

TRAINING PROGRAM

HAZARDS OF VINYL CHLORIDE

I. HEALTH HAZARD

Published information in February 3, 1975 issue of Chemical Marketing Reporter with source information from NIOSH and HEW indicated that a total of thirty-eight suspected cases of angiosarcoma of the liver had been uncovered among PVC and vinyl chloride workers worldwide. The number of deaths was reported to be at least twenty-three.

There have been 17 cases of angiosarcoma of the liver in the United States; nine of these cases were reported from the B. F. Goodrich, Louisville plant which employs less than 300 people. This plant has been in operation more than 25 years and personnel exposure to vinyl chloride was comparatively high.

A "safe" exposure level is not determinant at the present time; however, it must be concluded that VCl is carcinogenic to man at some level. OSHA set the maximum exposure level at 1 ppm based on 8 hour time weighted average (TWA) with possible excursions to 5 ppm for a 15 minute period.

II. NATURE OF OPERATIONS WHICH COULD RESULT IN EXCESSIVE EXPOSURE

<u>Typical Operations</u>	<u>Procedures and Precautions</u>
1. Cleaning autoclaves.	Wear full face mask, use supplied air. Wear rubber gloves and goggles.
2. Replace cartridges in VCl filter.	Use Nash pump to evacuate the VCl in the filter body. Fill with water, heat to 190°-200°F and hold for 2 hours, drain, check filter body atmosphere for VCl concentration using Drager tubes. Repeat hot water treatment if concentration is greater than 100 ppm. Wear full face piece and supplied air, wear gloves and goggles while opening filter body and replacing tubes. Dispose of cartridges in a closed container lined with polyethylene bag. Tie off top of bag and transfer cartridges to dumpster.
3. a. Breaking into VCl lines, VCl pumps or preparing to remove or overhaul Nash vacuum pump.	Vent the line or pump into the monomer collection system to gasholder then purge line with steam. After the line is warm, stop the steam purge. Check the atmosphere in the line or pump for ppm VCl using Drager tubes (should be less than 200 ppm). Repeat steam purge if necessary. Use full face piece and supplied air while breaking the line or opening the pump.
3. b. Breaking into VCl compressor or condenser liquid level controller.	Vent the compressor or condenser and lines to gasholder, then purge with L.P. nitrogen for five minutes. Check the atmosphere in the line for ppm VCl (should be less than 200 ppm).

Typical Operations

4. Cleaning monomer tanks.

5. Cleaning trenches and
sump on ground floor.

6. Processing coarse or
broken batches.

Procedures and Precautions

Vent the tank to gasholder and purge the tank with steam until the tank is warm (approx. 140°F). Fill the tank with water and heat the water to 200°F with L.P. steam and vent to the gasholder for an 8 hour period while maintaining the water temperature at 200°F with steam purge. Blank inlet and outlet lines on tank except drain and a line for adding air to break vacuum.

Drain the water, check the atmosphere inside the tank with Drager tubes; if it is less than 200 ppm, open the tank and purge with air to cool it prior to entering for cleaning. If the VCl concentration is greater than 200 ppm, repeat hot water treatment. Wear full-face mask and use supplied air while opening the tank.

Wear rubber gloves and goggles if using half face mask in addition to respiratory protection while cleaning the tank.

Dispose of solid waste in a closed container lined with a polyethylene bag. Tie off the polyethylene bag and transfer it to the dumpster.

Wear proper respiratory equipment commensurate with VCl exposure as measured by portable Century analyzer. Also wear rubber gloves, boots and slicker suit pants.

Any waste PVC resin, skins, pebbles, etc. should be put in a closed container lined with a polyethylene bag. Tie off the polyethylene bag and transfer it to the dumpster.

A coarse batch should be steam stripped to reduce the free monomer below 25 ppm; future installation of a type of granulator as a Reitz delumper may permit conventional processing of coarse batches which entails steam stripping.

Wear proper respiratory protection commensurate with VCl exposure as measured by portable Century analyzer while observing the slurry transfer into the slurry tank or broken batch transfer to the ditch. Also, wear rubber gloves and goggles if wearing half face mask and work on windward side of the release.

Typical Operations

7. Vinyl chloride compressor repairs.
8. Monitor and clean spray dryer head tank screen or perform work in spray dryer penthouse during dryer operation.
9. Monitoring emulsion resin pebble screen operation or working on top of emulsion storage tanks.
10. Laboratory analysis of resin emulsion.

Procedures and Precautions

Close the block valve on the compressor suction line, then purge this line and compressor into the gasholder using L.P. nitrogen gas for 3 to 5 minutes. Then check the atmosphere in the compressor discharge line by means of the Century analyzer or Drager tubes. Proceed with compressor repairs if VCl concentration is less than 200 ppm. Wear respiratory protection commensurate with VCl exposure potential; also, wear rubber or cotton gloves while removing valves or other compressor parts.

The atmosphere in the penthouses for each spray dryer has measured up to 50 ppm VCl. Use respiratory protection to enter the penthouse and use supplied air and full face mask while working inside the penthouse.

If the spray dryer system and head tank are empty, check penthouse atmosphere for ppm VCl, wear respiratory protection commensurate with VCl exposure while in penthouse.

VCl exposure will vary because the residual free monomer in the emulsion is variable. Either wear full face piece mask with supplied air or wear respiratory protection on basis of VCl exposure analysis as determined by Century analyzer or Drager tubes.

The sample of emulsion will be delivered to the Laboratory sample hood in a closed container. The analytical tests will be performed in the contamination hood. After tests are complete, the emulsion will be returned to sample bottle and the sample bottle placed in designated location in sample hood for pickup by operators. The emulsion will be returned to storage tank.

III. PURPOSE, USE AND LIMITATION OF RESPIRATORY EQUIPMENT

A full face mask with connecting hose to a manifold will be issued to each operator as part of his personal safety equipment. A canister or a mask air supply hose or a high pressure air cylinder can be connected to the manifold. Also, self-contained breathing apparatus, pressure demand type with full face pieces, will be stored in cabinets strategically located throughout the area; for example, in the operation control rooms.

A half face mask will be issued to autoclave cleaners. This mask hasn't been approved for use with the canisters. However, the half face piece mask with continuous air flow from the mask air header will provide the proper protection while cleaning an autoclave; this system has been approved for 1000 ppm VCl.

Each employee will be instructed in the use and care of this equipment by the Safety Department. Opportunities will be provided to handle the respiratory equipment, have it fitted properly, test its face piece to face seal and wear it in normal air and finally in a test atmosphere.

The facepiece to face fit is checked by covering the end of the mask hose with the palm of your hand. Then inhale gently so that the facepiece collapses slightly, and hold the breath for ten seconds. If the facepiece remains in its slightly collapsed condition and no inward leakage of air is detected, the tightness of the respirator is probably satisfactory. The facepiece fit should be checked by the wearer each time he puts on the respirator.

At the end of each working day the facepiece should be washed with water and sponge to clean the inside of mask and hose. Shake off excess water and hang the mask in your locker to permit water drainage and drying.

The limitations of the respiratory equipment which you will use is indicated in the tabulation below. The canisters for VCl service are so identified by markings and are to be used for 4 hours service. Moreover, all canisters which have had the seal broken are to be discarded as used canisters at the end of each shift in accordance with correct disposal procedures. The seal should not be removed until the canister is needed for use.

TABLE I

SELECTION OF RESPIRATORS FOR VARIOUS CONCENTRATIONS OF VINYL CHLORIDE

<u>Atmospheric concentration of vinyl chloride</u>	<u>Required apparatus</u>
(i) Unknown, or above 3600 ppm ----	Open-circuit, self-contained breathing apparatus, pressure demand type, with full facepiece. (Scott Air Pak or M-S-A).
(ii) Not over 3600 ppm -----	Combination Type C supplied air respirator, continuous flow or pressure demand type, with full or half facepiece, <u>and</u> auxiliary self-contained air supply for escape purposes.
(iii) Not over 1000 ppm -----	Type C, supplied air respirator, continuous flow type, with full or half facepiece. Air supply can be from either plant air mask system (while on job site) or from compressed air cylinder while traveling to job site.
(iv) Not over 25 ppm -----	Gas mask, front- or back-mounted canister which provides a service life of at least 4 hours for concentrations of vinyl chloride up to 25 ppm.

IV. FIRE HAZARD - ACUTE TOXICITY OF VCl AND PROTECTIVE STEPS

Vinyl chloride is a gas at atmospheric pressure and ambient temperatures. Breathing relatively high concentrations of VCl gas in air (several thousand ppm of VCl) can result in either nausea or dizziness. Also, very high concentrations of VCl in air (several percent of VCl) can be lethal.

The explosivity range is 3.6 to 22 percent VCl in air; all mixtures of VCl and air within this range will explode violently if ignited. Extensive precautions have been taken to build and operate this plant so as to avoid sources of ignition in the polymerization area. Some common sources of ignition which are to be avoided are open flames, hot spots, non-explosion proof electrical motors or switch gear, gasoline motors and static electricity.

If a VCl emission or a VCl fire should occur, the following action should be taken: (1) trip manual deluge valve if valve hasn't been tripped in order to sound an alarm and reduce the hazards, (2) rescue the injured, wear SCBA respiratory equipment, (3) look for the nearest block valve on the line supplying the release or fire and close it if possible; wear SCBA respiratory equipment.

In case of an emission, shut down ignition sources such as internal combustion engines by stopping motor vehicle and train traffic in the area.

Fires involving large spills of VCl are difficult to extinguish. Therefore, fire crews are being trained on each shift as to the most effective means for fighting VCl fires. Fire fighting should be the crew's function as soon as they arrive. VCl and water are immiscible and VCl will float on the water; therefore, fog nozzles or finely divided sprays are more effective than a heavy stream of water. The water fog or spray cools the burning area and helps protect adjoining equipment. The fire should not be extinguished prior to blocking the source of VCl fuel to the fire as reignition of a vapor cloud could be dangerous because it can cause a massive explosion. Large quantities of hydrogen chloride and carbon monoxide are produced in a VCl fire. All personnel who are in the fire area should wear SCBA respiratory equipment.

V. MONITORING

A personnel monitoring program will be conducted to determine job exposures on a monthly frequency. Also, continuous area monitoring will be obtained by use of two Miran II infrared analyzers.

(1) The Industrial Hygiene Section will initiate a program for determining the exposure for each employee on a monthly frequency without regard to the use of respirators. The monitoring frequency will be reduced to every 3 months when an employee's exposure is less than 1 ppm of VCl and may be discontinued if two consecutive monitoring determinations, not less than 5 days apart, show less than 0.5 ppm average exposure over 8 hour period.

(2) Each of the two Miran II analyzers will sample 11 locations within the respective units every 12 minutes. If a sample analysis is greater than 25 ppm, an alarm will sound and the scan board will indicate a high VCl emission. The Miran II recorder will indicate the area of excursion. A flashing red light will be installed in the vicinity of the excursion and will warn personnel in the area to wear their masks using supplied air while working in the area.

During the interim period before the flashing red light is installed, operators in the area will be warned verbally that the VCl exposure is above 25 ppm and that a supplied air respirator must be worn. (See Table I, III). The area foreman or a designate will give the warning and will try to determine the source of emission with the aid of the portable Century analyzer. Corrective measures will be initiated to reduce or eliminate the emission and report the excursion and corrective action taken on a standard log sheet. This information will serve as a basis for further engineering practices to reduce emissions.

VI. MEDICAL SURVEILLANCE

The Medical Department will conduct a medical surveillance program for detecting liver damage for each authorized employee who has been exposed to VCl in excess of the action level without regard to the use of respirators. Also, the Medical Department will establish a program for medical surveillance of certain other persons who have been exposed to VCl above the action level of 0.5 ppm.

All of the PVC operating and maintenance personnel received their initial examination in March 1974. These tests were specific for detecting liver damage. Ethyl's Medical Department will repeat these tests periodically on an appointment schedule. You will receive special instructions concerning diet 16 hours prior to examination. The examining physician will submit a statement as to the employee's suitability for continued exposure to VCl promptly after examination. If an employee's health would be materially impaired by continued exposure, such employee shall be withdrawn from possible contact with vinyl chloride.

Each employee exposed to an emergency shall be afforded appropriate medical surveillance.

VII. EMERGENCY PROCEDURES

An unexpected and uncontrolled massive release of vinyl chloride in a restricted area is an emergency. Some possible typical emergencies follow:

- (1) Autoclave charge discharged to the ditch by operating error.
- (2) VCl transfer line failure allowing liquid and large quantities of gas to be released.
- (3) Large VCl release from the top of autoclave as result of gasket failure.
- (4) Pump seal failure allowing massive release of vinyl monomer liquid or gas.
- (5) Vinyl chloride release from gasholder water seal because the bell is overpressured while being held by the stops at high level.

VII. EMERGENCY PROCEDURES (cont'd)

The magnitude of the emergency or VCl release as judged by the person discovering the situation will determine what immediate action is to be taken. However, in the event of immediate potential danger, the following action should be taken:

- (1) Actuate manual trip for the deluge system.
- (2) Rescue injured personnel; wear SCBA respiratory equipment.
- (3) Locate nearest block valve which will stop the release; close the valve if you can without endangering your life. DO NOT enter a vapor cloud or heavy concentration of vinyl chloride unless you have proper respiratory protection equipment. You should also have a standby person in the event you have difficulty.
- (4) The General Foreman or the Area Foreman will be responsible for emergency action as soon as he arrives on the scene.
 - a. All personnel in the restricted area will be notified by five (5) short blasts on the area whistle; repeat the warning signal.
 - b. Evacuate personnel not required for emergency work to Warehouse desk area.
 - c. Fire fighting should be handled by fire chief and his crew.
 - d. General Foreman will direct a complete polymerization unit shutdown and request shortstopping batches when the situation warrants. Also, if situation warrants he will order a shutdown of the drying area and compound unit.
 - e. The Compound Foreman will be in charge of all personnel evacuated to Warehouse; also, he will be in charge of locating personnel on the "sign in" roster.

All personnel who wish to leave the area must obtain permission from the Compound Foreman.
 - f. The General Foreman will determine when the emergency has been cleared. An "all clear" will be sounded on area whistle - ten (10) short blasts - repeat once.

Each operator should review the detailed emergency procedure (separate issue) and be familiar with his assigned emergency duties.

VIII. RECOGNIZING CONDITIONS WHICH MAY RESULT IN A VCl RELEASE

1. Operating conditions - temperature, pressure, flow.

- a. The operator should be familiar with normal operating conditions as a result of his training, his routine data log and equipment monitoring. Any abnormal condition should be reported to the unit foreman. The cause for an abnormal temperature or pressure should be determined immediately and corrective action initiated.
- b. Report any VCl leaks from valve packing, flange leaks, or leaks through valves to unit foreman. Corrective measures should be initiated immediately.
- c. Operator should check flange bolts and autoclave manhead closure mechanism routinely before charging an autoclave. Tighten loose flange bolts and report any mechanical defects to unit foreman for correction.

2. Mechanical Equipment

During operators' daily routine inspection of their mechanical equipment, attention should be focused on VCl pump seals for evidence of leakage. A slight VCl gas leak through the seal will cause the purge water discharge from the backup seal to sputter because of entrained VCl gas. Report this or other defective mechanical conditions to unit foreman.

Unusual gear or bearing noises should be reported to the unit foreman. Foreman will request a maintenance check and initiate corrective measures if necessary.

Excessive corrosion of piping or parts of mechanical equipment should be reported to foreman and a request made for an inspection by proper personnel.

IX. SIGNS AND LABELS

1. Entrances to regulated areas shall be posted with legible signs bearing the legend:

CANCER-SUSPECT AGENT AREA
AUTHORIZED PERSONNEL ONLY

2. Containers of polyvinyl chloride resin waste from reactors' tailings or other waste contaminated with VCl such as vinyl chloride filter cartridges shall be legibly labeled:

CONTAMINATED WITH VINYL CHLORIDE
CANCER-SUSPECT AGENT

3. Containers of polyvinyl chloride such as bags or boxes of PVC resin or compound shall be legibly labeled:

POLYVINYL CHLORIDE
CONTAINS
VINYL CHLORIDE
VINYL CHLORIDE IS A CANCER-SUSPECT AGENT

VC5286

X. REPORTS

1. Emergencies, and the facts obtainable at that time, shall be reported within 24 hours to the OSHA Area Director. The Area Director may request additional information, nature and extent of employee exposures and measures taken to prevent future emergencies of similar nature.
2. Within 10 working days following any monitoring or measuring which discloses that an employee has been exposed without regard to the use of respirators in excess of 1 ppm VCl, each such employee shall be notified in writing of the results of the exposure measurement and the steps being taken to reduce the exposure to within the permissible exposure limit.

XI. RECORDS

Records will be maintained of required personnel monitoring which include the date of monitoring, concentrations determined plus type of instrument and methods used. These records shall be maintained for 30 years or duration of employment plus 20 years, whichever is longer.

XII. REVIEW OF STANDARD

- a. As a result of hearings conducted in early 1974, OSHA issued a VCl Standard on October 4, 1974, major policy judgments follow:
 1. VCl is carcinogenic to man.
 2. "Safe" exposures cannot be determined with present information.
 3. Cannot wait to establish accurate "safe" limit.
 4. Employee exposure must be reduced to 1 ppm TWA over 8 hour day. Permissible excursions up to 5 ppm for 15 minutes.
 5. Industry will, in time, be able to attain this level of emission through engineering control. Technology is not now available.
 6. All employees can be protected from exposures above the permissible limit by respiratory protection.
- b. Ethyl will provide employees with required respiratory protection equipment.

Wearing of the respirators shall be at the discretion of each employee for exposures not in excess of 25 ppm until December 31, 1975.

Each employee who chooses not to wear an appropriate respirator shall be informed quarterly of the hazards of VCl and the purpose, proper use and limitations of respiratory devices.

After December 31, 1975, wearing of respiratory equipment will be mandatory in any area where VCl exposures are above 1 ppm.