two tank cars were on their sides, off the track, but did not vent or burn.

Authorities stated that some 3,000 to 5,000 residents in a two-square mile area surrounding the scene were evacuated at 6:00 p.m. when it became evident the second tank car might explode. The pressure relief device on this tank car was releasing and the time between releases was diminishing. The car exploded at 7:20 p.m.

One home, one-quarter mile from the scene, burned to the ground following the explosion, when the end of the tank car shot into the residence; and the porch of another home was sheared off. Fortunately, there were no injuries reported.

Penn Central officials notified CHEMTREC of the derailment at 5:35 p.m. The contents of the chemical cars was unknown for at least one-hour. The bills of lading were in the caboose but could not be reached at first, due to the proximity of the fire. The Calvert City plant was then contacted and confirmation made that the material was BFG's vinyl chloride.

Gene Phillips and Oran Johnston (Calvert City's CHEMTREC Team) were dispatched from the plant to the scene. Upon their arrival they were escorted directly to the derailment site and found the following: two tank cars coupled together and lying on their sides, both were cool with no leaks; another tank car on its side at a sloping angle, punctured in the initial derailment and burning; and ~~two hopper cars,~~ two box cars, and a piggy back flat that had also derailed. The team was advised that a fourth tank car had exploded and burned itself out.

After surveying the situation, the Goodrich team advised the fire chief to allow the burning vinyl car to burn itself out so escaping vapors did not saturate the area, re-ignite, and flash back.

A decision was then made to allow the evacuees to return to their homes, with the exception of those living in the immediate area. This decision was based on the likelihood that when the liquid was completely vaporized and the car pressure gone, there might be a flash back into the car, drawing in oxygen, and could result in an explosion.

To accelerate the burn off, the tank shell was warmed up with ambient temperature fire water. The tank shell had a heavy frost line at the liquid level, 4°-6°F., in comparison to the fire water at 60°-70°F. The warm water increased vaporization, accelerated the burn, and shortened the time required for burn off. The other derailed cars were retrucked and moved away. Penn Central brought two tank cars full of water and spotted them. Water was pumped from these cars which were continuously filled from a hydrant one-half mile away.

Early Monday morning the fire died down. After checking the frost line of the liquid on the exterior of the car, it was found to be down to approximately 150-200 gallons of liquid. The decreased surface of liquid reduced the amount of vaporization and the rate of burn. The water was cut off and after two hours the car was examined again; no frost line was found, indicating the liquid was gone and only the vapor remained.

At this point, not knowing what would happen in the final burn out with the loss of pressure, it was decided to snuff the flame. Two fire hoses were tied and aimed directly at the fire. One fireman started the pump and the fire was snuffed at 11:15 a.m. (Monday, July 23, 1973). Water was continued for some twenty minutes and then one hose was shut down and a twenty foot section of 1-1/2" pipe was attached to it. The pipe was inserted into the car through the puncture, which was only 3" in diameter. The water on this hose was turned on again, flooding the car.

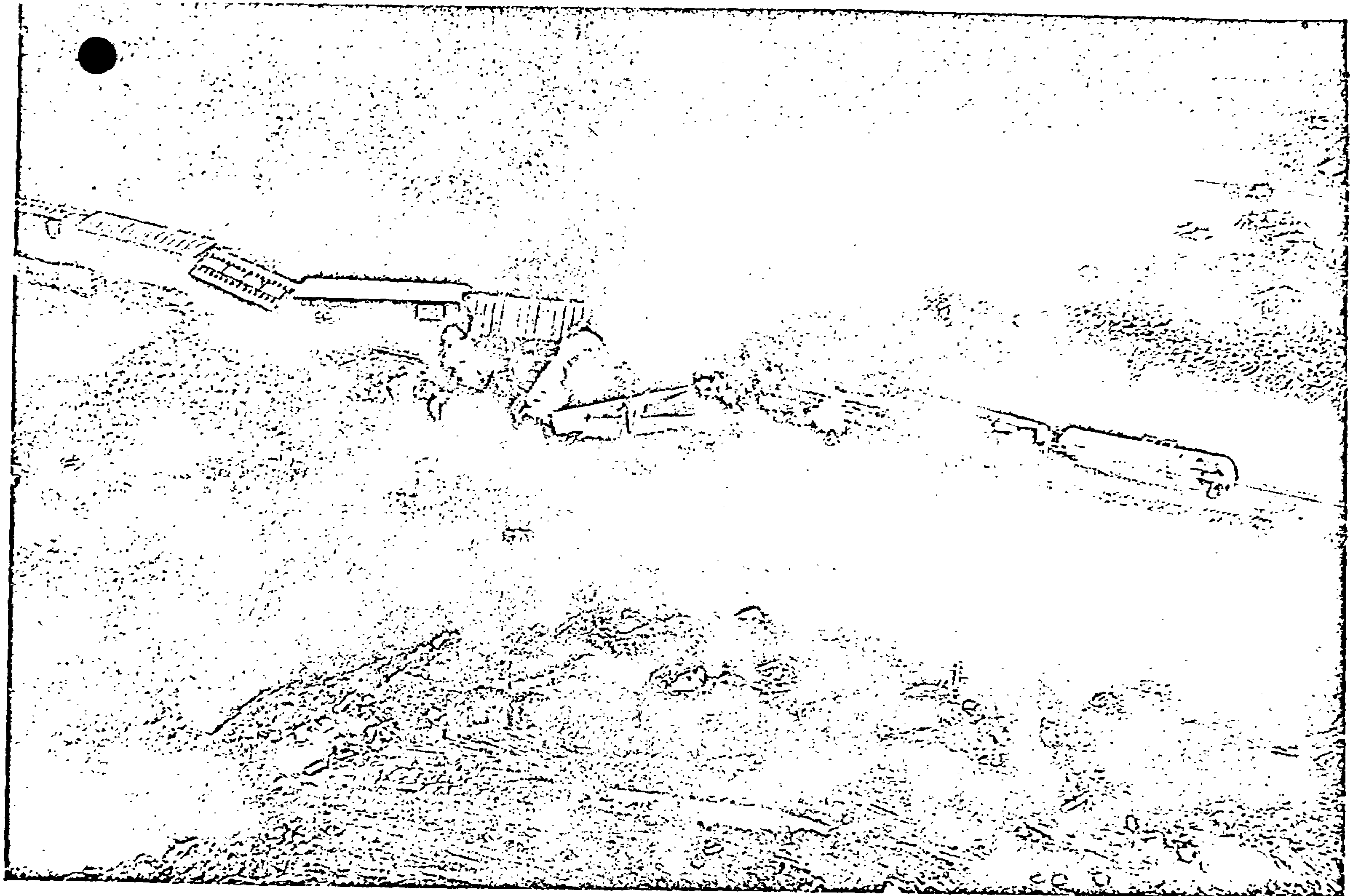
The adjacent area was then checked with explosimeters and found safe. The car was completely filled with water and monitoring of the area continued. At this point the Calvert City Team was released. The situation was well under control and their services were no longer needed. They left the scene at approximately 12:00 a.m., Monday, July 23, 1973.

H. Waltemate

HW/kats
Attachments

cc: Plant Managers
Plant Safety Engineers
Safety Council
T. H. Smith
R. A. Kelley
R. C. Johns

R&S 140796



R&S 140797

The Train Derailed, Then The Fire . . . Then Boom!

(Air Views by Allen County Police Chief Robert E. O'Reilly)

R&S 140798

Vinyl Chloride Mushroom

A red ball of fire brightened the skyline at 7:20 p.m. Friday when second tanker of a derailed Penn Central train exploded north of Indiana (Photo by News-Sentine . Photographer Carl Hartup).