

BFG TECHNICAL DOCUMENT

1981  
MINUTES

VINYL CHLORIDE SAFETY ASSOCIATION MEETING

J.F. MALONE/R.C. KAMINSKI

N.R. AQUINO/F.E. KRAUSE

R.A. KRUEGER/R.E. PASQUALI/R.A. TRAFAS

J.M. MADIGAN/G.F. LEFEBVRE/H.R. CALSING

~~E.C. MARTINELLI/H. WALTEMATE~~ → Tony M. → File

W.E. BRODINE/H.H. BORSVOLD/G.H. METZGER

E.L. BEELER AND STAFF

C.J. NOSAL AND STAFF

W.E. HORTON AND STAFF

J. CORONA AND STAFF

R.M. SANDFRY AND STAFF

R.D. MOORE AND STAFF

L.V. GOODE AND STAFF

C.L. WOODS AND STAFF

R.K. SCHLATZER/J.A. GLASS

C.E. FLEMING AND STAFF

D.A. BROOKS AND STAFF

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## VINYL CHLORIDE SAFETY ASSOCIATION MINUTES - 1981

### True Confessions:

- (1) Process Sewer Explosion - Jack McCauley, Conoco - An explosion occurred in the sewer system at the Lake Charles vinyl chloride plant. Vapors from the waste system were vented to the oxychlorination unit. A tank which was located aboveground contained a waste steam which was pumped to a belowground tank. The top drum blew off the aboveground tank and flew a considerable distance. This tank was 1" thick. There was a fire and/or explosion. They found a trace of peroxide. The cause of ignition was unconfirmed. One of the problems was the proper pH control of the material in the aboveground tank. In addition, they plan to nitrogen purge the vent stack. The feed nozzle will be such that it enters below the liquid level. The metal drums will be made of carbon steel.
- (2) Control Room and Laboratory Explosion, Dow - An explosion occurred in a lab sewer in Dow's Canadian vinyl chloride monomer plant. A system of tanks was connected to the industrial sewer and one of the valves leaked allowing vinyl chloride to get back into the sewer in the laboratory. The lab was adjacent to the control room for the vinyl chloride process. There was a liquid seal in the sewer line, but this must have blown out with the vinyl chloride vapor. The lab sewers were connected in with the process sewers. The lab itself was not explosion-proof. There were four Dow employees and one from the contractor injured, primarily from burns. Much damage was done to the roof and walls of the laboratory and the surrounding portions of the plant. It is standard practice at Dow to have their laboratories located in the production plant itself. This system permits some of the same employees to do the testing, as well as operation of the plant.
- (3) Nitrogen Inhalation Incident, Glen Schaaf, BFGoodrich - The Pedricktown incident with the mass autoclave was discussed with the group, emphasizing our commitment to proper vessel entry procedures. Emphasis was placed on obtaining operator commitment to following the procedures.
- (4) VCM Column Explosion at Convent, Ron Kaminski, BFGoodrich - Explained the explosion in the dehydrochlorination column at the Convent facility.
- (5) Reactor Lockout Device, Glen Schaaf, BFGoodrich - Itemized our work on reactor lockouts so that the bottom valve, the drain, vinyl chloride charge valves and the manway are interlocked in such a way to prevent accidental opening of the vessel when the reactor has a live charge in it. Castell is a company that provides a commercial lock-out systems for the PVC industry. Several companies, especially the English, reported that they have used the Castell system of lockout in their plants.

- (6) Polypropylene Plant Fire, Darwin Rhodes, Tenneco - This incident occurred in the Amoco plant near Philadelphia. Propylene and hexane solvents were involved. Two of the mechanics involved in the incident were killed. Amoco does not plan to rebuild this plant. The timing of the accident was very unfortunate. It occurred during the time that Philadelphia was playing the last game of the World Series. It was very difficult to get people to work overtime and people with limited experience were used. The incident occurred when a recirculation line on a reactor was being cleaned. The normal practice is to put two men on top of the reactor and two men on the bottom of the reactor and clean the recirculation line. After lunch, these operators then change places putting the people who are working on the top on the bottom. They were cleaning a section of the line which extended into the reactor. This was isolated by a valve. They were working on a valve located on the top of the reactor. The valve contained an actuator. The idea was to remove only the valve actuator, since the reactor had pressure on it. However, they removed the wrong set of nuts allowing the valve to completely come apart venting propylene and hexane into the area. The source of ignition was not known. Much damage occurred to the total plant. The blast took out the electrical pumps for fire water. Water for firefighting had to be supplied from a local stream. Propylene is a very volatile solvent. One of the theories for the accident was that overpressurization can cause an explosion. This incident is similar to a mechanical error that took place in the vinyl chloride tank farm in the Premix plant in Mexico a number of years ago. The salvage work at this site was hampered by the asbestos used for insulation.

A survey was taken during the discussion of this incident concerning the number of companies that use a blowout protection for vinyl chloride pumps. Ten companies use this type of protection.

#### General Topics

- (7) PVC Dust, John Vaughn, ICI - He reported that the effect of PVC dust on worker health had confirmed that it is not really a health hazard. An independent organization had studied 800 operators and issued a preliminary report early in 1979. Just last year, an additional 300 operators were included in the analysis and a final report was issued. Some of the pertinent details are included in an attachment.
- (8) Hazardous Material Notification, Harold Dubeck, Hooker - Harold reported some problems when they installed a new shortstop system in their mass polymerization plant. (They were installing our license technology involving the use of nitric oxide shortstop). Most of the problems occurred because the employees were not adequately briefed on the hazards of nitric oxide. There was a walkout by the people and they stayed out for about two weeks. The mistake was made by not spending enough time with the people explaining the hazards and defining the system and the safety features built into

its operation. They decided to implement this technology without first developing good operating procedures. OSHA even refused to enter the plant during the strike, and the landfill operators refused to take material for three weeks.

The discussion indicated there was also a need to inform the local community people when important changes were made which might result in different materials being vented. A survey was taken among the group indicating 13 companies do have a formal plan for informing the local people when changes are made and 13 have informal policies.

- (9) OSHA Inspection Respiratory Protection, Dave Lull, Diamond Shamrock  
The major factor during this inspection was the discussion of the practice of permitting fertile women to work in the vinyl chloride and PVC areas. In 1978 and 1979, most companies would not allow that. Since that time, five companies have changed their policies. Now there are only nine companies that do not allow fertile women to work in the vinyl chloride and PVC areas.
- (10) Operator Training, Steve Brouillard, Diamond Shamrock - Diamond has an excellent safety program at their Independence vinyl monomer plant. The plant was extremely well built during the 1978 period following all OSHA and EPA guidelines. It has a total of 157 employees, and have now gone 1.2MM manhours without a lost time accident, so their training and safety program must be very effective. One of the important points stressed in this program is the involvement of people, equipment, and programs. Roy Henderson, the plant manager, is out in the plant frequently on a day-by-day basis to promote safety. Their people were hired off the street, but were well trained before plant start-up. Now after three or four years, retraining will be done. Programs for training were developed specifically for this plant and they were flexible during the progress of training to gain the input of the operating personnel. Safety meetings have required attendance and people are paid for this time. Their safety department consists of one loss control supervisor and a combination safety and environmental engineer. Both of these people report to the human resource manager. A survey on operator training is attached.
- Quoted  
BFC*

Seven companies indicated that they test operators for certification after training, John Vaughn, ICI - indicated they train operators for three months, and then test to determine if he is certified to do a particular job.

- (11) Video Tape, John Barr, Air Products - John Barr presented a video tape made by OSHA and Air Products to explain the hazards of vinyl chloride to the new employees. A copy of this video tape for our use will be requested from Air Products.

Mr. John Stafford of ICI was mentioned as the person who has the best list of up-to-date data on angiosarcoma deaths.

- (12) Small Reactor Safety, Jerry Brumbaugh, General Tire - Jerry summarized the results of the questionnaire sent out to the members on small reactor safety. A copy of this questionnaire is attached.
- (13) Computer Control Survey Report, Jim Gabbett, Georgia-Pacific - Jim summarized the results of the survey on computer safety. Georgia-Pacific have a 98% reliability factor with their computer. The computer improves quality and increases output. A master switch is used to connect the plant to analogue control when required. A copy of this summary is attached.

ICI reported that they go through a hazard analysis when any changes are made to computer programs. Georgia-Pacific reported that they are adding equipment to expand the memory of their computer since it is too small.

- (14) Vinyl Chloride Safety Condensation System, Bernd Terwiesch, Chemische Werke Huls - They designed a system to handle the emergency relief of large polys. This was commissioned in 1973 with a 200 cubic meter poly. In a runaway charge, a shortstop is added, but its effectiveness depends upon good agitation. Bernd indicated the shortstop affected product quality. They now have a system to handle runaway batches. The kinetics of the runaway reaction is fairly well defined. Usually you have the reaction going from an isothermal to an adiabatic condition. Their system is designed to vent the contents from the poly through a knockout tank, and condenser, into a vinyl chloride accumulator. A supply of cold water is kept in a separate tank to operate the condenser. The condensation system is activated after the pressure in the vessel reaches a predetermined value and if the recovery system does not lower this pressure. In addition, it can be manually activated by a switch. This system design is covered under U.S. patent 4004880 dated January 25, 1977, a copy of which is attached. Since the installation of this system, it has been used effectively one time. No venting of vinyl chloride to the atmosphere has occurred. The system is designed to be used for two polys.
- (15) Fluid Bed Dryer Explosion, Conoco - Conoco reported on a fluid bed dryer explosion which occurred in the second stage. The air temperature reached 250°C. Normal conditions are 100°C. The explosion occurred in the plug flow section. The PVC fused so badly it had to be chopped out with axes. A stainless steel baffle melted. In addition, there was some HCL damage in the dryer. This occurrence is similar to dry blend problems in gaylords where they have experienced hot cores in the center of the gaylord.
- (16) Tank Car Derailment, Pt. Pleasant, West VA, Everson Weakly, Pantasote - A copy of this incident is attached. One of the important factors was to keep people of the community informed concerning the progress of cleanup operations. In this particular case, the leak in the vinyl chloride car was patched and the car was then turned upright and returned for repair. The use of portable radios to communicate with a command post was recommended. OSHA people were present, but did not interfere with the operation.

EPA Update

Attached is the following information:

- (a) Regulatory update - comments by J. Barr.
- (b) Highlights of a luncheon speech by Garry Baise.

Business Matters

Next year's meeting will be held in Toronto, Canada. More input will be sought from the European Co. (Their representation seems to increase at each meeting).

Officers for 1982:

|                  |                                   |
|------------------|-----------------------------------|
| Doug Fry         | Diamond, Chairman                 |
| Jim Wallace      | ESSO Canada, Vice Chairman        |
| Henry Rzempoluch | Program Chairman <i>Pantasote</i> |
| H.G. Olson       | Ethyl, Secretary                  |
| Bill Hager       | Formosa, Treasurer                |

The offices of Secretary and Treasurer are continuing.

Ron Kaminski

Glen D. Schaaf

/3359j  
10/13/81

19 August 1981

INSTITUTE OF OCCUPATIONAL MEDICINE

EPIDEMIOLOGICAL AND CLINICAL STUDIES OF POLYVINYLCHLORIDE WORKERS

by

C A Soutar, S Gauld, M Lloyd, L H Copland, J F Hurley

ABBREVIATED SUMMARY

We have reported previously a medical survey of 818 present and past workers at a factory making polyvinylchloride (PVC) in which we showed that exposure to fine PVC dust was associated with a slight average reduction in tests of breathing capacity, and with the presence of small spots visible in X-rays of the lungs.

The present studies were designed to identify any chest illness in men who had worked in dustier plants in the factory but who had not been seen in the previous survey, and to examine similarly men working at a second factory manufacturing PVC; to re-examine the relationship between PVC dust exposure and small spots in the chest X-ray since in the first study there had been some disagreement between expert readers over the interpretation of the X-ray appearances, and to discover how seriously men may have been affected by PVC dust.

Two hundred and twenty-nine additional men were seen at the first factory, and little chest illness was found among them. One hundred and twenty-seven men were seen at the second factory, and even less illness was found in this workforce. Each man was sent a brief confidential medical report

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The X-rays were re-read by the same three experienced readers whose results were reported previously, and also by another panel of five readers. The readings confirmed the results of our earlier study, in that PVC dust exposure was found

Again, only some readers detected the effect of PVC dust, and the reasons for these differences probably include the slight degree of the abnormalities, which cannot be distinguished in an individual X-ray from changes related to age.

These changes of the chest X-ray were slight, on the borderline between normality and abnormality, and clinical examinations of a group of men who had these spots indicate that the health of their lungs was no worse than that of a group of men of similar age and smoking habits who had normal chest X-rays (except for a slight increase in sputum). We conclude that the presence of these spots does not indicate that PVC dust has seriously affected the lungs. Some men who had experienced relatively high estimated dust exposures were also examined if their breathing tests results were lower than those of other men. The non-smokers selected in this way all had healthy lungs, but some of the smokers had serious reductions of their breathing tests. This was probably the result of their smoking habit, and there was no evidence to suggest that PVC dust had seriously damaged their lungs.

We conclude that exposure to PVC dust has been shown to cause a slight reduction of tests of breathing and slight abnormalities of the chest X-ray, but that there is no evidence that PVC dust has caused serious illness among the workforce, although the possibility of a rare idiosyncratic response to dust cannot be excluded.

For details of this work, please refer to Institute of Occupational Medicine Technical Memorandum TM/81/8.

9/24/81

SUMMARY OF OPERATOR TRAINING QUESTIONNAIRE

The following is a summary of the 32 responses to the operator training questionnaires:

1. What is the approximate number of people in your total work force involved in manufacturing?

|            |    |
|------------|----|
| 0 to 100   | 19 |
| 100 to 300 | 8  |
| 300+       | 6  |

Some responses covered several different plants.

2. Do you have a formal training program for operating personnel:

|     |    |    |   |
|-----|----|----|---|
| Yes | 28 | No | 4 |
|-----|----|----|---|

3. Does your plant organization have a full-time person whose primary responsibility is training?

|     |    |    |    |
|-----|----|----|----|
| Yes | 17 | No | 15 |
|-----|----|----|----|

4. If your answer to No. 3 is "yes," to which functional part of the organization does this person report? (Employee relations, manufacturing, technical, etc.)

Typical responses:

- a. Manufacturing department (8 responses)
- b. Employee relations department controls overall program with a coordinator from the manufacturing department implementing most of program at unit level (4 responses)
- c. Employee relations
- d. Safety
- e. Technical

5. If your answer to question No. 3 is "no," who in your organization is primarily responsible for training?

Typical responses:

- a. Operating supervisor or foreman
- b. Safety Department
- c. Manufacturing engineer
- d. Personnel

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6. How long does the typical operator spend in the training program?

At least half of the respondents indicated the length of their program as 3 to 6 weeks.

Page Two  
Summary of Operator Training Questionnaires

7. Is your program one continuous cycle or is it divided into several stages separated by practical on-the-job experience? Could you please describe (Example: Orientation/limited training - 1 week, advanced - 1 week, recycle training - 2 days)

Typical responses:

- a. Five phases (I - Orientation - 3 weeks; II - Departmental Training - 2-3 weeks; III - On the Job and Advanced; IV - Self-study Pilot Book Training; and V - Advanced Classroom Training)
- b. Three weeks operator training; 2 weeks supervisor training. 3 months OJT, annual review
- c. One continuous cycle of classroom and OJT
- d. Three days formal classroom, 1 month OJT, 2 days recycle classroom training per year
- e. 90-day apprentice training; 45 days OJT and classroom, qualification courses in process, mechanical, electrical, instrument
- f. Orientation one-half week; Buddy on the job 2-3 months, probationary period until passes test.

8. Please check those of the following topics which are included in your training program:

|                             |                                       |
|-----------------------------|---------------------------------------|
| <u>X</u> Orientation        | <u>X</u> Regulatory (EPA, OSHA, RCRA) |
| <u>X</u> Safety             | <u>X</u> Industrial Hygiene           |
| <u>X</u> Fire Fighting      | <u>X</u> Respirator Protection        |
| <u>X</u> Process Technology | <u>X</u> Company Philosophy           |
| <u>X</u> Instrumentation    | <u>X</u> Company Organization         |
| <u>X</u> Basic Equipment    |                                       |

List others not mentioned above: EEO, Company Policy.

9. As a part of your operator training program, do you use proficiency tests to evaluate the effectiveness of the program?

Yes 22          No 10

10. Do you use tests to qualify operators for promotion:

Yes 14          No 18

11. What do you feel are the strengths of your program?

Page Three  
Summary of Operator Training Questionnaires

Typical responses:

- a. Six weeks formal training
- b. Locally produced video tapes
- c. Management support
- d. Operator input
- e. Uniform format for procedures
- f. Company philosophy and attitude

12. What area of your program would you like to improve:

Typical responses:

- a. Supervisor training
- b. Detailed orientation for advanced program
- c. Operator retention of material
- d. Improve higher technology training
- e. Add formal followup
- f. Formalized testing
- g. More formal procedures
- h. Full time supervisor for training
- i. Follow-up on a more formal basis

13. Which, if any of these training aids do you use in your operator training program?

All of the following are being used to some degree:

Film  
Slide/tapes Presentation  
Video Tape  
Commercially Produced Video Tapes  
Home-made Video Tapes  
Mock-up Equipment or Process Area  
Demonstration Instruments

14. Do you use video tape recordings produced at your facility by your own people?

Yes 11      No 19

If "yes," could you please comment on the effectiveness of this technique? Do you recommend this technique to others?

Page Four  
Summary of Operator Training Questionnaires

Typical responses:

- a. Good for repetitive routine information
- b. Very good because of local background
- c. Very relevant
- d. Prepared by a special training division
- e. Good - but still learning how to do it
- f. Only 25% good enough to re-use
- g. Two respondents said not using but plan to start.

9/18/81

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Question No. 1: Most Important Safety Considerations

What are some of the most important safety considerations that you would investigate to evaluate the overall plant safety status?

|                                                                                  | Number of<br>Replies |
|----------------------------------------------------------------------------------|----------------------|
| (a) Containment of vinyl chloride                                                |                      |
| 1. Relief valve and rupture disk system and condition                            | (6)                  |
| 2. Emergency relief containment capacity and recovery system                     | (3)                  |
| 3. Cooling and electrical backup for reactors                                    | (3)                  |
| 4. Reactor controls                                                              | (2)                  |
| 5. Unloading and storage and handling of VCM                                     | (2)                  |
| 6. Reactor S/S system                                                            | (2)                  |
| 7. Control of reactor bottom valve                                               | (1)                  |
| 8. Emergency shutdown systems                                                    | (1)                  |
| 9. Agitator alarms                                                               | (1)                  |
| 10. Reactor area manned at all times                                             | (1)                  |
| 11. Maintenance records for vessels in VCM service                               | (1)                  |
| 12. Vessel integrity program                                                     | (1)                  |
| (b) Contingency - preventing fires and explosions<br>in the event of V.C. escape |                      |
| 1. Fire protection system                                                        | (6)                  |
| 2. Plant layout                                                                  | (4)                  |
| 3. Presence of safety equipment                                                  | (2)                  |
| 4. Plant emergency plan                                                          | (1)                  |
| 5. Electrical equipment properly grounded                                        | (1)                  |
| 6. Use of fire safe valves                                                       | (1)                  |
| 7. Ability to handle large quantities of V.C. gas                                | (1)                  |
| (c) Good safety and operational management                                       |                      |
| 1. Up to date procedures - complete operating manual - plant follows procedures  | (11)←                |
| 2. Training and education of all personnel                                       | (10)←                |
| 3. Maintenance status - P.M. program                                             | (7)                  |
| 4. Housekeeping                                                                  | (6)                  |
| 5. Attitude of management and personnel                                          | (5)                  |
| 6. Safety organization                                                           | (2)                  |
| 7. Operator involvement in safety                                                | (1)                  |
| 8. Inspection system                                                             | (1)                  |
| 9. Engineering standards - design criteria being followed                        | (1)                  |
| 10. Proper raw material storage                                                  | (1)                  |
| 11. Regular safety sessions                                                      | (1)                  |
| 12. Inter-action between Production and Maintenance                              | (1)                  |
| (d) Indicators                                                                   |                      |
| 1. Past Records - frequency and severity records                                 | (4)                  |
| 2. Monitoring and emission records                                               | (2)                  |
| 3. Most recent systems safety analysis review                                    | (1)                  |

Question No. 2: Reactor Discharge Valve Control

How do you prevent the wrong reactor from being opened?

|                                                                                | Number of Replies |
|--------------------------------------------------------------------------------|-------------------|
| 1. Operator training and procedures                                            | (8)←              |
| 2. Clear identification of reactors                                            | (6)←              |
| → 3. Mechanical locking system - two people to open                            | (4)               |
| → 4. Discharge port is covered with a locked cover                             | (4)               |
| 5. Fixed discharge piping - batch always contained                             | (4)               |
| → 6. Reactor discharge valve interlocked with reactor pressure                 | (3)               |
| 7. Two valves                                                                  | (2)               |
| 8. Software interlocks                                                         | (2)               |
| → 9. Warning light system - indicates safe to open                             | (2)               |
| → 10. Electrical interlocks                                                    | (1)               |
| 11. Communications                                                             | (1)               |
| 12. Pressure gauge mounted beside valve                                        | (1)               |
| 13. Slow opening valves - time to discover mistake                             | (1)               |
| 14. Drop valve actuated from reactor top - near pressure gauge and sight glass | (1)               |
| 15. Working on a locking device                                                | (1)               |

Question No. 3: Charge Volume Control

(a) How do you measure water, VCM, catalyst, suspending agents?

|                   | <u>Weight</u> | <u>Meter</u> | <u>Volume</u> |
|-------------------|---------------|--------------|---------------|
| Water             | 0             | 15           | 1             |
| VCM               | 7             | 10           | 1             |
| Catalyst          | 9             | 0            | 3             |
| Suspending Agents | 8             | 2            | 1             |

(b) How do you prevent over or under charging?

|                                                            |     |
|------------------------------------------------------------|-----|
| 1. Visual checks on levels                                 | (7) |
| 2. Operator training, procedures, signing charge sheet     | (6) |
| 3. Calibrating meters - maintenance                        | (3) |
| 4. No independent mechanism to prevent over/under charging | (2) |
| 5. N/A                                                     | (2) |
| 6. Dual meters                                             | (1) |
| 7. Computer controlled                                     | (1) |

(c) How do you control charging sequence?

|                                                     |      |
|-----------------------------------------------------|------|
| 1. Operator training and procedures                 | (12) |
| 2. Computer                                         | (3)  |
| 3. Sequence controlled by mechanical stepper switch | (1)  |
| 4. N/A                                              | (2)  |
| 5. No answer                                        | (2)  |

Question No. 4: Gasket Replacement Control

(a) Do you replace gasket --

Number of  
Replies

|                            | <u>Yes</u> | <u>No</u> | <u>No Answer</u> | <u>N/A</u> |
|----------------------------|------------|-----------|------------------|------------|
| 1. After each opening      | 7          | 5         | 7                | 1          |
| 2. After major maintenance | 15         | 0         | 4                | 1          |
| 3. Once per year           | 3          | 1         | 14               | 2          |

(b) Pressure of the pressure test --

1. After each opening      psig - 50, 200, 90, 30,  
Vacuum, 80% of R/D rating, 15" Hg vacuum
2. After major maintenance      psig - 100, 140, 150, 85, 120, 150, 135,  
120, 180, 60, reaction pressure,  
rating - 10%
3. Once per year      psig - 170, 175, 180

(c) How often is a manway gasket re-used?

- |                                                        |     |
|--------------------------------------------------------|-----|
| 1. Inspected visually and re-used if passes inspection | (8) |
| 2. Never re-used                                       | (3) |
| 3. 10 - 15 times                                       | (3) |
| 4. 10 - 20 charges                                     | (1) |
| 5. 50 charges                                          | (1) |
| 6. 100 - 150 charges                                   | (1) |
| 7. No answer                                           | (2) |

(d) Are your manway gaskets O-rings or flat gaskets?

| <u>O-Rings</u> | <u>Flat</u> | <u>N/A</u> |
|----------------|-------------|------------|
| 10             | 8           | 2          |

Question No. 5: Safety Valve Control on Reactors

(a) How often do you inspect your safety valve nozzle?

- |                                                                                        |     |
|----------------------------------------------------------------------------------------|-----|
| 1. Each time the reactor is entered or opened                                          | (7) |
| 2. After every charge                                                                  | (4) |
| 3. Approximately every 3 days                                                          | (1) |
| 4. Once per week                                                                       | (1) |
| 5. Once per month                                                                      | (1) |
| 6. Once every 30 - 50 batches                                                          | (1) |
| 7. Two parallel relief nozzles - each with 2 rupture discs<br>and no pop safety valves | (1) |
| 8. Do not use safety valves on reactors - use double rupture discs                     | (1) |
| 9. No answer                                                                           |     |

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Question No. 5: Safety Valve Control on Reactors

|                                               | Number of<br>Replies |
|-----------------------------------------------|----------------------|
| (b) How often do you test your safety valves? |                      |
| 1. Once per year                              | (14)                 |
| 2. Every 6 months                             | (1)                  |
| 3. N/A                                        | (5)                  |

(c) Are safety valves removed and cleaned  
after each release?

Yes 15

No 0

Yes was the only answer if the question was answered, except -- "no  
reactor releases - should be done - no policy."

Question No. 6: Reaction Shortstop

(a) Do you have a reaction shortstop system?

Yes 17

No 2

N/A 1

(b) Is the injection automatic or done by  
an operator?

Automatic 5

Operator 16

No answer 3

If automatic, what initiates the operation?

- Agitator RPM
- High reactor pressure
- Loss of power to agitators
- Over pressure or temperature or loss of agitation
- Loss of agitation, agitator motor, high water pressure,  
power failure

Question No. 6: Reaction Shortstop

Number of  
Replies

(c) Is this system independent for each reactor  
or a common system for several reactors?

|              |    |
|--------------|----|
| Independent  | 10 |
| Common       | 6  |
| Both systems | 1  |
| No answer    | 4  |

(d) How often was your system operated last  
year?

|                 |   |
|-----------------|---|
| Less than 10    | 6 |
| 10 to 100 times | 4 |
| Over 100 times  | 4 |
| N/A             | 6 |

Many times the shortstop system was used in non-emergency situations.

(e) How often was your system tested last  
year?

|         |    |
|---------|----|
| Daily   | 2  |
| Weekly  | 1  |
| Monthly | 3  |
| Yearly  | 1  |
| N/A     | 13 |

Question No. 7: Reactor Pressure Control

(a) How do you prevent pluggage in reactor  
pressure transmitters?

|                                   |      |
|-----------------------------------|------|
| 1. Water injection                | (6)  |
| 2. Inspection and manual cleaning | (10) |
| 3. Solvent cleaning system        | (1)  |
| 4. Dual pressure systems          | (2)  |
| 5. N/A                            | (1)  |
| 6. Not a problem                  | (1)  |

Question No. 7: Reactor Pressure Control

Number of  
Replies

(b) Do you have alarms for high pressure?

Yes 18

No answer 1

N/A 1

(c) Approximately what percent of normal  
operating pressure is the alarm set for?

- |                       |     |
|-----------------------|-----|
| 1. Less than 110%     | (9) |
| 2. Between 110 - 120% | (5) |
| 3. Over 120%          | (2) |
| 4. No answer          | (4) |

Question No. 8: VCM Pump Control

What protection do you have to prevent remote  
operated VCM pumps from starting with suction  
and discharge valves closed?

- |                                           |     |
|-------------------------------------------|-----|
| 1. Operator training, procedures, etc.    | (5) |
| 2. Automatic valves interlocked with pump | (5) |
| 3. None                                   | (6) |
| 4. No answer                              | (2) |
| 5. CRT display                            | (1) |
| 6. No remote pumps                        | (1) |

Question No. 9: VCM Storage Tanks

(a) Do you have sprinkler protection for  
your VCM storage tanks?

Yes 20

No 2

- Use monitor nozzles on older installations.  
-- No, for some larger tanks

Question No. 9: VCM Storage Tanks

(b) How often are these tanks opened for internal inspection:

|                                                      | Number of Replies |
|------------------------------------------------------|-------------------|
| 1. Once per year                                     | (3)               |
| 2. 2 - 5 years                                       | (8)               |
| 3. 6 - 10 years                                      | (3)               |
| 4. Over 10 years                                     | (2)               |
| 5. No regular basis (many use ultrasonic inspection) | (3)               |
| 6. No answer                                         | (1)               |

Virgin monomer tanks inspected infrequently. Day tanks inspected more frequently.

(c) Have you had any corrosion problems in VCM storage tanks?

Yes 4

No 16

Those indicating they have corrosion problems are in recovered VCM tanks or day tanks, not virgin VCM.

Question No. 10: Recovered VCM Handling

(a) Do you distill your recovered VCM?

Yes 3

No 17

N/A 1

(b) How do you control polyperoxide formation in your recovered VCM system?

|                                   |     |
|-----------------------------------|-----|
| 1. Short retention time           | (7) |
| 2. Add an inhibitor               | (6) |
| 3. pH control - keep basic        | (4) |
| 4. Keep O <sub>2</sub> levels low | (3) |
| 5. No precautions taken           | (3) |
| 6. No answer                      | (3) |

Question No. 11: Reactor Entry

Do you require:

|                                                                                                        | <u>Yes</u> | <u>No</u> | <u>N/A</u> | <u>No<br/>Answer</u> |
|--------------------------------------------------------------------------------------------------------|------------|-----------|------------|----------------------|
| 1. All flanges blinded                                                                                 | 13         | 6         | 1          |                      |
| 2. VCM flanges blinded only                                                                            | 3          | 12        | 1          | 5                    |
| 3. Manway watch                                                                                        | 16         | 4         | 1          |                      |
| 4. Mechanical manway watch                                                                             | 4          | 11        | 1          | 4                    |
| 5. Safety belt only                                                                                    | 6          | 11        | 1          | 3                    |
| 6. Safety belt and wristlets only<br>(3 answered - wristlets only)                                     | 2          | 11        | 1          | 3                    |
| 7. Safety belt and wristlets with<br>line attached<br>(2 answered - safety belt with line<br>attached) | 2          | 12        | 1          | 3                    |
| 8. Lab entry analysis VCM/O <sub>2</sub>                                                               | 2          | 14        | 1          | 3                    |
| 9. Portable analyzer entry analysis<br>VCM/O <sub>2</sub>                                              | 17         | 2         | 1          |                      |
| 10. Respirator worn at all times                                                                       | 15         | 3         | 1          | 1                    |
| 11. Respirator worn at certain jobs                                                                    | 6          | 6         | 2          | 6                    |
| 12. Gloves to be worn                                                                                  | 13         | 4         | 1          | 2                    |

COMPUTER CONTROL SAFETY QUESTIONNAIRE

Dear VCSA Member,

Computer control of PVC plants has very definite safety benefits. However, there are some safety problems which computers introduce which are not readily apparent. The purpose of this questionnaire is to survey computer-operated plants to discover any special problems related to computers, either design or operator interface related, and how these have been solved.

1. COMPUTER/MANUAL OPERATION

A) Do you have provisions for independent computer and manual operation? \_\_\_\_\_

1. No
2. Yes
3. Not Totally
4. Yes
5. Yes
6. Yes

B) How do you isolate the computer from the plant during manual operation or when the plant is down for computer repairs?

1. The portion of the computer used for temperature control is kept active when the computer is in repair. No manual control is possible in other portion when computer is down.
2. A key switch which turns complete plant control into manual operation.
3. Mechanical disconnect, at I/O and at remote (air supply to valve, etc.)
4. Switch all devices to manual operation
5. There is a relay switching system that is activated on computer failure or by manual request. This system deactivates panel push-buttons during computer operation and isolates the computer I/O from the device relays during manual or panel mode.
6. Have MANUAL/AUTO switch which electrically isolates computer. Had one incident during trouble shooting of computer when switch was bypassed accidentally. Future design will consider more tangible isolation than switch.

C) Have you had any problems with the computer opening valves or reactors which were out of service for maintenance?

1. No operation is possible without computer.
2. No-air is removed from solenoid operated valves when out of service.
3. Once - installed lockout on positioners.
4. One occasion due to human error.
- G/p 5. No - All valves on reactors down for maintenance are "air-failed" so that they cannot open.
6. Air supply to reactors is locked out during maintenance.

D) How do you maintain operator proficiency on manual operation during long periods of computer operation?

1. No manual operation is made.
2. We do not run full production without computers.
3. Don't try.
4. Once per month each operator must operate manually for at least four hours.
5. We do not, at this time, have a specific program or method. This has not been a problem for us because our computer up-time averages about 98%.
6. Schedule periods of MANUAL operation in order to maintain proficiency.

*GP can not run as fast without the computer.*

2. OPERATORS TRAINING

A) How do you train new operators?

1. Through education in special lecture program and on the job training.
2. On-the-job with a background of basic theory once familiar with job.

3. Some classroom and theory - mostly on the job buddy system.
4. Formal Class Room Training for approximately four weeks. Then work with existing operator for approximately two months.
5. New computer operators receive most of their training by working with experienced operators. They also spend approximately eight hours with one of the computer programmers for technical instruction about the computer.
6. New operators are not trained on the computer until all other jobs in plant are mastered. Training involves several weeks of on the job dual operation with experienced operator, on both MANUAL and COMPUTER modes.

B) Do you have refresher training for experienced operators?

1. Yes
2. Yes - Limited to last job rotation otherwise operators are encouraged to keep current at all times.
3. Yes
4. Sometimes when operating procedures are updated.
5. We do not have regularly scheduled retraining classes for experienced operators, but retraining is done if operational performance indicates the need.
6. No

C) How do you retrain after major program revisions?

1. By lecture and simulation training.
2. Process and staff engineering will assist in this effort.
3. Written, classroom, and demonstration.
4. Systems Engineer conducts training sessions. Includes practice on CRT.
5. When possible, major changes are made gradually and training classes are held to inform operators of the effects of the changes on them.

6. (1) 12-15 hours classroom
- (2) 1 to 3 days water batching

D) How do you communicate minor program revisions to all operators?

1. Either by an official transmittal note or either by starting meeting of the day.
2. Memos and log book.
3. Written - notice and description.
4. Operator log book and notices.
5. This is done through operation department communication channels. (IE., instructions in supervisors instruction log).
6. Have separate log book to record all revisions.

3. FIRST-LINE SUPERVISOR TRAINING

A) How do you train new supervisors?

1. By on the job training.
2. Allow upgrade system to cover vacancies.
3. A - Senior operator system leads to promotion.  
B - No formal method - probationary period.  
Both - Use outside training programs.
4. New first line supervisors are promoted from the operators ranks and are already familiar with operation. Other training consists of familiarization with maintenance procedures, company policy, etc.
5. New supervisors do not undergo any formal training because they are all ex-computer operators.

6. Had problems during startup of plant because supervisors had no time for first hand solo operation of computer, following the classroom sessions. Since then, however, all new supervisors selected have come from best computer operators.

B) Do you have refresher training for experienced supervisors?

1. Not done usually, except on emergency training.
2. They participate in all training sessions for each unit.
3. Yes
4. Yes - Same as with operators. In addition they get refresher on supervisory skills.
5. No
6. No

C) How do you retrain after major program revisions?

1. By a lecture and simulation training.
2. Process engineering will assist in this effort.
3. Same as operators.
4. Same as operators.
5. They attend the same training classes that operators attend for major changes.
6. (1) 12-15 hours classroom.  
(2) 1 to 3 days water batching.

D) How do you communicate minor program revisions to all supervisors?

1. By an official transmittal note.
2. Memos and log book.
3. Written and discussions.
4. Same as operators.
5. The same as for operators, through operation department's communication channels.
6. Separate log book to record all revisions.

E) Have you had any problems with first-line supervisors losing proficiency with computer operations because of problems in other non-computer-operated parts of the plant? How are these problems overcome?

1. Very few case only. We give them refreashing education and make them supervisors.
2. No - Most first-line supervisors have only a limited working knowledge of computer operations.
3. Some refresher period and assignment with capable operators.
4. No
5. We do not attempt to keep a supervisor completely up-to-date on computer operations. We feel that with two console operators and two senior operators on each shift, it is unnecessary to keep supervisors proficient on the computer.
6. Yes - Require supervisors to spend more time in control room and place more responsibilty on outside operators.

4. INFORMATION OVERLOAD

A) Have you had any problems of operators being swamped with computer messages and alarms so that some are ignored? How are these problems overcome?

1. No - Only important messages and alarms are kept, so there will be no neglecting possible.
2. Yes - Use of two people helps to overcome problems when the extra person is available.
3. Yes -
  1. Establish higher threshold for emergency alarms.
  2. Have some data indicated, not alarmed.
  3. Hardwire really critical alarm.
  4. Training employees.
4. Yes - Added a second operator in control room to handle all operations after the reactors. In another plant - the supervisor assists the operator.
5. Yes - We are constantly working to eliminate unnecessary messages and redundant alarms to reduce the amount of information being fed to the operators.
6. Yes -
  1. Revised program to reduce number of alarm messages.
  2. Use separate printers for messages and alarms.
  3. Some critical alarm messages are printed with exposed type in order to make them stand out.

5. OPERATOR COMPLACENCY

A) Have you had any problems with operators relying too heavily on the computer to correct all mistakes? How are these problems overcome?

1. No - Cross checks by operators are inserted at important locations.
2. No
3. A- No  
B- Yes - have mandatory log sheets to record reaction to alarm.
4. No - Not since instituting manual operations once per month.
5. No
6. Yes - Diligent follow up on all incidents (major and minor) where mistakes using the computer are made. Operator making mistake is counseled and other operators are informed.

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6. MAJOR PROGRAM REVISION SIMULATIONS

A) Do you perform any plant-scale simulations when major program revisions are made?

1. No
2. On start-up we provide dummy batches to walk through the program.
3. No - Except water batch tests.
4. No
5. No
6. Yes - Charge full batch quantities of water, VCM, and all additives except catalyst. Use catalyst solvent to simulate catalyst. Simulate alarm conditions, including emergency shortstop. Period lasts from 1 to 3 days.

7. OPERATOR/SUPERVISOR PROGRAM VARIABLE CONTROL

A) Do you use an operator/supervisor control key to limit changes to program variables through the CRT?

1. No
2. Yes - Key switch
3. Yes - Many are not accessible to operators.
4. No
5. Yes
6. Have key - but do not use it.

B) How do you limit program variable changes by operations?

1. \_\_\_\_\_
2. Some parameters cannot be charged from CRT - engineer has to charge (key-switch).
3. Yes - written authorization and record.
4. Through directed operator CRT keyboard function.

5. By requiring them to obtain permission and key from supervisor.
6. Program variables are changed by engineers. Have not had problems with operators changing program variables. Had some problems with operators tampering with FLAG changes in order to get programs to run. Educated operators to high danger of this and revised programs for better operability.

C) How do you change formulation variables, such as catalyst and suspending agents?

1. No operators are involved in recipe changes.
2. Done with consultations with process engineering group through supervisor. Engineer normally makes changes.
3. By CRT, but only as written authority.
4. Process Control Engineer or Shift Supervisor accomplishes through CRT keyboard.
5. We have programs that allow operators to change the amount of ingredients used within certain limits and this is not a permanent change. Permanent changes to recipes are made by the programmers on request from the technical group.
6. Formulation page has variables which can be changed from CRT entries. The change must be input twice in order to be accepted. CRT changes are valid for one batch only. Long term formulation changes are made by engineers.

8. REACTOR CHARGE VOLUME CONTROLS

A) If you have primary and secondary measurement devices on charge quantities, how do you allow operator acceptance of deviations between primary and secondary devices?

1. Only one measurement is present.
2. Yes - Deviations are questioned by operators, and supervision makes decision. Also process engineering can be consulted.
3. Computer queries, then operator must get visual field verification before proceeding.
4. Variance limits set, but Shift Supervisor has some discretion if barely over limit.

5. We have no secondary measuring devices.
6. Deviation during charge - steps charge, operation must repair problem or deselect one of devices. Deselection procedures are written, with acceptable limits. On some chemicals, high value is accepted, on others, low value is selected.

9. VALVE STATUS INDICATIONS

A) How do you handle problems with valve status indicators, such as microswitches? Do you override the computer hold or alarm, or do you manually adjust in the field on each batch?

1. \_\_\_\_\_
2. a) We override only after manually checked in field.  
b) Adjust in field if problem persists.
3. Allow override after field inspection, then write ASAP work order.
4. Device is visually checked in the field before overriding computer hold status. Device is not operated post next work day without repair.
5. If a position indicator fails (valve in the proper position and in contact with switch) an "override" can be placed on the device by using the "supervisory key" until it can be repaired by the I & E Group.
6. Diligent maintenance is required to keep microswitches in good condition. Use override and manual field adjustment to overcome problems. Neither is an acceptable solution, but is necessary for operation. Repeat that follow up on problems must be prompt and diligent.

10. PLEASE DESCRIBE OTHER COMPUTER-RELATED SAFETY PROBLEMS OR INCIDENTS AND HOW YOU RECOMMEND TO CORRECT THEM.

1. \_\_\_\_\_
2. Operators do not always respond to computer initiated emergency type alarms - Computer print-out is reviewed duly by process engineer and recommendations made to production - Training sessions W/operators helps.
3. Preparing thorough fault-free analysis of computer operations on corporate basis.

4. None

5. In some instances, operators in the field have resorted to manipulating the instrument to process transducers (I to P's) by hand to force a valve or device to move contrary to computer command. This is a rather simple procedure that, only involves unscrewing the cover and using a finger, nut, bolt, rock or some other object to hold the pneumatic switch in the desired position.

Our solution to the problem was to make this act a severe violation of safety procedure with resulting severe penalties for violators. Since instituting this policy, we have had no further problems.

6. \_\_\_\_\_



# METHOD AND APPARATUS FOR CUSHIONING CONTINUOUS EXOTHERMAL REACTIONS

## CROSS REFERENCE TO A RELATED APPLICATION

Applicants claim priority under 35 U.S.C. 119 for Application Ser. No. P 24 287 05.6, filed June 14, 1974 in the Patent Office of the Federal Republic of Germany.

## BACKGROUND OF THE INVENTION

The field of the invention is chemical apparatus having tanks, and the present invention particularly relates to a method and apparatus for cushioning continuous exothermal reactions with, or in the presence of liquefied gases.

The state of the art of the present invention may be ascertained by reference to U.S. Pat. Nos. 3,636,331; 3,749,555; 3,793,258 and 3,794,471, and German Published Patent Application No. 2,032,700 of Georg Schroeder et al, having a publication date of Jan. 13, 1972 the disclosures of which are incorporated herein.

U.S. Pat. No. 3,793,259 discloses the state of the art of continuous bulk polymerization of vinyl chloride while the remaining references disclose the state of the art of continuous polymerization reactors.

When carrying out exothermal reactions, for instance polymerization reactions, unevenness in the reaction sequence or failure of heat exchange may force a resort to gas expansion from the reaction chamber as the only way to prevent the reactor from bursting.

Until recently, such exothermal reactions were carried out on a large scale in reactors containing about 20 cubic meters. When the pressure in such reactors became excessive, or when heat generation grew too large, the gases were expanded into a gas vessel at normal pressure or into the atmosphere. The quantities of escaping gas in the prior art are relatively minor and generally harmless through dilution into the atmosphere.

Such expansion into the atmosphere is impossible as regards the recently developed large reactors holding up to 200 cubic meters, as disclosed in German Published Application No. 2,032,700 because of ecological and safety hazards. Furthermore, appreciable amounts of input materials are lost in this manner. High costs eliminate the feasibility of catching the gases escaping from a reactor into a sufficiently large gas vessel under normal pressure.

## SUMMARY OF THE INVENTION

Having in mind the limitations of the prior art, the present invention has as an object means for containing continuous exothermal reactions with or in the presence of liquefied gases, without there being a loss of same and simultaneously observing ecological and safety regulations, and to do so in as simple a manner as possible.

This object is achieved in the present invention in that upon initiation of the reaction, the liquefied gases are expanded into a condenser, then they are condensed in same, and are collected in an accumulator.

Furthermore, in order to implement the method, the present invention makes use of apparatus comprising at least one gas exhaust line from the reactor with a blocking valve responding to over-pressure, a condenser so

cooling means without application of external energy flows into the condenser through a blocking valve actuated simultaneously as that of the gas exhaust line, and an accumulator connected to the condenser.

When the pressure in a reactor holding liquefied gases rises excessively either because of unevenness in the reaction sequence or because of failure in the heat exchange, for instance if there is total power failure, or if the heat generated becomes excessive, then according to the present invention the liquefied gases are expanded through at least one gas exhaust line provided with a blocking valve responding to over-pressure. Because of the expansion evaporation, both pressure and temperature rapidly drop inside the reactor.

The gases escaping from the reactor are fed through a gas exhaust line into a condenser and are condensed therein. Conventional condensers of the state of the art, for instance boiler-tube nest heat exchangers are used as condensers.

Those liquids are used as cooling media which will boil in the cooling process, and also those which will not boil. To ensure that the method of the present invention may also be carried out if there is total power failure, the cooling means must be capable of flowing from the cooling medium supply vessel into the condenser without requiring external power, such as by gravity or by means of compressed gas.

Cooling liquids boiling during the cooling process allow the mounting of the cooling medium supply vessel and the condenser at the same height or elevation, provided the self-generated pressure or fluid head of the cooling medium is large enough to make the same flow also in such a case into the condenser without requiring external power.

The use of media boiling in the cooling process, such as ammonia, holds the advantage of the cooling medium supply vessel being kept smaller in size. However, an additional absorption system for the evaporated cooling medium is then required, to prevent the matter from entering the atmosphere.

For reasons of safety, the cooling medium supply in the supply vessel is large enough to condense the entire gas content of the reactor.

It is important in the method of the present invention that the blocking valves at the reactor and at the cooling medium supply vessel are opened synchronously and that the supply of cooling medium to the condenser is large enough to rapidly condense the gases escaping from the reactor. This is achieved through mechanical, electrical or pneumatic coupling of the blocking valves at the reactor and at the cooling medium supply vessel.

When the reaction in the reactor is computer controlled, as disclosed in U.S. Pat. No. 3,636,331, then opening and closing of the blocking valves at the reactor and at the cooling medium supply vessel are controlled by a computer. In this system of U.S. Pat. No. 3,636,331, one uses for instance "feed-forward" control, in which the blocking valves are controlled by a program developed from exhaustive process analysis. The blocking valves then are opened prior to reaching excessive pressure. Pressure, but also the temperature gradient in the reactor may be used as the control parameter. Such an embodiment is especially reliable in operation.

The condensate obtained in the condenser is collected in a pressure accumulator and may be used again. If the condensate tends toward polymerization,

stopper solution are placed in the accumulator. It is especially advantageous to place the stopper solution in a "liquid bag" at the bottom of the accumulator, the condensate being made to pass by means of a dip-pipe through this liquid bag. This achieves especially good mixing.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The present invention is better understood by reference to the attached drawings, wherein:

FIG. 1 is a diagrammatic plan view of the apparatus of the present invention having one blocking valve in the gas escape line synchronously controlled along with one blocking valve in the cooling medium line;

FIG. 2 is a diagrammatic plan view of the apparatus of the present invention having two blocking valves in the gas escape line and two blocking valves in the cooling medium line; and

FIG. 3 is a diagrammatic plan view of the apparatus of the present invention having three blocking valves in the gas escape line and three blocking valves in the cooling medium line.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

With particular reference to FIG. 1, when the pressure in reactor 1 rises excessively, the gas is expanded through a gas escape line 2 and a blocking valve 3 into condenser 4. Once blocking valve 3 is opened, blocking valve 5, located in line 24, is also opened synchronously, thus releasing the supply of cooling medium through line 22 from the cooling medium supply vessel 6. Valves 3 and 5 are actuated by pressure controller 20. In a particular embodiment of the pressure controller 20, similar to that in FIG. 5 of U.S. Pat. No. 3,794,471, the pressure controller receives an electric signal output from a pressure transducer in the vapor space of reactor 1 and opens valves 3 and 5 beyond a given excess pressure and then closes them when the pressure drops off. The opening of valves 3 and 5 can also be controlled by pneumatic means. The condensate obtained is collected in accumulator 7.

To prevent solid or foamed particles from being carried along with the gases escaping from the reactor, a separator is suitably mounted ahead of the condenser. A cyclone, for instance, or a suitably designed pressure vessel may be used as the separator.

When easily polymerized materials, with respect to the particular reaction conditions, are located in the reactor, the latter's blocking valve preferably should be rinsed with a suitable liquid to prevent clogging of the blocking valve.

A preferred embodiment is shown in FIG. 2. Besides the elements shown in FIG. 1, there is a further gas exhaust line 8 provided with a blocking valve 9. Valve 9 is coupled to another blocking valve 10, which controls the supply of cooling medium from the cooling medium supply vessel 6. A separator 11 is mounted ahead of the condenser 4.

When the pressure in the reactor rises excessively, blocking valves 3 and 5 are opened first. If the pressure in the reactor fails to drop rapidly enough, a subsequent pressure controller 26 additionally opens blocking valves 9 and 10, and more expansion takes place. When materials are present in the reactor, which under the particular reaction conditions are easily polymerized, then rinsing blocking valves 3 and 9 with a suitable liquid through line 12 prevents clogging

The method of the present invention may be applied to all exothermal reactions with or in the presence of liquefied gases, for instance in polymerization reactions of vinyl chloride, ethylene, propene, butene, butadiene or the like, as disclosed in U.S. Pat. Nos. 3,749,555 and 3,793,259.

The apparatus of the present invention comprising accumulator, condenser, cooling medium supply vessel and where desired separator, may be designed in very compact form. Parts of the apparatus of the present invention also may be used during the normal sequence of a reaction in order to recover the residual gases still in the reactor at the end of a reaction taking place therein.

As shown in FIG. 3, the residual gas under pressure is expanded through an additional gas exhaust line 13 provided with a blocking valve 14 at the reactor and actuated by controller 28. In this case, the cooling medium is not supplied from the cooling medium supply vessel but rather through line 15. It can flow through blocking valve 16, which is coupled with blocking valve 14, into the condenser, the moment blocking valves 14 and 16 are opened. When the apparatus shown by FIGS. 1 and 2 is required, then blocking valves 3 and 5 or 9 and 10 are simultaneously opened with blocking valve 17.

A back pressure valve 18 prevents the cooling medium from flowing out of the cooling medium supply vessel into line 15 when, according to the present invention, the cooling medium flows from the cooling medium supply vessel into the condenser during a complete reaction in the reactor.

The method and apparatus of the present invention surprisingly protects in simple manner the reactor from bursting in the presence of complete exothermal reactions, without requiring discharging explosive or toxic gases into the atmosphere. The method of the present invention furthermore suffers no loss of input materials. Also, high reliability and safety is achieved for large reactors, while simultaneously preventing damage or jeopardy of any kind to the environment.

#### EXAMPLE

FIG. 2 shows the apparatus of the present invention. The reactor holds 200 cubic meters and contains about 60 metric tons of vinyl chloride, 110 tons of water, activators and suspension means. The temperature in the reactor is about 60° C and the pressure is about 10 atmospheres. The capacity of the cooling medium supply vessel is about 200 cubic meters and it holds 200 cubic meters of cooling water at about 20° C. A nest of boiler tubes heat exchanger is used as condenser 4. Sliders with pneumatic control are used as the blocking valves at the reactor and at the cooling medium supply vessel. These valves are coupled through an electrical circuit. A direct digital control (DDC) system monitors whether the pressure in the reactor drops fast enough upon opening blocking valves 3 and 5. If not, the DDC system additionally opens blocking valves 9 and 10 and the control variable is pressure.

If through failure of heat exchange, the pressure in the reactor rises to about 14.5 atmospheres, the pneumatically driven blocking valves at the reactor and at the cooling medium supply vessel are opened by means of the electrical circuit. Thereupon within about 10 minutes, approximately 180 cubic meters of cooling liquid flows through the condenser. The pressure in the reactor is about 10 atmospheres.

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utes, and the temperature drops to about 60° C. Approximately 30 metric tons of vinyl chloride are condensed in this step.

We claim:

1. A method for cushioning continuous exothermal reactions by the expansion of gases during an over-pressure condition during a power failure, comprising:
  - a. conducting a continuous exothermal reaction in a reactor under elevated gas pressure in the presence of liquefied gases;
  - b. at pressures beyond a given safe pressure, expanding said liquefied gases into a condenser to lower said elevated gas pressure below said given safe pressure;
  - c. condensing said gases in said condenser;
  - d. collecting the condensed gases in an accumulator;
  - e. supplying cooling medium to said condenser at a pressure head sufficient to discharge the cooling medium through the condenser; and
  - f. initiating said expanding and said supplying for cushioning said exothermal reaction during an over-pressure condition during a power failure.
2. An apparatus for cushioning continuous exothermal reactions by the expansion of gases during an over-pressure condition, comprising:
  - a. a reactor having an elevated gas pressure therein generated by liquefied gases and said reactions;
  - b. means for exhausting gas from said reactor beyond a given safe pressure;
  - c. means for condensing connected to said means for exhausting and receiving the exhausted gas;
  - d. means for accumulating connected to said means for condensing and receiving the condensed gas;
  - e. a cooling medium supply vessel connected to said means for condensing and having a pressure head

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sufficient to discharge the cooling medium through said means for condensing; and

- f. means for initiating flow from said cooling medium supply vessel and means for activating said means for initiating flow synchronously with said means for exhausting gas.

3. The apparatus of claim 2, wherein said pressure head of the cooling medium is a gravity feed.

4. The apparatus of claim 3, wherein said means for exhausting gas is a first blocking valve responding to a first given excess pressure and said means for initiating flow is a second blocking valve actuated synchronously with said first blocking valve.

5. The apparatus of claim 3, wherein said means for exhausting gas are a first blocking valve responding to a first given excess pressure and a second blocking valve responding to a second given excess pressure greater than said first given excess pressure and said means for initiating flow are a third blocking valve actuated synchronously with said first blocking valve and a fourth blocking valve actuated synchronously with said second blocking valve.

6. The apparatus of claim 3, further comprising a commercial water supply source connected in line between said cooling medium supply vessel and said means for condensing and said means for exhausting gas are a first blocking valve responding to a first given excess pressure and a second blocking valve responding to a second given excess pressure greater than said first given excess pressure and said means for initiating flow are a third blocking valve actuated synchronously with said first blocking valve and initiating flow from said commercial water supply source and a fourth blocking valve actuated synchronously with said second blocking valve.

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# United States Patent [19]

Langheim et al.

[11] 4,004,880

[45] Jan. 25, 1977

## [54] METHOD AND APPARATUS FOR CUSHIONING CONTINUOUS EXOTHERMAL REACTIONS

[75] Inventors: Franz Langheim; Michael Braasch, both of Marl, Germany

[73] Assignee: Chemische Werke Huls Aktiengesellschaft, Marl, Germany

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[58] Field of Search ..... 23/285, 230 A, 253 A, 23/284; 62/54; 48/175; 260/78.5 R

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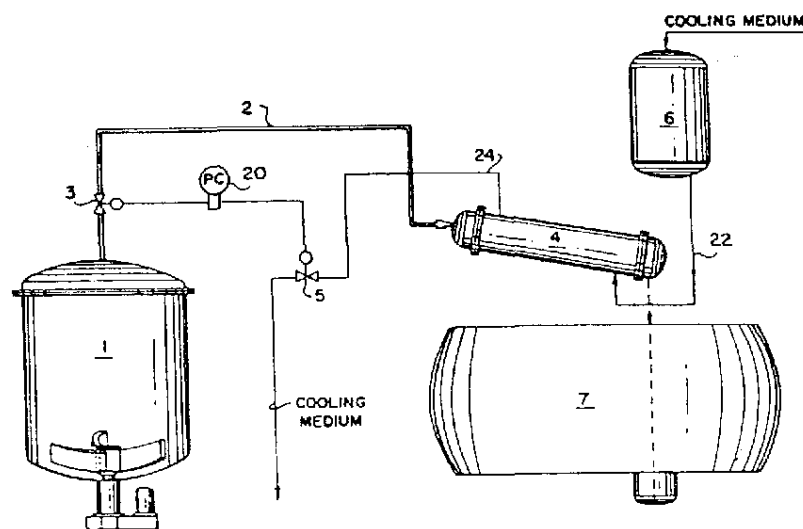
Primary Examiner—R.E. Serwin

Attorney, Agent, or Firm—Gilbert L. Wells

### [57] ABSTRACT

Method and apparatus for cushioning continuous exothermal reactions with or in the presence of liquefied gases having a reactor, a condenser connected to the reactor, an accumulator connected to the condenser and a gravity fed cooling medium supply vessel providing cooling to the condenser. A first blocking valve which responds to excess pressure is inserted in the line between the reactor and the condenser and a second blocking valve, actuated synchronously with the first valve, activates the flow of the cooling medium through the condenser.

6 Claims, 3 Drawing Figures



NGC 23291

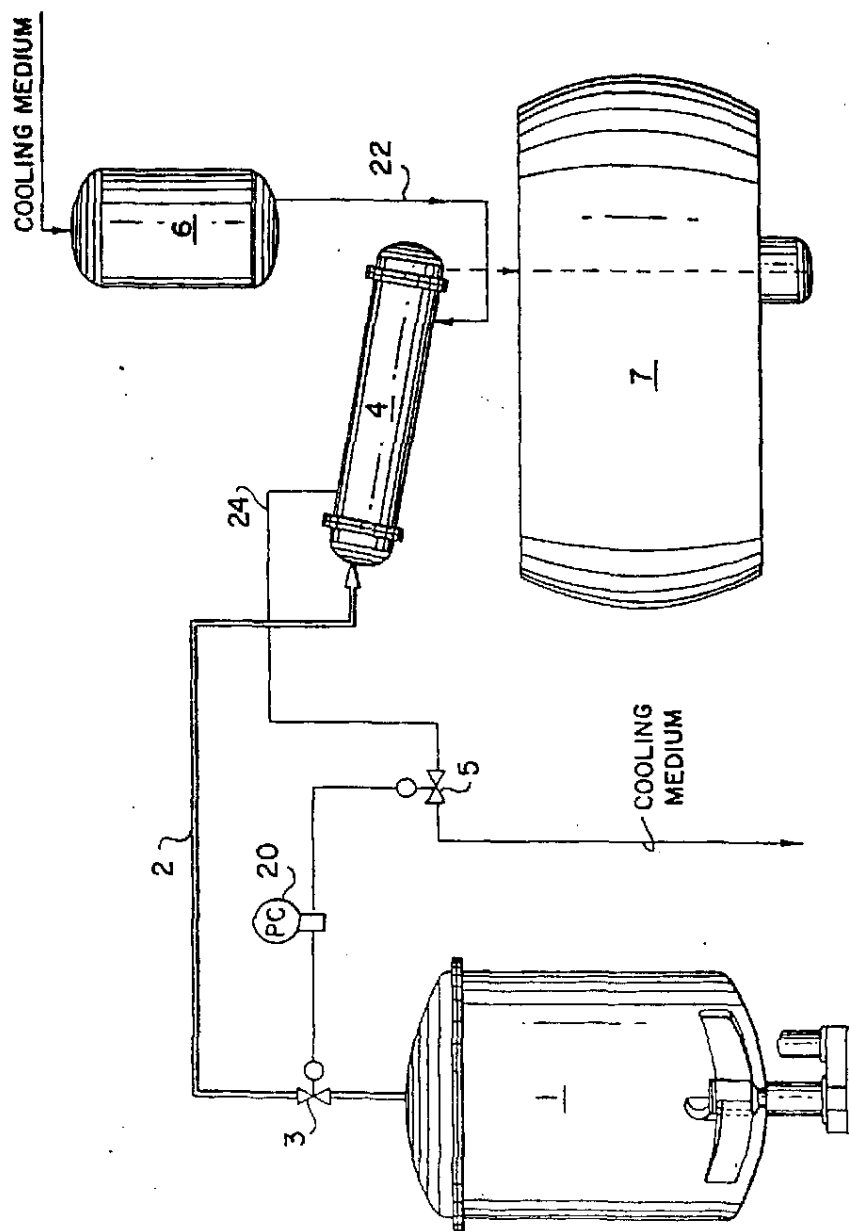


FIG. 1

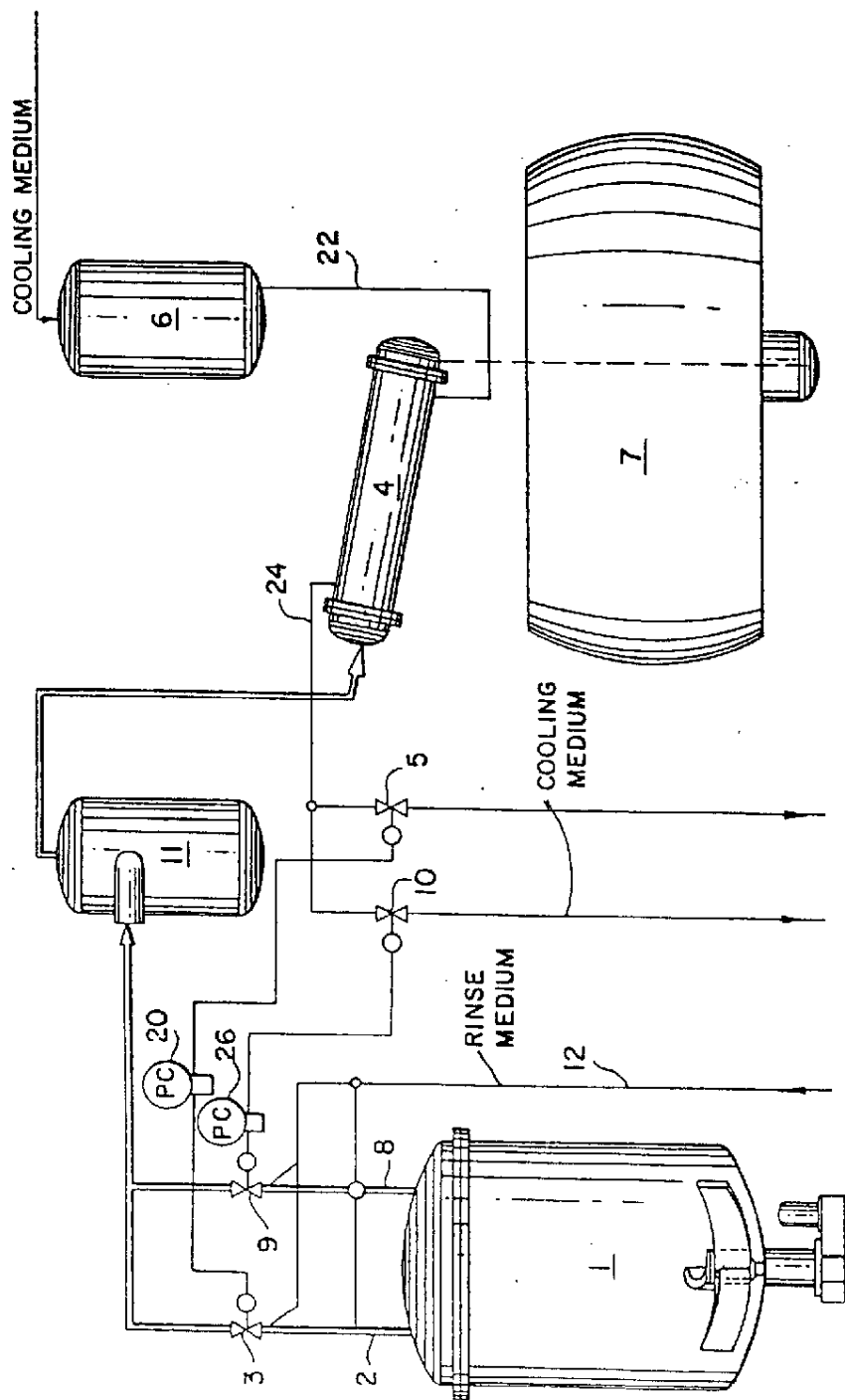


FIG. 2

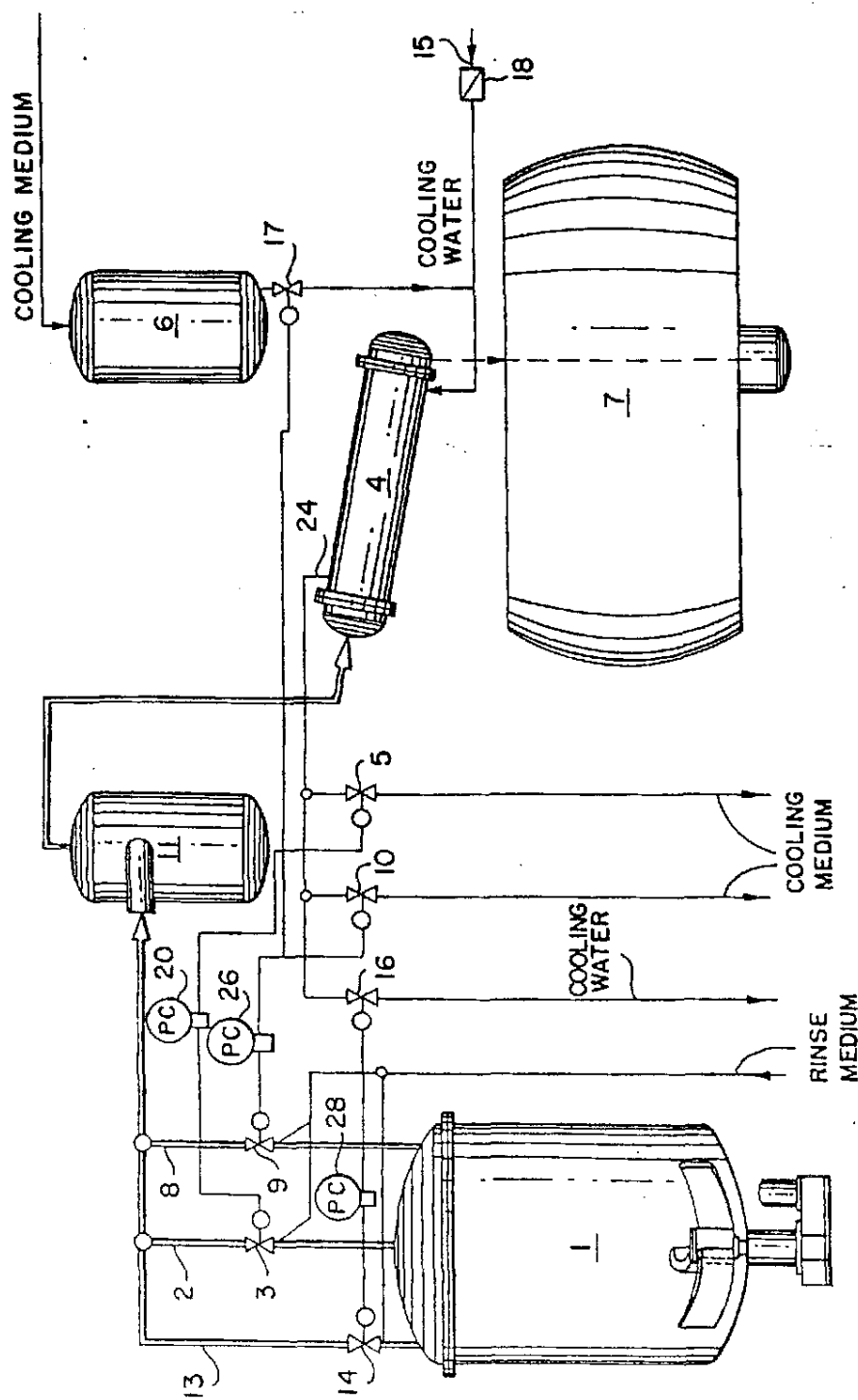


FIG. 3

VCM  
TANK CAR  
DERAILMENT

NGC 23295

Thursday, January 8, 1981

- 5:30 AM Henry Rzempoluch, Plant Manager, is contacted by railroad and informed of VCM tank car derailment.
- 6:00 AM Rzempoluch visits the disaster site and finds two hopper cars and five VCM tank cars involved. At least one VCM car has a serious leak.
- 6:30 AM Jim Ferrell, Traffic Manager for Pantasote, and Rzempoluch are at the scene with local authorities and railroad employees. It was decided by local authorities at the suggestion of Pantasote to secure the area. By this time, the railroad had contacted CHEMTREC.
- 7:00 AM CHEMTREC contacts PPG in New Martinsville, West Virginia. Union Carbide in Charleston is also contacted in case their expertise is needed.
- 7:30 AM Vapor cloud had increased to about one half acre. Local authorities and railroad evacuate families within one half mile radius.
- 8:00 AM Ferrell contacts Bob Baker of PPG in New Martinsville; advises him of the situation and requests a response team.
- Rzempoluch; three Pantasote production foremen; and Everson Weekley, Safety Supervisor, visit the scene to determine extent of damage. Scott Air Paks are used by two men who examine the overturned cars. At this point we feel only one car has a serious leak. We find that dome valves have been completely sheared off allowing VCM to escape.
- 9:00 AM Rzempoluch and Weekley formulate a program to monitor vinyl leaks. This is done by a Century Unit. A command post is set up at the plant and "walkie talkies" are used to relay information from the scene.
- 11:00 AM Weekley returns to the plant and briefs local authorities, railroad officials and Pantasote personnel. Levels in the area are 60 ppm at 500 yards and 150 ppm at 200 yards.
- Pumps for the city water wells are shutdown since they could prove to be an ignition source and cause an explosion. Public is informed that there is no contamination problem.
- 12:00 NOON Sheriff Bob Fruth is appointed to read a statement to the press and answer questions on the extent of the disaster.
- Bill Shaw, Train Master for Chessie System, arrives. Several railroad officials are now at the scene.
- Hulcher Emergency Service is called in to handle the cleanup.
- Security is now stepped up and local authorities (sheriff, city and state police) are joined by railroad police.

NGC 23296

- 1:00 PM Task force from PPG arrives and are taken to the site to make an assessment.
- Richard Fleece, Regional Manager for the Chessie System, arrives and helps to coordinate cleanup efforts. EPA, West Virginia Department of Health, and West Virginia Air Pollution Control Commission by now have contacted us by telephone.
- 2:00 PM A conference is held to determine how to patch the leak. We know that all dome valves have been sheared off and that we must plug leaks and clear the atmosphere before cars can be raised. We must also be able to unload the remaining monomer.
- 5:00 PM Regional Supervisor for Hulcher arrives and inspects the damaged car.
- 7:00 PM Meeting held at the Point Pleasant Motor Inn to discuss progress on patching the leak, the possibility of explosion, health hazards involved, security, evacuation, etc.
- Consensus is that since all valves have been sheared, this is a unique situation.

Friday, January 9, 1981

- 10:00 AM PPG states that they are beginning to fabricate a patch.
- 12:00 NOON Ron Escue, an employee for Huntington Piping, is called to the disaster site; and he then takes the lead in designing and fabricating a patch.
- 3:00 PM The leak from the Safety Relief on the tank car is patched. Gauge and vapor lines are also secured by the same patch.
- 5:00 PM Both liquid lines are patched and the car is ready to be raised.
- 6:00 PM Meeting at Point Pleasant Motor Inn to discuss progress made up to this point. Another task force from PPG's Lake Charles VCM plant arrive.

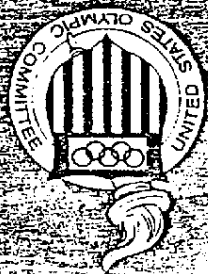
Saturday, January 10, 1981

- 8:00 AM - 3:00 PM Cars are raised, set back on tracks, and moved to Pantasote's yard for unloading on Monday morning.

NGC 23298



# PORTABLE COMMUNICATIONS



# Applications

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## Radio Communications At Three Mile Island

On October 16th, August 15th, and July 23rd, Three Mile Island technicians including a health physicist, a senior reactor operator and two nuclear engineers, entered the Unit 2 Reactor Building at Metropolitan Edison's Nuclear Station. The purpose of the missions was to assess damage and survey radiation levels in the building, take notes and photographs of what was found, and to take samples.

Since the required breathing equipment covers the face, a conventional microphone could not be used. A microphone which would operate in high noise without compromising the safety of the face mask had to be found. Additionally, to prevent radioactive contamination, the use of gloves and full-coverage protective clothing meant that a method for completely hands-free radio keying was required.

Each man was equipped with a Setcom GM-312 Face Mask Kit and a Setcom/Portable radio cable assembly to interface the kit to a Motorola MX series radio worn on a belt. The Setcom Kit included a bone conduction microphone, a unique device designed to respond to voice vibrations transmitted through the skull. Since



Technicians entering the Unit 2 Reactor Building at Three Mile Island.

this microphone was not in the facial portion of the face mask, mask integrity was maintained. Also included in the mask kit was a small, lightweight speaker suspended over the ear by a nylon loop.

The Cable Assembly used for the entry operations included a body-mounted switch for radio keying. This switch was used two different ways depending upon personal preference.

In one application it was belt-mounted and activated by pressing an arm against it; in the other approach it was taped to the individual's wrist and activated by pressing his wrist against his side. Both ways eliminated the need for hand use in keying.

In the three entry operations, all conversations and verbal notes were recorded, permitting careful study of the data collected.

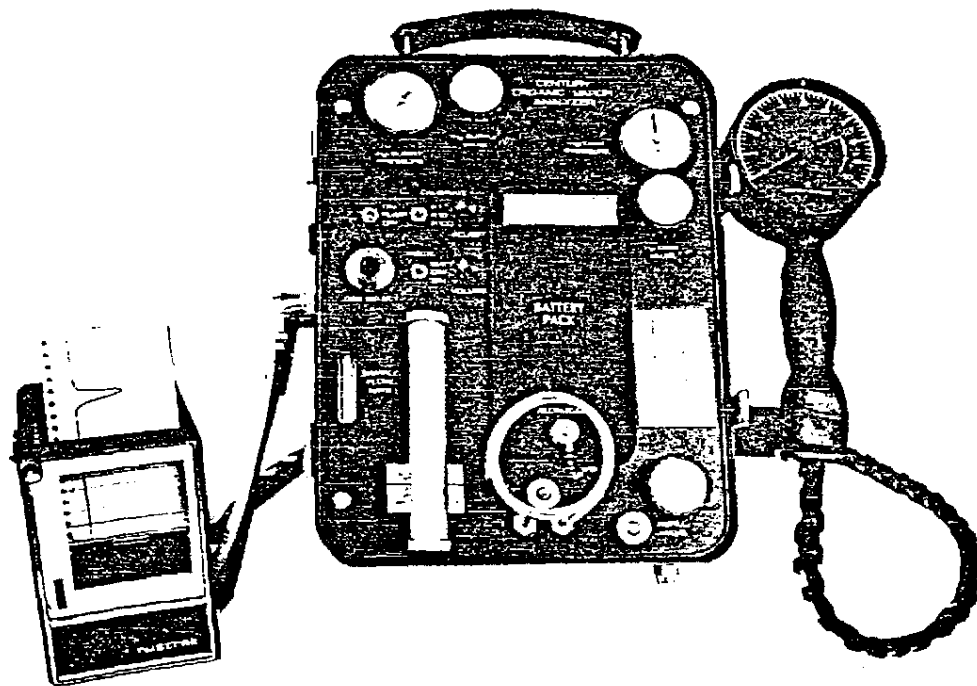
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# Communications

# ENVIRONMENTAL AIR MONITORING FOR THE 80's

Foxboro offers the individual concerned with air monitoring studies a broad capability in instrumentation ranging from charcoal tubes for personnel monitoring to portable infrared or gas chromatographic analyzers for on-site measurements to complete infrared or GC

stationary systems for multi-component, multi-location monitoring. If your work involves ambient air measurements of gas and vapors, call Foxboro. The newest addition to the Foxboro line of environmental monitoring equipment is the CENTURY Organic Vapor Analyzer.



## Air Monitoring Utilizing Portable GC

The CENTURY Organic Vapor Analyzer (OVA) provides the operator with continuous data on organic vapor concentrations for screening and survey purposes. Qualitative and quantitative analysis is also possible utilizing the gas chromatographic option. Since most industrial hygiene work is performed in the low and sub parts per million (ppm) concentration range, the OVA incorporates an extremely sensitive flame ionization detector which can, in many cases, analyze to parts per billion (ppb) levels. For analyses which involve monitoring in potentially explosive environments, the OVA has been certified by Factory Mutual Corporation for use in Class I, Division 1 areas.

The CENTURY Organic Vapor Analyzer has been proven by years of field experience to be exceedingly durable. Its integral power supply and light weight make it a "go anywhere" instrument capable of dependable operation over a wide range of environmental conditions.

The versatility of the OVA has manifested itself in a wide variety of applications, such as:

- OSHA compliance testing where both qualitative and quantitative data are desirable.
- Source identification and measurement for fugitive emissions as defined for refineries and chemical plants by EPA.
- Studies of hazardous waste and spill sites.

The OVA can operate in either of two modes. Mode 1—the survey mode—directs sample air directly to the detector. The built-in meter reflects the total organic vapor concentration in the environment being monitored. This mode is ideal to detect areas of high concentration as part of leak detection programs or to define locations requiring further study.

Mode 2—the chromatographic mode—incorporates a sample valve for injection of the air sample into a chromatographic column. In this way, the chemical components of an environmental air sample are physically separated and delivered to the detector in sequence, forming a chromatogram.

Regulatory Update  
September 1981

OSHA

Carcinogen Policy

Amended to meet benzene case, January. Other amendments proposed and withdrawn. Under review, with 2-3 year goal. Candidate list unlikely.

Cotton Dust case stops cost/benefit analysis for health, reaffirms need for rule.

Lead Standard

Some details of rate retention still unsettled.

Qualitative mask fitting proposed.

Partial stay until October 11.

Medical Records Access

Proposal to tighten labor access to data.

Labeling

Reproposal scheduled for September-October.

Women in Workplace

General acceptance of employer right to exclude.

Reopening of VC/PVC Standard

Not expected for 2-3 years.

EPA

Carcinogen Policy

Being rewritten as response policy. Timing uncertain.

Vinyl Chloride Standard

Administrative changes this fall?

General Fugitive Rule

Hearings last spring.

Water Quality Criteria

Revised version out-lowered limit.

RCRA Listing - improbable.

Superfund repairing limit due next year.

All RCRA, Pretreatment, etc. rules reviewed.

Fluorocarbon action likely delayed.

FDA

Still no final action on PVC packaging, BATF request no help.

Plasticizer action unlikely until more tests.

SPEECH HIGHLIGHTS

GARY BAISE - SEPTEMBER 24, 1981

EPA - VCM REGULATORY STATUS

- . The 1977 EPA standard contained a 0 goal; however, this is not practical and will probably be replaced with a 1.0 level.
- . O<sub>2</sub> chlorination vents - some companies use air instead of O<sub>2</sub> - but further study is required. Some companies will have no problem complying while others may.
- . Reactor opening requirements will remain the same, but waivers can be obtained on some of the testing required.
- . The stripping requirements for suspension and dispersion resins will remain at the present levels. This would appear to be "Best Available Technology".
- . Fugitive emissions - Phase II no change in regulation if your plant is following the present guidelines.
- . Relief valve discharge - will continue to enforce the "Best Available Technology" concept - may divide into preventable and non-preventable categories.
- . Land fills - no problem.
- . No off set regulations.
- . Administration - will accept the malfunction argument if level of contamination would cause no problems.
- . It will probably be 2-3 years before the VCM standard is revised - even longer if we want to keep bottled up in litigation.

/3359j-13