

Air Products

Date 19 October 1977

INTEROFFICE
MEMORANDUM

Subject Vinyl Chloride Safety Association Meeting

October 6, 1977.

To T. L. Carey

(Location, Organization, or Department)

From J. T. Barr

(Location, Organization, or Department)

cc: R. Burnham
D. Francke
R. Gilbert
C. A. Heiberger
R. McGinnis
J. Novak
E. Primeau
F. Riddle
J. Russell
R. Schenck
W. Silowka
W. M. Smith
W. Stuben
L. Tepper
D. Ward

Escambia

COPY:

SAM

Ed

Randall Jones

The Vinyl Chloride Safety Association held its annual meeting at Valley Forge, Penna., on October 6 - 7, 1977. A total of 83 persons from 32 companies attended, with 13 of the companies being outside the U.S. This was a record attendance in both categories. Attendees from Air Products were the writer and Dale Francke and Jim Russell.

The officers elected for next year were:

Chairman,	H. Waltemate, Goodrich
Vice-Chairman,	H. Lloyd, Georgia Pacific
Secretary,	H. Olsen, Ethyl
Program	J. Flores, Gt. American
Treasurer	R. Hager, Stauffer

In a general discussion of the aims of the Association it was concluded that no major changes were needed. A copy of the by-laws will be circulated to all members for review.

A copy of the agenda is attached, and a brief review of each subject is given below.

PHYSIOLOGICAL EFFECTS

Dr. R. W. McBurney of Diamond-Shamrock discussed the hazards of vinyl chloride. He described it as a relatively non-toxic narcotic which could cause death from arrhythmia in high doses. It is detoxified in the liver by sulfhydryl-bearing enzymes, and the chief target of the metabolites is the lining of the small blood vessels. This leads to two types of disease. Scleroderma is a reversible result of small vessel

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plugging which is seen more in Europe than in the U.S. In a few especially susceptible people it can cause sensitivity to cold (Reynaulds Phenomena) and if the bone tufts are starved, resorption of the bone, resulting in finger clubbing, called acroosteolysis. It can also cause liver fibrosis, or cirrhosis, and enlargement of the spleen from high portal vein pressure. The above symptoms are relatively rare.

Even rarer is angiosarcoma, a cancer of the liver blood vessel lining. The body seems to detoxify low doses safely, but at higher dosages the primary metabolic pathway is swamped and attack on the body occurs from secondary metabolites. This disease is very rare, about 25 cases per year in the U. S. It is sometimes seen in infants, and can also be caused by arsenic and thorium. Chemotherapy is not effective, and it usually occurs at multiple sites in the liver and is not operable. It would be reasonable to expect sarcomas at other sites as well as the liver, if this mechanism is correct.

He expressed the opinion that the threshold for rats to develop cancer was about 35 ppm, and felt that anything below 15 ppm was safe for humans, thus most of the effort spent on OSHA and EPA compliance is a waste. About one person in 3400 develops cancer at high exposures, and he postulated a genetic predisposition to the disease.

He further said that no medical screening program can be really effective, because there are no early warning signs. The normal population has 15-20% "abnormal" blood tests. Diamond-Shamrock returns men to VC exposure with 2 abnormal results in the SMA - 12 blood test if their liver scan is normal. They do not perform a biopsy on employees, but refer them to their own physicians.

Medical Surveillance

H. Lloyd, of Georgia-Pacific led a discussion of medical surveillance practices. All companies have similar preplacement medical exams, and generally use the same tests as in their annual re-exam. Many report problems with alcohol consumption before the tests.

Treatment after an "emergency" was not consistent between companies. Some give blood tests, although they are not sure why. Even the definition of an emergency was not uniform, although most held that exposure to greater than 100 ppm without breathing protection as a definition.

The employment of women of child-bearing capacity is still an unsettled topic. About two-thirds do not permit them in exposure areas.

Most companies make the annual re-exam a condition of employment, but where this rule has been challenged by an employee, the company has lost. Many have consolidated the VC exam and their routine physicals, especially where the company examines all employees. The average cost per employee was about \$100. Some have eliminated one of the x-ray tests for employees with two exams/yr.

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Chromosome Studies

Per Ranges, of Norsk Hydro, gave a report on a recheck of their chromosome breakage study of 3 years ago. In the original study, they found that heavily exposed workers had a breakage count of about 4%, compared to 1.8% for controls. They repeated the study this year, three years after heavy exposure ceased, and found that carefully matched controls had 1.2% breakage and workers had 1.6%. They assume from this that the damage is reversible.

He was asked to transmit this to SPI and MCA as soon as the report is formalized.

OSHA ENFORCEMENT

H. Waltemate of Goodrich reported on four OSHA inspections at their plants which all occurred in the first week of August of this year.

The Calvert City plant had a general KOSHA inspection and received 15 citations, all non-serious, with 2 penalties totalling \$100.

The Long Beach plant was inspected by CALOSHA, with sampling being done for VC, benzene, lead, noise, dust and ammonia. This was prompted by the "Gregario Amendment", a new law on carcinogens passed this summer. They expect to receive citations for a respirator on which they had changed the connector and thus nullified the NIOSH certification, an employee with a beard (whom they claimed could not get a good respirator fit), drinking coffee in a regulated area, and an improper dust mask in the compound area, where dust levels were high.

The Louisville plant had a 12 day inspection, prompted by an employee complaint. They expect no citations there. The problem was that their employees do not believe the published results of the monitoring program, and want an independent check on exposures. Hooker said they have the same problems, but most companies reported otherwise.

Their Pedricktown plant reported two massive releases in three weeks just before the inspection. A four day visit included sampling for VC, cadmium, carbon black, and noise. They expect citations for dust and an improper respirator in the compound area.

Waltemate offered to act as a clearing house for citations and policy letters from OSHA. Those having information of general interest can send those items to him, and he will circulate them to the group.

Pantasote was cited and fined for storage of tankcar outside their regulated area. They now have the City Police patrol a section of track for them.

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Tenneco has had 19 inspections in two years, 13 of which included monitoring tests. They have received two citations.

Borden was cited when OSHA sampling showed exposures of men in masks to 1.5 and 3 ppm. They were also refused the OSHA data, and were told that the decision was made in Washington.

Stauffer contested a citation for an exposure over 25 ppm. The alleged number was reduced, then the citation dropped.

Several companies have been told that employee complaints account for 60 - 70% of all inspections, and have a very high priority.

Most companies contest their citations routinely to reduce the probability of serious repeat violations.

Four companies use only area monitoring to calculate employee exposure, and seven use a combination of area and personal monitoring. The average concentration of the reactor area was indicated to be as follows:

below 0.5 ppm	= 2 companies
0.5 - 1.0	= 6 companies
1.0 - 2.0	= 8 companies
2.0 - 5.0	= 8 companies

No one admitted to an average over 5.

Goodrich did not establish a regulated area around their new large reactors at Louisville. They have been inspected twice, with no comments.

No one is using the LSU badge-type personal monitor at present, although ICI and DOW are testing it, and preliminary results are good.

A show of hands indicated that essentially all plants experienced ten or more excursions per month over 5 ppm, and many go above 25 ppm on occasions. Pumps and compressors are still the major sources of leaks. Great American reports more than a year of satisfactory service on their sealed pump.

More companies alarm at 5 ppm than any other value. Most also use the zone alarm method, as do we, and the majority use both lights and audible alarms.

EPA UPDATE

D. Kuhn of Conoco reviewed the EPA situation. No new information was presented except that Region 6 has questionnaires out on fugative emissions and controls, and that EPA has a contractor inplant at DOW working on the same problem.

Firestone reported that Maryland is setting a fence-line limit on emissions. Massachusetts has also done so in at least one case, and Texas is proposing a similar rule, along with emission limits below that of the Federal EPA.

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EMISSION CONTROL METHODS

The writer led a discussion of the methods of disposal of vinyl chloride. An outline is attached. Twenty seven companies are using incinerators, four carbon beds, and two use solvent extraction.

In a discussion on frequency of opening large storage vessels, the minimum frequency seemed to be about three years, with many taking five to seven years, or longer. Only British Plastics reported any evidence of any corrosion problems, and that after 5 - 15 years of service.

VCSA HISTORY

G. Schaff of Goodrich reviewed the history of the group, and led a discussion of its future. Most seemed satisfied with the present arrangements. The question arose as to the time necessary to retain the tapes made of each meeting, and members were asked to get advice from their legal groups.

TRANSPORTATION

R. Wilson of Stauffer discussed the recent DOT rule HM144, published 15 Sept. and effective 19 October. It requires modification to existing or new uninsulated cars in the transport of hazardous liquids, including VC, EDC, ammonia, and similar products.

Shelf couplers will be required by 1979 on existing, and after Jan 1st, on all new cars. Estimated cost is \$1000/car.

Head Shields are also required, at a cost of \$3500, and weighing 1300 lbs.

Insulation is required to protect against a pool fire to maintain the wall below 800°F. after 100 minutes. Cost will be \$5 - 10M, weight will be increased 1 - 8 tons, and cars will be out of service 45 - 60 days.

Relief valve requirements have also been changed. The Compressed Gas Association has petitioned for a review of this requirement.

Placards and shipping papers have new requirements. One change has eliminated the cancer warning from the placard, so it will now be stencilled on the car near the dome. Specific wording on the cancer hazard and handling methods are required on shipping papers.

Midland ball float gauges and Drexelbrook capacitance gauges have replaced the older slip gauges.

P. Bogart of Tenneco urged that those who have not signed up for the mutual response group of Chentreck, do so (we have not.). He said that Congress seemed to be taking some action to consolidate the 200 - plus organizations now involved in emergency responses. The DOT and EPA have not resolved their disagreement over shipping hazards.

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TRUE CONFESSIONS

J. Alvarez of Primex described a fire in their Pueblo, Mexico plant which occurred in June. Monomer was stored in 7 bullet tanks, 5 x 90 and 2 x 60 M gals. each. On the date in question, about 2.9 MM lbs. was on hand. An experienced mechanic was removing the top works from a plug valve on the bottom of one tank, and removed the plug bonnet plate rather than the top works bracket. The plug blew out and the 3" valve vented liquid. A visible vapor cloud formed in an area about 1100 x 800 ft. by 500 ft. high, and ignited at a neighboring plant. The liquid stream then became a torch playing on adjacent tanks which then ruptured one by one until all were destroyed. They used the ASME - UPV code for relief valve area calculations rather than the NFPA code, so had only 25% of the relief area that the latter would have furnished. They also had an inadequate water supply.

One man was killed and three other burned. Damage was over \$3MM. The fireball of the initial ignition destroyed the laboratory, library, and offices. Books were charred through, and bottles were melted from the heat of the fireball, but blast damage was minor.

They have installed a 200 ton bullet tank and are installing a 2000 ton sphere as replacements for these tanks. To reduce hazards in the future, these tanks are insulated, and have relief valves according to the NFPA code. The pump line is reduced to 2" size, with an excess flow valve. This reduced flow rate requires a day tank for charging. They have revised their safety program and emergency action instructions.

By a show of hands from the floor, it developed that most attendees do not know which code their plants used for reliefs. One company reported use of a special 4 way valve that allowed use of one or both attached reliefs, but would not permit both to be shut off at the same time.

*notes showed
w/ 4 way flow valves
w/ foam systems*
Ten companies use excess flow valves on storage vessels, and many commented on the unreliability of those in sizes over 4 inches. Twelve companies now have foam systems installed. Nineteen use remote pneumatic valves, and 10 have fire-safe valves in this service.

Bob Franz of Union Carbide described briefly an explosion of a bulk polymerizer in their Texas plant on Labor Day. The final investigation report has not been presented to management, and will be made available to us later. A 6000 gal "non-solvent" reactor exploded with little or no apparent warning, burning two men who were about 75 ft. away, one of whom died later. There was severe damage in the immediate area, and the blast was heard 20 miles away. One large piece of the reactor was found 1600 ft. away. I was told by another Carbide employee a few days after the explosion that at that time they suspected an overcharge of initiator.

Esso of Canada reported on the corrosion failure of 304 vessels in PVC service which they told us about on our trip there earlier this year. They have seen severe corrosion adjacent to welds in their 11 yr. old clad 304 strippers. None was found in 316 equipment. Being clad, there was no vessel failure as Goodrich reported two years ago. They now make a dye penetration test every two months. Dow said that they had seen the same,

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and at chloride concentrations of 10 - 40 ppm the worst rates were at pH of 3 - 5. They also have had ss bolts fail in the salt air in Texas. The vapor phase of their recovery system seemed to be the worst area.

Dale Francke described the incident of last January in the Escambia plant. The only comment from the floor was from Goodrich, who disables automatic valves in a work area by disconnecting the air supply lines.

They do this after each use to prevent inadvertent opening. Dis?

Union Carbide reported that a reverse buckling rupture disk and knife assembly was reversed by hydraulic pressure without the knife cutting the disk, thus preventing the relieving of the disk in any future overpressure. They are going to a B S & B reverse buckling scored disk that does not require a knife. Borden said that they have three years successful experience with a scored Fike disk that does not require a knife, and have operated within 20 pounds of the set pressure without premature failure.

INJURY STATISTICS

H. Waltemate of Goodrich reviewed their accident history for the past few years. He pointed out the problem with the change in the data base from ANSI to OSHA, and suggests that the VC-PVC industry compile its own statistics, as do other special groups. This would be done by abstracting annually the OSHA log of injuries on the attached form, using data for the entire facility, not just PVC, and he will act as the clearing house for the data. I recommend that we cooperate in this.

The Goodrich experience has been well below general industry rates, but the incidence increased in 1974-5 as the result of discovering the angiosarcoma cases. Their on-the-job rates are about one-fifth of injuries at home.

EMERGENCY PLANNING

J. Van Winkle of Diamond Shamrock described several incidents at their plants which pointed up the failures in their planning methods. By a show of hands only 10 companies had held drills in the past year.

He suggested several common failings in this area.

1. Too much reliance on supervisory personnel.
Emergencies usually happen on off-shifts.

2. Too much involvement by supervision and guards.
They have better things to do in an emergency than lay hoses, and are exposed to too much danger.

3. Failure to allow for turnover of personnel. Inadequate training or assignments to keep the emergency group effective.

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He discussed the strong effort to certify and unionize firemen in the Houston area. One result would be to shut down a plant in case of a strike.

INITIATOR STORAGE

A. Dixon of Goodyear discussed initiator handling techniques. The favorite storage method still is a walk-in freezer house with dual mechanical coolers, emergency power, and high temperature alarms. Eighteen companies use this method, and 10 of these are sprinklered. Twelve companies use the freezer chest method that we have.

His main points were as follows:

- 1) Follow IRI standard on storage quantities and separation distances.
- 2) Never return material to primary stock or reuse containers.
- 3) Rotate stock.
- 4) Assure air space between individual containers.
- 5) Workers should use plastic or rubber protective clothing.
- 6) Protect all containers on the work floor from heat and sparks.

Tenneco reported that they had a fire when a hydraulic shock in the fire header lifted the valve to the storage house sprinklers and filled the house with warm water. When this was discovered, the water was drained out and the cooling units restarted. A few hours later the whole lot of initiator fumed off.

A few companies use nitrogen or carbon dioxide instead of water. This does not seem useful, since there is enough oxygen in the peroxides to make the fire self-supporting.

There is a move in Europe to bulk transport and storage of a 25% solution of initiators. Lucidol is considering a frozen 25% suspension in water for those who wish to use the Goodrich procedures.

MISCELLANY

Georgia-Pacific has selected Crawford and Russell for their present PVC expansion program. This will include 3 contact fluid beds and two flash fluid beds, all from Niro, to get their rates up to 450 MM lb/yr. They also plan continuous stripping and additional blow-down vessels. They have no construction permits on this project yet. The monomer project has not been approved by the Board, but the caustic-chlorine expansion is going ahead.

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KemaNord has hopes that the Denmark project can move ahead. Local opposition has reversed itself and they are appealing the permit refusal.

JTB:djm



J. T. Barr

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VINYL CHLORIDE SAFETY ASSOCIATION MEETING

THURSDAY, OCTOBER 6th - FRIDAY, OCTOBER 7th, 1977

STOUFFER'S VALLEY FORGE HOTEL, PHILADELPHIA, PENNSYLVANIA

<u>rsday - 10/6/77</u>	<u>Agenda Subject</u>	<u>Discussion Leader</u>
0 - 0900.....	Registration	
0 - 0915.....	Business Meeting & Election of Officers for 1978.....	R. Henderson Diamond Shamrock
5 - 1000.....	Vinyl Chloride Physiological Effects.....	Dr. R. W. McBurney Diamond Shamrock
0 - 1030.....	Medical Surveillance Problems.....	H. Lloyd Georgia Pacific
30 - 1045.....	Coffee Break	
15 - 1115.....	OSHA Enforcement Action.....	H. Waltemate B. F. Goodrich
15 - 1200.....	OSHA Compliance Practices Review.....	D. Rhodes Tenneco
1300.....	Lunch	
00 - 1345.....	EPA Update.....	D. Kuhn Conoco Chemicals
45 - 1430.....	Emission Control Methods Review.....	J. Barr Air Products
30 - 1445.....	Coffee Break	
45 - 1515.....	VCSA History.....	G. Schaaf B. F. Goodrich
15 - 1600.....	Transportation Update.....	R. Wilson Stauffer Chemical
00 -	Major Accidents, Near Misses.....	J. Alvarez Primex
<u>riday - 10/7/77</u>		
00 - 0830.....	Industry Injury Review/Survey.....	H. Waltemate B. F. Goodrich
30 - 0900.....	Planning for Disasters.....	J. Van Winkle Diamond Shamrock
00 - 0930.....	Catalyst Handling.....	A. Dixon Goodyear
1015.....	Open Discussion Period	

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METHODS OF EMISSIONS CONTROL

I. CHEMICAL

A. Acid Permanganate

Used in UEI tape monitor system, and disposable cartridge masks. Very expensive and limited by solubility in water.

B. Hypochlorite

Produces EDC. Less expensive, solubility limited.

C. Ozonalysis

Laboratory scale only. Patented. Very expensive, ozone disposal problem, possible explosion hazard.

D. Incineration

Most popular method, capable of low exit concentrations. Requires scrubber in most states, some reliability problems. Some companies use steam boilers.

E. Catalytic Destruction

Apparently used by two or three companies. Operates at somewhat lower temperatures than incineration, little or no auxiliary fuel.

II. PHYSICAL

A. Absorption in Solvent

Capable of good control, becomes progressively more expensive as exit limit is reduced.

B. Adsorption

Carbon only adsorbent used commercially. Capable of very low exit concentrations if unit staged and properly regenerated. Problems with impurity recycle, may need small incinerator in addition.

C. Cryogenic

Expensive. Also has impurity build-up problem. Not used commercially.

VINYL CHLORIDE SAFETY ASSOCIATION

Company Name _____

Location _____

Date _____

RETURN TO: H. Waltemate
 BFGoodrich Chemical Division
 6100 Oak Tree Boulevard
 Cleveland, Ohio 44131

YEAR	NON-RECORDABLE CASES	TOTAL CASES	DEATHS	LOST WORKDAY CASES				NONFATAL CASES WITHOUT LOST WORKDAYS	TERMINATIONS OR PERMANENT TRANSFERS	TOTAL CASES RECORDABLE INC. RATE *	LOST WORKDAY CASES INCIDENCE RATE **	CASES INVOLVING DAYS AWAY FROM WORK INC. RATE ***	DAYS AWAY FROM WORK ****
		Total Lost Workday Cases	Cases Involving Days Away From Work	Days Away From Work	Days of Restricted Work Activity	Number of checks in Col. 10 of the log. (7)	Number of checks in Col. 11 of the log. (8)						
		Number of entries in Col. 7 of the log. (1)	Number of entries in Col. 8 of the log. (2)	Number of checks in Col. 9 of the log. (3)	Number of entries in Col. 9A of the log. (4)			Sum of entries in Col. 9A of the log. (5)	Sum of entries in Col. 9B of the log. (6)				

Case Histories:

* $\frac{\text{No. in Column (1)} \times 200,000}{\text{No. Man-Hours Exposure}}$

** $\frac{\text{No. in Column (3)} \times 200,000}{\text{No. Man-Hours Exposure}}$

*** $\frac{\text{No. in Column (4)} \times 200,000}{\text{No. Man-Hours Exposure}}$

**** $\frac{\text{No. in Column (5)} \times 200,000}{\text{No. Man-Hours Exposure}}$

NOTE: On the reverse side include a brief description of accidents, injuries, fires, etc., having experience value.

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