

MEMORANDUM

DATE: DECEMBER 14, 1971

SUBJECT: VINYL CHLORIDE SAFETY ASSOCIATION MEETING
ROCHESTER, N. Y. - NOVEMBER 10 - 12, 1971

TO: W. M. REITER

Attached are the minutes of the Vinyl Chloride Safety Association Meeting held November 10 - 12, 1971 in Rochester N. Y. Allied attendees were R. F. Schwab and J. E. Cooper.

The minutes consist of three sections:

- I - Business Meeting
- II - Agenda Presentations
- III - Accident Experiences of Individual Companies

New activities for the association as proposed in this meeting include the following two major items:

1. The group passed a motion to have the new executive committee outline a procedure whereby the association would prepare uniform safety standards and procedures for the industry. One method under consideration would require the submission of edited procedures from all member companies from which consolidated procedures could be formed. (Refer Section II-G of the minutes).
2. Likewise a proposal was made for the development of uniform procedures for handling Acroosteolitis (AOL) prevention and hand examinations.

A number of the members requested aid in refining their programs, particularly in the area of finding qualified physicians for x-ray diagnosis. It was suggested that individual companies send information regarding their AOL programs to the association secretary who would then distribute same to all members.


J. E. Cooper

JEC:cl

cc: Messrs. A. P. McGuire
E. C. Schule
R. F. Schwab
G. R. Millar
R. L. Fawcett
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J. E. Ertel
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MINUTES - VINYL CHLORIDE SAFETY ASSOCIATION MEETING
NOVEMBER 10 - 12, 1971 - ROCHESTER, NEW YORK

I. BUSINESS MEETING

A. Affiliation with the SPE or SPI

The steering committee moved to discontinue consideration of affiliation with the SPE or the SPI. Motion Passed.

Both SPE and SPI regulations would require the presence of a representative at all meetings, who would take and prepare minutes. Minutes would be held on file by either society.

B. New Officers

Nomination for new officers were presented and approved by the group. They are:

Chairman - M. G. Glenn - General Tire
Vice Chairman - R. A. Aste - Stauffer Chemical
Program - H. G. Smith - Ethyl Corporation
Treasurer - J. C. Flores - Great American Chemical Corp.
Secretary - J. R. Mehall - Hooker Chemical

II. AGENDA PRESENTATIONS

A. Catalyst Handling, Storage and Reactor Addition - How can the hazards be minimized?

Discussion Leader - Glenn D. Schaaf - B. F. Goodrich

Goodrich presented their internal catalyst handling policies and experience which include the following:

1. A committee composed of representatives from manufacturing, research, engineering and safety was formed to develop safe handling procedures.
2. Catalysts were given a hazard rating consistent with Factory Mutual Insurance Bulletin FM-7-80. It was mentioned, however in the group that the AIA has a bulletin which is more restrictive than Factory Mutual. And secondly, that the NFPA is trying to set up standards for organic peroxides. The government would probably adopt the latter as a Federal Standard. It was thought that it might be a couple of years before the NFPA standards were issued.

The following Table No. 1 defines the B. F. Goodrich hazards rating:

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TABLE NO. 1

BFG CRITERIA FOR CATALYST HAZARD RATING

<u>CLASS</u>	<u>CRITERIA</u>	<u>EXAMPLES</u>
I	Greatest hazard - can cause severe explosion.	100% IPP
II	Intermediate Explosion Hazard	100% ACSP, 100% SBP
III	Moderate Explosion Hazard - Severe Fire Hazard	20% IPP in n-Hexane (BFG solution)
IV	Moderate Fire Hazard	
V	Little Fire Hazard	LPO

It should be noted that a solution of IPP was designated as a Class III catalyst as opposed to Class I for solid IPP. Members of the group recommended caution be exercised for this criteria as IPP solution can crystallize out to solid if temperature is allowed to get too cold.

3. Storage criteria were then established based on catalyst hazard ratings in FM standards. Storage was divided into two areas:
 - A. Primary storage where the bulk is held, and
 - B. Secondary storage for service or immediate use.

Dry ice or mechanical refrigeration with possible back-up liquid nitrogen cooling should be used for primary storage. Storage should be a minimum distance from other facilities as determined by following Table No. 2:

TABLE NO. 2

BFG CRITERIA FOR CATALYST PRIMARY STORAGE

<u>WEIGHT PEROXIDE (LBS)</u>	<u>DISTANCE FROM PROCESS BUILDING (FEET)</u>			
	<u>Class I</u>	<u>II</u>	<u>III</u>	<u>IV</u>
10-50	50	50	50	50
50-100	75	50	50	50
100-500	100	50	50	50
500-1000	125	60	50	50
1000-3000	200	95	50	50
3000-5000	300	140	65	50

Allowable secondary storage of catalyst is determined by the following Table No. 3:

TABLE NO. 3

BFG CRITERIA FOR SECONDARY STORAGE OF PEROXIDE

CATALYST HAZARD RATING	ALLOWABLE STORAGE (POUNDS)			
	MAIN PROCESS AREA (IN CONTAINERS)	"CUT-OFF OR ATTACHED AREA" (1)		DETACHED AREA (IN CONTAINERS)
		CONTAINER STORAGE	DISPENSING OR MIXING	
I	None	None	50	5000
II	Intermediate Needs (1 batch)	24 hr. supply (200 lbs. max.)	100	10,000
III	"	"	"	"
IV	"	200,000	20,000	500,000
V	"	Unlimited	"	"

- (1) Goodrich defines a "cut-off" or attached area as a room or building of non-combustible construction with a "blow-out" wall - Class I Group D.

Note that according to Table No. 3 no Class I catalyst can be stored in the Polymer Building and that Polymer Area Storage for all other classes is restricted to an amount sufficient for one batch. B. F. Goodrich stated that they adhere to these regulations. Others in the group stated that they do not. One admitted having a Class III catalyst freezer on the Poly floor.

4. The following points developed from discussion of catalyst charging techniques:

- (a) Nine companies use charge pots attached to the reactor and five use portable charge pots.

General Tire described their portable system as a small tank on a cart with an air driven positive displacement pump. Catalyst is charged and followed by an equal quantity of solvent. This procedure was started 3 years ago when a reactor charge pot blew up. The same system is used for charging short-stop.

- (b) Most members of the group believe that charge pots should be equipped with rupture discs. Monsanto stated, however that their internally developed data indicates that same will not prevent explosion. Monsanto's charge bombs are jacketed and kept under brine recirculation. An automatic vent valve stays open except during physical transfer of catalyst to the reactor.

PPG, however disagrees with Monsanto. They have developed pressure build-up data supporting the use of and sufficient for sizing of rupture discs.

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- (c) The general group consensus was that fast catalysts should go into the reactor last. The notable exception was Hooker who charges fast catalyst first then monomer in their bulk polymerization process.
 - (d) Regarding methods for flushing in the catalyst almost all who use pots flush with copious amounts of water. A few however flush with VCM, then water.
5. With regard to disposal of catalyst containers it was noted that most from the group do not flush with 20% caustic and water as has been recommended in the past. Likewise few follow new recommendations of flushing with caustic and isopropyl alcohol. Nearly all slit the containers before disposal. Some flush with water before disposing and some do not. One argument given to support flushing with water is the prevention of partial bottles of catalyst being left in the disposal bin or leaving the plant. One company has had experience with used containers leaving the plant with catalyst still in them which later started fires in the local dump. It was noted that vermiculite should be used to soak up all catalyst spills. However, many were not certain whether this practice is being adhered to at their plants.
6. B. F. Goodrich recommendations:
- (a) Better publicity should be given to accidents of both producers and users.
 - (b) Internal committees should be set up to establish catalyst handling procedures. Goodrich stated this system worked well for them.
 - (c) Operators must be adequately trained. Procedures must be uniform and enforced - with disciplinary action if necessary. Manufacturing, technical and safety should jointly enforce the safety practices. Once the operators have been trained a continual re-education system, showing films, etc. should be employed. In addition to the obvious operators should also be trained to cope with charging delays, how to dispose of catalyst - they should know the proper storage temperature and handling temperature and how much time they have before decomposition will occur.
 - (d) Closed refrigerators and freezers can be a hazard as the catalyst is contained. Latches must be removed from all freezer lids.
7. Catalyst Accident Experience:
- (a) Goodyear had a bottle of 25% Lupersol 11 in mineral spirits burn on their polymerization floor. It was later estimated that the bottle had sat on the floor for 12 hours at approximately 75°F. Once the fire started it could not be put out until decomposition was complete.

- (b) Dow had an experience where the contents of an entire freezer chest decomposed. No explosion occurred, however a vigorous fire continued until decomposition was complete. In this incident the freezer had malfunctioned and the high temperature alarm sounded. The alarm however was silenced and forgotten. It was recommended by Dow that time delays be used which will reactivate the alarm if the situation has not been corrected in a specified amount of time.

B. Lucidol Plant Tour and Panel Discussion

A tour was taken of the Lucidol plant in Geneseo, New York on November 10, 1971. The tour included the inspection of the Lucidol power plant, the IPP production remote control center, IPP pack out station, intermediate freezing section, primary storage section and a refrigerated shipping container.

Following the tour a panel discussion was held on catalyst handling procedures. The following items are those discussed that supplement the earlier group discussion on this subject:

1. Initial discussion centered on Lucidol's standard testing program to determine safe handling procedures. All catalysts are tested for sensitivity to shock (impact & blasting cap), heat, flame and contamination.

One of the more important tests for the fast catalysts is the determination of the self-excelerating decomposition temperature (SADT). The largest commercial container is placed in an oven for one week at varied temperatures to determine the SADT and a safe storage temperature. SADT statistics for IPP thus determined are as follows:

	<u>SADT</u>	<u>FORM OF DECOMPOSITION</u>
100% IPP	35°F	Gas and Fire
45% IPP solution	45°F	Vigorous Gas Liberation
30% IPP solution	75°F	Mild Gas Liberation

As this data shows dilution of the peroxydicarbonates tends to prevent auto ignition of the gas liberated by their decomposition. In addition as package size decreases the chances of auto ignition decreases. Ignition of off-gas, however can always occur as a result of static spark, etc.

2. The danger of confining catalysts such as IPP was again re-emphasized. In event of decomposition pressure rises so rapidly that any confinement can lead to a detonation. PPG has conducted tests where a small amount of catalyst is allowed to decompose in a 7 milliliter bomb and the resulting pressure rise is measured. 0.1 grams of pure IPP created an 850,000 psi per second pressure rise while 0.2 grams of a 50% solution of IPP created a 20,000 psi per second pressure rise.

Monsanto's earlier comment on the insurance provided by rupture discs was somewhat supported by the examples given showing how little con-

finement can be required to produce a detonation. In one test, where the decomposition of a tray of solid IPP was initiated by, blasting cap, a steel tray detonated while that in a polyethylene tray, where confinement was less, did not. In the second case liquid IPP was placed in an open vessel with two feet of water on top of the IPP. Decomposition of the IPP caused a severe detonation. The water blanket was sufficient confinement.

3. With regard to earlier discussion on universal catalyst safety standards Lucidol reported that the peroxide manufacturers had agreed upon classifications which will probably be published in 1972. These standards will be based on three primary classifications: "Danger" - "Warning" - "Caution".
 4. Disposal of catalyst was discussed. Where catalyst cannot be burned or "weathered off" in an open trench, because of pollution considerations, Lucidol suggested neutralizing it with caustic. In this case two moles of caustic should be agitated with one mole of peroxide to yield alcohol, hydrogen peroxide, and carbon dioxide.
 5. Lucidol reported some details on a recent explosion at their facility. In this incident a 70 gallon batch of IPP decomposed in the pack-out tank, just up-stream of the packaging station. The tank peeled apart and shrapnel was found 1/2 mile away. Some IPP had apparently been left in the line leading to the packaging faucet. This coincided with an unexplained valving off of the brine recirculation intended to keep this line cold. Decomposition in the line flashed back to the tank and the detonation occurred.
 6. Lucidol recommended having stand-by liquid nitrogen for all walk-in freezers for use in event of power failure. In addition the liquid nitrogen can be used to control an initiated decomposition.
- C. Operator Training Programs - Is it possible to adequately train production and maintenance employees?

Discussion Leader - Joe Mudd - General Tire

General Tire presented their philosophy of maintenance training and organization as initiated in 1965. The new program reportedly transformed an ineffective maintenance force into one that is highly efficient today.

Direct results of the training program are as follows:

1. Maintenance cost split of 67¢ material per dollar of labor in 1965 has improved to \$1.22 material per dollar of labor.
2. There was one grievance registered this year where floods of same used to come in.
3. Unscheduled overtime was significantly reduced to 2% of the total payroll. (General Tire utilizes one shift mechanic and one shift instrument electrician)

The primary basis for the program is a schedule of advancement based on acquired skill and knowledge. Men are divided into three groups, mechanics, instrument electricians and service (laborer). There then

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are a number of skill levels within each group. To advance to higher pay levels training must be received (when program was initiated training amounted to 3 hours per week of overtime for 12 weeks). Home study is given along with work training. The man must then pass the test to advance. A poor test showing, however can result in the man being bounced back one level. A minimum of 6 months must now be spent at one level and it takes a minimum of 42 months to move from the lowest to the highest paying grade (\$4.60 per hour vs. \$4.40 per hour for a top production operator). The entire maintenance force can theoretically move to top pay grade.

In addition, outside study (local shop courses) is promoted and 100% paid by the company. If a man takes a course he is given related shop assignments at work. He is also tested on what he learned after the course is completed.

The key to the success of this system is that promotion and pay raises are dependent on acquired skill - not vacancies at the top.

When the program was first initiated the following goals were set up:

1. More thorough maintenance.
2. More efficient maintenance.
3. Less breakdown - preventative maintenance.
4. Better ratio of material to labor dollars.

The cost books were opened to the men. Most refused to believe how much it cost to rebuild a pump, etc.

The men themselves were included in the re-writing of all safety procedures - their ideas were included.

Outside vendors were invited to show films on how to install bearings, etc. The importance of record keeping and work order systems were stressed. In addition to the training aspects the revitalization included better maintenance scheduling (to include a specific percentage of preventative) and a revival of the equipment numbering system. Better control over stores is now being achieved by use of a local vendors computer (A.Lewis Supply).

D. Emergency Procedures

Discussion Leader - William J. Bradford - Olin Corp.

Discussion in this area centered in ways to prevent procedures from "becoming lost in the files", and always accessible when the need suddenly materializes. One good suggestion called for emergency procedures to be permanently placed at each phone. They would be applicable for that immediate area and the man working in it. In addition

all procedures would be overlapping to insure no missed assignments.

A survey on emergency power showed that twelve member companies have sufficient generator capacity to maintain reactor agitation and cooling in the event of power failure.

On the subject of shortstops only isoprene was mentioned. One level cited was 2 quarts for a 2200 gallon reactor.

E. Job Safety Analysis

Discussion Leader - William J. Boyle, Jr. - Monsanto Co.

Monsanto detailed a case where JSA's were used to effectively straighten out a sloppy plant. An accident focused attention to poor safety standards. A committee was set up to draw up JSA's for each job, based on interviews with each hourly and salaried employee. In the process JSA's were formed that were adhered to because they incorporated the ideas of the men, and all employees' gripes were heard. These "beefs" were incorporated into a maintenance punch list that was given highest priority. When the operators' area problems were solved it was found that the foremens' personnel problems began to disappear and within a short amount of time all aspects of operation dramatically improved. Production hit new records, yield and quality improved, and grievances disappeared.

Monsanto warned however that success was met in this instance because it was a joint internally motivated program. After its success was apparent management ordered a similar program at another plant. Complete failure there resulted from strict time-table pressure placed on individuals, the lack of a group spirit, and outside "force" vs. internal motivation. Appendicized is Monsanto's recommended procedure for conducting job safety analyses.

F. Bulk Handling and Storage of VCM

Discussion Leader - William Miringoff - Hooker Chemical

Points made in the Hooker presentation follow:

1. Personnel should use self contained air packs if work is required in a VCM atmosphere. Seven to eight hour exposure to less than 500 ppm of vinyl chloride will cause drunkenness.
2. The group generally conceded that copper can probably be used now that acetylene content of today's monomer is very low. Explosive copper acetylides won't be formed. Use of aluminum however should be avoided as explosive chlorinated aluminum alkyls can be formed. A severe explosion has occurred where a chlorinated solvent was placed in an aluminum tank.
3. Hooker uses a 125,000 gallon sphere for monomer storage. A dike is used with a large concrete run-off trench leading to a remote pit. Hooker convinced their insurance company that a run-off ditch was a safer approach than a continuous dike not able to contain a large spill.

4. Oxygen in stored VCM should be maintained below 500 ppm. Provision for inerts venting should be made. Hooker employs a 5 psig low pressure cut-off on their unloading compressors as well as maintaining a nitrogen blanket on the compressor seals to avoid oxygen intake when on the vacuum side. A pump and vaporizer are used for liquid unloading. Hooker uses a Hays Oxygen Analyzer for monitoring oxygen content. B. F. Goodrich uses a Teledyne Oxygen Analyzer. For more extensive discussion on the subject of oxygen in the VCM refer to Diamond Shamrock's experience with polyperoxides in their vinyl chloride found in the accident section of this report.

G. Industry Wide Safety Standards

Discussion Leader - Edward T. Biehl - Pantasote

In view of increased government attention towards safety it was felt by Pantasote and the group as a whole that it would be better for our industry itself (The VCM Safety Association) to develop uniform safety standards (which might then be adopted by the government), than to allow the government to do the same on their own. After some discussion on how best to get started, a motion was passed to have the new officers act as, or appoint a committee to prepare detailed recommendations and a feasible approach. One method offered was for each member company to submit his own safety procedures (edited as necessary to protect confidential information) for the preparation of conglomerate standards.

Pantasote reviewed aspects of their company's safety programs which include the following:

1. Elimination of vapor using detectors to pinpoint problem areas. Frequency of detector alarms is monitored and is used as an indicator of required action, whether it be maintenance or employee reprimand, - not just as a warning for water deluge. If venting must be done it is done slowly enough to keep safe readings on the VCM monitors.
2. Rules for hard hats and proper clothing are enforced with time off or even dismissal if necessary. All clothing is cotton to prevent the occurrence of sparks. Shirt pockets are removed to prevent "fall-out" into tanks, etc.
3. Vessel entry rules are strict and compliance must be complete. All permits are filed and reviewed.
4. Bottom drop valves cannot be opened until 0 pressure releases the lock on the valve.
5. No solids are sewered: Linen bags are placed on reactor drop lines to catch reactor cleaning. A "b.b." batch is bagged off in like manner.

H. Pressure Vessel Inspection and Record Keeping

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Discussion Leader - Walter M. Iliff - Uniroyal Chemical.

Uniroyal's system for pressure vessel inspection was given as follows:

1. One man is responsible for all pressure vessel inspection.

2. All vessels are given annual external and internal inspections. Vessels subject to corrosion such as knock-out pots off the reciprocating recovery compressors are checked more frequently. Suspect vessels are downgraded into lower pressure service.
3. Vessel thickness can be gauged using an electronic caliper by drilling and getting an actual thickness or by hydrostatic using one and one-half times working pressure and a 25 lb. hammer test. In the latter case if the tank does not fail the assumption is made that it is in good condition. Conoco recommended the use of Bronson's sonic measuring device. A tank wall can be measured while tank is full and a thickness profile can be obtained.
4. A record is drawn up each time a test is made. An 8-1/2 by 11 sheet of the tank unfolded is prepared and the point of inspection is designated.

I. Pressure Test Procedures

Discussion Leader - Charles E. Bowman - Union Carbide

1. Nearly all pressure vessel testing is hydrostatic at Union Carbide. Hydrostatic testing is required every 5 years for autoclaves in high pressure storage and every 10 years for low pressure storage (less than 50 psig). All equipment is entered on computer and after an allocated period has expired computer prints out an "overdue" on the particular item. Safety, engineering and production get a print out every six months of the overdue items.
2. Union Carbide spray paints relief valves after inspection with a color representing that given period of time.
3. Union Carbide also pressure tests each time the reactor is opened (1 to 10 batches dependent on grade). The reactor is pressurized to 165 psi with nitrogen, held for 15 minutes and the reactor is then soap tested for leaks. If no more pressure drop is experienced that 1 psi in 15 minutes and if no soap leaks are found the reactor is vented. 100 gallons of water are then charged to cover the dump valve and vacuum pulled. The operator then looks for leaks through the sight glass. At this point it was determined that 12 out of the group used sight glasses on their reactors.

General tire hydrostatic tests after each reactor clean.

Four to five of the group use hydrostatic tests after each reactor open. About 8 to 10 test with nitrogen and the remainder apparently do not pressure test that often.

Diamond at Deer Park, Texas, is in the process of grinding down all their reactor nozzles and manheads to get a good single gasket seal.

J. Plant Supervision - How much is really required to maintain the proper balance between Operations and Safety?

Discussion Leader - Clay G. Thompson - Tenneco Plastics ASI 000016477

Tenneco believes this is normally a bigger problem area in older plants.

New plants are or can be designed to eliminate much of the human value judgement using VCM detectors, etc. Tenneco believes that eventually all plants will be computer controlled. Tenneco's new plant is semi-automatic.

Since Tenneco's Flemington disaster, operating and emergency procedures have been revised and an additional safety foreman and one shift foreman have been added. The foreman has check sheets where he must follow a minimum of the operation, men, methods, equipment, instrumentation, etc. each day. Tenneco's measures to promote safety reportedly cost them 0.2¢ per pound of resin.

New operator training follows the following general format:

On the first day he receives policy orientation. During the second and possibly the third day the foreman gives him safety indoctrination and a tour. The first day on the job is his third or fourth day. At this time he follows a buddy and does no work himself. At the end of the first week he takes a safety and procedures test. If he passes, he can start work. He can, however be discharged at this point. Further evaluation of the man is taken after 10 more working days. 75% pass the 30 day probation period.

From this point, follow up training is given using the employee contact system. Two men must be contacted each day by each supervisor. A record card documenting the talk must be turned in. In addition, a one hour per month, over-time basis, safety meeting is held. The meeting is run by the foreman and a higher supervisor is present, who in turn critiques the foreman's written report.

The point was made however that regardless of the system used for strengthening and enforcing safety, consistent repetition can lead to the death of same. New ideas are constantly required to keep safety vitalized.

- K. Vapor Cloud Dispersion - The current status of the FIA proposal to research this subject.

Discussion Leader - Sherwood J. Moll - Borden Chemical

The major hazard being investigated is a VCM spill releasing large volumes of vapor thus creating a high disaster probability. Many have believed in the past that water spray is a good defense in a vapor cloud situation. Southwest Research Institute will perform required testing to provide definition of the above for a fee of \$38,000. Eight to ten months would be required for completion of testing and 12 months for total completion of work. The FIA is contributing \$5,000 and organization members are contributing \$2,000 each. The contract will now be awarded for the work on the basis of \$35,000 in pledges committed to date.

- L. New Federal Safety Standards - What do they mean to the vinyl chloride industry?

Discussion Leader - Peter Bogarc - Tenneco Plastics

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Discussion here focused on implications of the Occupational Safety and

Health Act (OSHA). It was pointed out that the federal inspectors are men with technical background that are given 8 weeks of intensive training. They are generally well qualified.

We will have state and OSHA inspectors and whichever criteria is tougher will apply.

What can be done to prepare for a visitation? Tenneco outlined what they have done:

1. A copy of the Federal Register was sent to all plant managers and plant engineers.
2. All shift foremen were told what to expect and the basics of the law, that an inspector can see all safety and accident records and can talk to any employee.
3. A critique of the law was sent to all executive management and the law itself to the plants.
4. An OSHA bulletin was sent to the plants - telling them what OSHA is picking on. Here they often are after the "nitty gritty", a drill not grounded, an open electrical junction box, no shocks under truck wheels, no guard on a fork lift truck. They can get worse - such as, a faulty bathroom door knob, an uneven bathroom floor and doors without exit signs. You can however bargain with the inspectors. He may not give a citation if he thinks you are trying. Good housekeeping and records of safety activities ready at hand will help give him that impression. Poor housekeeping on the other hand may give an impression such to guarantee a citation.

It was recommended that a program for good communication feed back be developed. Employee gripes must be heard as they may call the government in for a visitation.

Most common citations given are for noise, dust, fumes and mist. It was recommended that if a noise program does not exist, one had better get one developed.

The inspector will ask to see your safety procedures and manuals. You will have to be able to have them on display. Likewise he can and often will go after operating procedures and evidence of adherence.

You are expected to show engineering approaches to solve your problems. Ear muffs and respirators as solutions are considered second rate.

You may be required to log exposure time to noise and to tell worker he is exposed to a hazard - how much of a hazard and how much exposure time is safe.

Fines will be levied for violations of the act and signs declaring an area unsafe by the U.S. Federal Government must be hung until the violation is remedied.

M. VCM Sniffing - How serious a problem is it?

Discussion Leader - L. A. Lemaster - Dow Chemical

This subject came as a surprise to many members of the group. Others however could list numerous examples of suspected or proven in plant cases where persons intentionally went out of their way to sniff VCM to achieve a "high". Persons prone to this kind of activity are reported to be known alcoholics and persons with emotional problems.

Ways in which employees have been known to sniff VCM are as follows:

1. A cotton wad is soaked with VCM and placed in a plastic bag. The bag is then held up to one's nose and he breathes deeply until he gets high. This method is probably safest of any because if he gets to the point of passing out, the bag drops away and he breathes fresh air.
2. An employee enters an enclosed area, such as a closet, and closes the door. He then opens the bleed on a sample bomb of VCM. This method of course can be highly dangerous as he will continue to breathe the vinyl chloride after passing out.
3. Other instances were cited by the group where an operator simply goes to an area of the plant where there is vinyl chloride. He may open a sample valve, lie on the ground underneath the valve and breathe deeply.

This problem of course is not restricted to VCM. Many cases have been cited of freon and trichloroethylene sniffing. The two latter however, like most chlorinated hydrocarbons, can severely damage the liver and kidneys. The medical information accumulated by Dow however indicates that vinyl chloride does not produce physiological damage. It can of course produce death due to advanced anesthesia or asphyxiation. Aside from the above there is apparently another cause of death related to the sniffing of chlorinated hydrocarbons called sudden sniffing death (SSD). There have been over 110 recorded cases of SSD. They have been unexplained by anesthesia effect and autopsies did not indicate suffocation. Here it is thought that the combination of low oxygen, high adrenalin and the chlorinated hydrocarbon in the blood stream causes the phenomenon. The person who is the victim of SSD will suddenly jump up, run furiously and then drop over dead.

N. Noise Suppression

Discussion Leader - Harold E. Kling - American Chemical

OSHA standards for allowable exposure to noise are 90 decibels for no more than an 8 hour shift per day or 115 decibels for no more than 15 minutes per day. One method to reduce noise level is to include specifications for same in original purchase requisitions. For existing equipment, engineering ingenuity must be used. American Chemical gave an example where the insulation of a blower with polyurethane reduced noise level from 95 to 80 decibels. "Vinyl Custafab" (filled with lead) can be used for curtaining off noise areas.

If engineering cannot solve the problems, ear plugs or good ear muffs that remove only high frequency noise can be used.

It will be very important to keep exposure records to combat liability. General Radio produces a good audiometer for about \$350.00. Many of the group felt that employee hearing tests should be given regularly. Others felt that it would be like opening a can of worms.

III. ACCIDENT EXPERIENCE

1. Conoco

a) PVC Plant - VCM Exposure

Two persons have been overcome by vinyl chloride exposure, one inside a reactor and one at a dump strainer.

b) VCM Plant - Sinking of a VCM Barge

In October, 1970 a small 50 meter long barge bearing 300 metric tons of vinyl chloride left Belgium with crew and crews' families in a 50 mile an hour wind. They were making a 30 mile trip. The barge flipped over and sunk. The barge was loaded with 6 tanks of 50 tons vinyl chloride each. The two deck tanks washed ashore with some liquid vinyl chloride still remaining. Three days later the bow of the barge started floating. About 120 tons remained on the barge, which started coming out when the barge surfaced. The leaks in the tanks were fixed and some vinyl chloride remained uncontaminated. The vinyl chloride that remained was transferred from the structurally damaged tanks to another barge at sea.

Very little ice was observed on the water while VCM was spilling out. Most of the VCM was vaporizing very rapidly, producing very dense clouds of VCM.

c) VCM Plant - Major Fire

This accident involved the use of a standby pump not normally in operation. When process flow was swung to the pump no flow occurred. It was thought that a downstream check valve was plugged. An 8" Monel plug valve with gear operator at the discharge of the pump was closed and the line between it and the check valve was bled down. At this point the check valve was removed, found to be clean. It was open for about 15 minutes while the operator was going to get a new gasket, when a sudden release of vinyl chloride, ethylene dichloride and HCL ignited against the cracking furnace.

The indicator on the plug valve said that the valve was closed. However, later investigation revealed that the indicator was set 90° off true so that the apparent closed position was in fact an open valve position. A plug in the 8" line upstream of this valve had allowed the line to be bled down and the check valve removed. It was at this point that the plug let loose, releasing full flow from the 8" line up against the cracker.

Six persons were slightly injured and 5 schools downwind had to be bailed out because of HCL emission.

2. Diamond Shamrock - Delaware Plant

This account did not involve an actual accident. However, the circumstances were such that one could easily have occurred. In June, 1970 an operator reported hearing crackling sounds wherever he walked in the monomer area, and muffled crackling sounds inside centrifugal pumps. Residue left from a distilled sample was composed primarily of explosive polyperoxides. Subsequent investigation revealed that the inerts valve which removed inerts from both the condenser and the storage tank had malfunctioned, and the oxygen level in the system had risen to 1,000 to 2,000 ppm. It was believed that the combination of the high oxygen level and the hot weather had led to the formation of the polyperoxides.

Action taken included the following:

- a) The monomer area was saturated with a dilute solution of caustic. In addition caustic was injected into the storage tank.
- b) A better method of controlling monomer pH was found to be the use of ammonia from cylinders. Using ammonia Diamond has had no problems controlling pH in the range of 7 to 9.
- c) Whereas recovered monomer had been frequently held for several days before purification monomer is now purified immediately after recovery.
- d) The inerts relief valve is now kept well maintained.

Tenneco mentioned that they in the past have had polyperoxides and acetylides problems even while employing a caustic scrubber. Their experience indicates that air and oxygen getting into the system is the main cause of the peroxide formations. Tenneco uses Nash pumps and keeps the seal water basic with caustic. They also have an alarm for oxygen in the system and keep nitrogen on the compressor seals to further safe guard against oxygen leaking in. Tenneco and Firestone believe that reciprocating compressors are bad in this regard due to higher heat build up and an increased likelihood of oxygen admittance to the system.

Airco stated that they have definitely related oxygen and polyperoxides in the monomer to fisheyes in the end resin. Many in the group believe that an oxygen spec. on delivered VCM of 500 ppm is too high. A better spec. would be 100 ppm of oxygen.

Firestone stated that they used 20% or higher caustic to decompose already formed polyperoxides in the system.

With regard to removing polymer buildups in the monomer area many in the group believe that the deposits should be caustic soaked prior to cleaning. Others believe that adding water and holding at elevated temperatures for an extended period will decompose any peroxides formed to allow safe deposit removal. Many of the group have witnessed very definite different rates of polymer build up in the recovery area dependent on type of catalyst used for polymerization.

3. Norsk Hydro A.S. - Norway

a) Monomer Plant - Major Fire

Norsk experienced a fire almost identical to the one previously presented by Conoco. The difference was that the blockage that let go was held back by ice. An explosion and major fire resulted. In addition, the shock caused by the explosion ruptured a vinyl chloride underground storage tank which apparently had been defective when installed. The vinyl chloride seeped up through the ground in a number of places and the fires feeding on same lasted for five days.

b) PVC Plant - Reactor Valve

This was a case where an operator simply opened the wrong bottom valve. Instead of opening the one to be dropped, he opened a reactor that had just been charged and was on heat up. The reactor contained 5 tons of vinyl chloride. The operator tried to close the valve, realizing he had opened the wrong one. He could not. Two other operators tried to help him with no success. No fire resulted.

The group made several suggestions to prevent the occurrence of similar accidents:

The suggestion was made to install red and green lights at the bottom of the reactor to indicate pressure.

Tenneco suggested changing lever operated to wheel operated drop valves. This makes the operator turn the valve several times before it is actually opened.

It was recommended that a double key interlock system be installed where the operation of the second key is only possible if the reactor is not under pressure.

c) PVC Plant - Runaway batch

A suspension reactor had just been heated up when a pressure rise was noted to be heading straight up. The control board operator went out to see if the agitator was on and it was. He went back to the control room and told the foreman. The foreman then instructed venting. At this point the safety valve blew. The operator then opened the manual vent. As he was walking away the reactor gaskets blew.

When the reactor was opened the next morning it was found that the glass had shattered off the reactor. In addition there were signs of bulging both in the upper and lower domes. It was estimated that pressure must have risen to 640 to 710 psig. From the I.V. of the polymer produced it was estimated that temperature had been as high as 160°C. It is believed by Norsk that the pressure relief valve did not open at the proper pressure. Further it was theorized that polymer may have forced into the valve further restricting flow.

Secondly Norsk accumulated evidence that indicated that the reactor agitator had been initially off during the first portion of the polymerization and then had been turned on by the operator realizing his mistake. Several in the group recalled having similar phenomenon with reactors where the agitator had been initially off and then turned on later in the polymerization. Monsanto in particular had noticed that when the agitator is turned back on in such a case reaction is runaway. They recommend that if the agitator is initially off that all available cooling be placed on the reactor before it is turned on. Monsanto relates the rapid increase in reaction to a phenomenon that occurs when a bulk polymerization proceeding in the separated upper layer of monomer is agitated back into the water phase. The phenomenon that occurs is contrary to what might be believed based on more efficient heat transfer once agitation is achieved.

4. Dow - Reactor Lighting

Dow has had two occurrences where the standard type of explosion proof drop light with glass globe has exploded. The drop lights were used to drop into the reactor to give light during high pressure water cleaning. It was thought that water had leaked into the globe producing pressure when the vapor was heated by the lamp. In both instances the glass globe shattered and pieces of glass flew as far as 20 feet. Dow now uses an Atlas Air Turbo Lamp. This is judged to be safer but is heavy and cumbersome. Dow also wished to know whether anyone was considering fiber optics. They did not see any reason why they could not be used. In discussion the comment came from the floor that OSHA will not allow 110 volt lighting for use in reactors. The lighting must be powered by a 6 volt source.

5. Ethyl

a) Persulfate Fire

This incident involved a drum of inorganic persulfate that had caught fire in the weigh room. The fire could not be put out with water. It was later found that there had been an inadvertent addition of flake caustic into this drum which catalyzed the decomposition of the persulfate.

b) Reactor Gasket Failure

This incident occurred shortly after a reactor had been heated up. A temporary loss of reactor cooling occurred and reactor pressure approached 220 psig. The rupture disc was set to blow at 250 psig and the relief valve was set to open at 225 psi. The disc failed early and the relief valve then opened. The relief valve then reset however, the gasket under the valve failed and a large VCM release into the room occurred. Later investigation revealed that maintenance had installed the wrong gasket having too small an outside diameter.

6. Tenneco - Near Fatality from over-exposure to VCM

ASI 000016484

Some years ago a man died from over-exposure to VCM at a slurry tank at Tenneco. Following this accident manways were all bolted down and

automatic spray systems were installed to wash down the slurry tanks. New procedures stipulated that a man could not go on top of the slurry tank alone but must take a buddy. Even then an operator could only look through a sight glass.

Over two years this procedure eroded entirely and another man nearly lost his life in similar manner. The operator was found hanging from his boots from the slurry tank manway. He had apparently been hosing out the heel of the tank with the top portion of his body entered in through the manway when he became overcome with monomer. The investigation revealed the following:

- (1) After the latter accident management finally found out that the operators never could see through the sight glass. Further it was found that the automatic spray system never did work. The operators now said "We told you this at our safety meetings".
- (2) Management never really supported the new procedures after the first accident. An operator would go for a buddy and the foreman would give him the brush off.
- (3) The foreman had apparently ignored complaints by the operator involved in the latter accident that he had vomited several times while hosing down the slurry tanks.
- (4) The location of the slurry tanks was such that no one could hear a cry of help coming from that area.

Corrective actions taken by Tenneco were as follows:

- (1) All hatches in remote vessels were chain locked.
- (2) Man-savers were placed in all hatches.
- (3) A lifeline belt and overhead rail were installed where man-savers could not be installed.
- (4) Systems were redesigned to work. Sight glasses were equipped with spray washes and automatic spray systems were designed to clean all areas.
- (5) Since it was found that supervision knew of the problems and ignored them the assistant plant manager and the production superintendent were fired. Letters of reprimand were sent to all foremen.
- (6) Falcon Aerosal Horns were given to all the buddies.

The group recommended that as an alternative to Falcon Horns a common garage opening device can be used to signal a central alarm horn.

7. Great American Chemical - Reactor Entry Fatality

ASI 000016485

This incident involved complete disregard for vessel entry procedures. The cleaner and safety watch were preparing to enter a reactor when the safety watch decided to take a break. He returned 10 to 15 minutes

later and found the cleaner passed out inside the reactor. The atmosphere inside the reactor had not been tested nor was anyone aware that the cleaner had entered. The man was removed from the reactor 3 to 5 minutes from the time he was found. However, he was dead on arrival to the hospital. As a result of this accident new procedures required that (1) all reactor manholes have locks and that the lead operator has the only key, (2) the operator must have approved his completed check list before the manhole is unlocked, and (3) a 0 to 2000 ppm J & W gas detector with a push button alarm goes into the reactor with the man once the atmosphere has been tested from the outside.

Great American uses high pressure water for most of their reactor cleaning and enter only occasionally. They are so satisfied with the performance of the portable J & W analyzer that they are thinking of eliminating safety watch.

Conoco uses the Wellco stripping agent. Wellco makes two compounds - one for glass and the other for stainless steel. Conoco reports that they are very pleased with the performance of the latter - it works much more efficiently than previously used 150 to 250 psi water. Conoco stated however that the Wellco equipment - the whirl nozzle and the heating tank and pump are poorly designed. They recommend that if Wellco stripping agents are used that equipment be designed internally.

8. Monsanto - Kettle Entry Violation

In this instance an operator dropped a tool inside an empty reactor and immediately entered to retrieve it. He bent over to pick it up, stood up and then collapsed, cracking his head on the agitator. The senior operator walking by noticed him in the reactor and immediately grabbed the hose from the air blower and threw it in on the man's face. He then called for help. The man inside quickly revived and crawled back out himself. The senior operator demonstrated quick action, as the result of training.

The man who ignored entry procedures was not disciplined. Instead the incident was replayed as it occurred and a slide presentation was prepared. The man involved led safety meetings for all shifts and narrated the slide demonstration. Monsanto felt that this approach worked very well.

9. B. F. Goodrich - High Pressure Water Accident

Goodrich stated that they had been using high pressure water for 12 years without an incident. Recently however an accident occurred while a "Hicar" reactor was being cleaned with 10,000 psi water.

It had been B. F. Goodrich's policy not to allow the use of short lances, however same became necessary to clean the new cooling coil configuration in "Hicar" reactors. To do this a man stands in a cage adjacent to the coils with an air tent over his head and shoulders. Cleaning can only be accomplished using a 20" lance.

In the incident discussed the cleaner casually lowered his lance while inspecting the coils and the gun cut through his shoe just , in back of the safety toe and lacerated his foot. The man was off work two weeks.

The accident happened so quickly that neither the man above or the cleaner below released their respective "deadman" switches in time. The incident emphasises the importance of using long lances whenever possible.

Goodyear related a fatality they experienced 3 to 4 years ago where a high pressure water gun was propped up precariously against a beam. It fell over and the "deadman" switch activated momentarily as it hit the floor. The resulting squirt from the gun punctured the heart of a man who happened to be walking by.

10. Allied Chemical - Vacuum Pump Incident

The vinyl chloride over exposure incident that occurred concurrent with vinyl chloride entry into the vacuum system was presented to the group. Goodrich and Tenneco both stated that they use steam jets to pull vacuum and recommended that this method might be used to reduce the hazards evident in the Allied incident.

APPENDIX

JOB SAFETY ANALYSIS

Vinyl Chloride Safety Association
November 10-12, 1971
Rochester, New York

William J. Boyle, Jr.
Monsanto Company
Springfield, Massachusetts

ASI 000016488

SAFETY ANALYSIS

1. THROUGH THE EXPERIENCE AND KNOWLEDGE OF THOSE WHO PERFORM THE WORK, TO METHODICALLY IDENTIFY HAZARDS ASSOCIATED WITH THE WORK AND TO DEVELOP STEP BY STEP SAFE PROCEDURES WHICH ELIMINATE OR MINIMIZE THESE HAZARDS.
2. TO INCREASE EMPLOYE SAFETY AWARENESS AND IMPROVE SAFETY ATTITUDE BY EMPLOYE PARTICIPATION IN THE FORMULATION OF SAFE WORK PRACTICES.

ASI 000016489

SEQUENCE OF ACTIONS

1. LIST ALL TASKS WITHIN THE DEPARTMENT:

- EXAMPLES:
- a. CHARGING A KETTLE
 - b. PREPARING PREMIX
 - c. BREAKING INTO A LINE

2. RANK THE LIST OF TASKS FOR ANALYSIS PRIORITY.

FIRST: THOSE TASKS HAVING THE HIGHEST FREQUENCY OF INJURIES.

SECOND: THOSE TASKS PRODUCING THE GREATEST NUMBER OF VIOLATIONS OR UNSAFE ACTS.

THIRD: THOSE TASKS THOUGHT TO BE PARTICULARLY HAZARDOUS EVEN THOUGH NO INJURIES MAY HAVE OCCURRED.

FOURTH: THOSE TASKS HAVING HIGH SEVERITY POTENTIAL.

3. BREAK THE TASK DOWN INTO STEPS:

*CAUTION -- NOT TOO DETAILED

NOT TOO GENERAL

- a. EACH STEP WILL GIVE "WHAT IS DONE - NOT HOW."
- b. MAKE A PRELIMINARY BREAKDOWN TO ENSURE ALL STEPS ARE LISTED.

4. DETERMINE HAZARD AND ACCIDENT POTENTIALS.

- a. EXAMINE MATERIALS AND TOOLS USED IN EACH STEP.
- b. LIST CONTACT POSSIBILITIES.

ASI 000016490

SEQUENCE OF ACTIONS

Continued

5. ELIMINATE HAZARD AND ACCIDENT POTENTIALS.
 - a. DESCRIBE THE SAFE PRACTICE TO BE FOLLOWED.
 - b. LIST PROTECTIVE CLOTHING AND/OR EQUIPMENT NEEDED.
FOR SAFE TASK PERFORMANCE.
 - c. LIST CHARACTERISTICS OF MATERIAL USED.

METHOD QUESTIONS

WHO WILL ACTUALLY DO THE J.S.A.?

FOREMAN - OPERATING SUPERVISOR - ENGINEER.

WHO WILL PARTICIPATE IN THE J.S.A. FOR A PARTICULAR JOB?

A CROSS SECTION AS A MINIMUM. ALL WHO DO THE
JOB, IF POSSIBLE.

WHEN WILL THE J.S.A. BE CONDUCTED?

DAY OR NIGHT - AVOID "BUSY" TIMES.

HOW LONG SHOULD THE SESSION LAST?

DEPENDS ON THE AVAILABILITY OF THE PERSONNEL.

15 MINUTES - 45 MINUTES.

WHERE SHOULD THE J.S.A. BE CONDUCTED?

A QUIET, RELAXED ATMOSPHERE OUT OF THE PRIME
WORK AREA.

WORK AREA MAY BE USED FOR DEMONSTRATIONS.

SAFETY ANALYSIS

ADVANTAGES OF THIS APPROACH.

1. MEN FAMILIAR WITH THE OPERATION CONTRIBUTE FROM A LARGE POOL OF EXPERIENCE.
2. TRAINING ADVANTAGE - LEARN FROM EACH OTHER.
3. A PARTICIPATING ROLE FOR EMPLOYEE.

POINTS TO PONDER

1. THE PERSON CONDUCTING THE ANALYSIS MUST APPROACH THE WORKERS WITH ENTHUSIASM AND SINCERITY.
(AS YE SOW - SO SHALL YE REAP!)
2. THE WORKER MUST BE TOLD:
 - A. THIS IS NOT A TEST OR TIME STUDY.
 - B. HE IS THE AUTHORITY - HE KNOWS THE BEST WAYS AND THE SAFEST WAYS TO DO THE JOB.
 - C. THE END PRODUCT WILL BE THE PUTTING TOGETHER ALL OF THE "BEST" FROM EACH WORKER.
3. SITUATIONS THAT MAY OCCUR.
 - A. WORKERS WILL ADMIT MISTAKES AND ERRORS THAT THEY HAVE MADE. (ESPECIALLY IF THEY WERE MADE A LONG WHILE AGO.)
 - B. NEW WORKERS TALK MORE - THEY MAY WANT TO PROVE THEMSELVES.
 - C. ANALYZE ONE JOB AT A TIME. DON'T LET THE ANALYSIS TURN INTO A GENERAL GRIPE SESSION.