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CONTROL TECHNOLOGY ASSESSMENT
OF
CHEMICAL PROCESSES

Preliminary Survey Report for
the Site Visit of
December 7, 1981

DuPont Company
Fabrics and Finishes Division
Chicago, Illinois

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Submitted to:

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BACKGROUND INFORMATION ON CONTRACT

This visit was conducted as part of the Control Technology Assessment of Chemical Processes, NIOSH Contract No. 210-80-0071. The purpose of this contract is to identify and assess superior control techniques for limiting worker exposure to hazardous substances during chemical processing. This is being done through extensive visits to industrial facilities. Preliminary surveys are intended to generate information about the control strategies used at various facilities and will be used to determine which facilities warrant further in-depth surveys. Information collected from the visits will be compiled into a control technology reference source to aid in the solution of worker exposure problems in industry. It should be noted that control techniques cannot be extrapolated to other situations without careful evaluation of all factors involved.

II. PLANT AND PROCESS DESCRIPTION

This facility was established in 1865. It was acquired by DuPont in 1920. It is a small plant with approximately 47 employees working 7 days/week. The plant consists of several multi-story buildings which house the major processes. Storage, loading, and unloading facilities are located outdoors.

This plant mainly produces alkyd resins which are sent to other compounding facilities to be made into paints. This survey was concerned only with the process used to make acrylic emulsion coating for copper wires. Acrylonitrile is used in the formulation of this coating. The following paragraphs briefly summarize the process and identify emission points and associated control techniques used. Figure 1 depicts the process.

Raw materials for the process, including acrylonitrile, are delivered to the plant and unloaded from tank trucks or rail cars to storage tanks. To prevent release of acrylonitrile vapors during unloading, a special vapor recovery system is used. This system is described in Chapter III.

The various raw materials are tranfered from storage to a weigh tank. This tank is never opened and does not normally present a source of exposure. When appropriate amounts of each of the materials have been added to the weigh tank, a monomer feed pump transfers them to a reactor vessel. The monomer feed pump was a problem exposure area in this process in the past. A positive displacement Viking Model #4724 pump with a teflon mechanical seal has reduced this problem. Local exhaust ventilation has also been installed in the area.

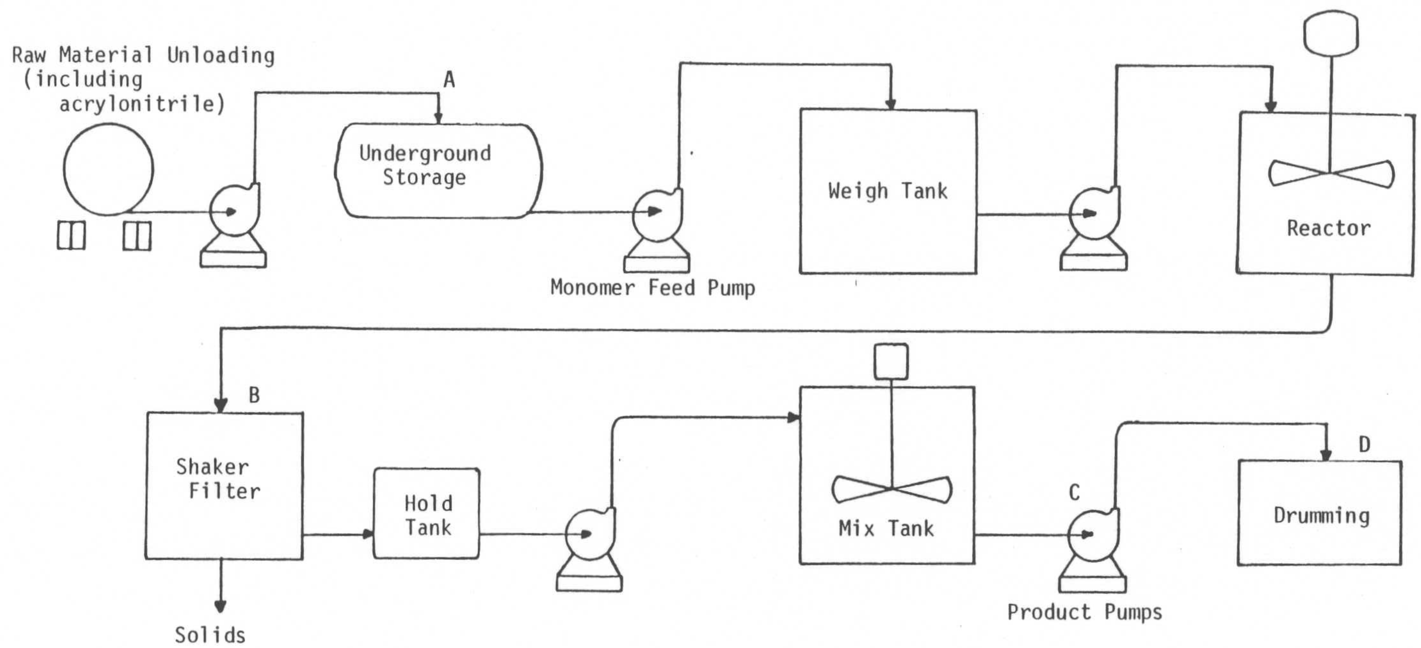
In the reactor the raw materials are heated at atmospheric pressure to polymerize them to an acrylic emulsion with water. The raw materials are fed to the reactor stepwise to allow the mixture to stabilize. In the past all reactants were dumped into the reactor at once, sometimes resulting in the batch solidifying in the reactor. When this happened, the vessel had to be opened and workers would chip out the solid with resultant exposure to residual acrylonitrile. Stepwise addition of reactants prevents the batch from solidifying and thereby eliminates potential worker exposure.

Potential Emission/Exposure Points

A. Raw material unloading
B. Emulsion filtration
C. Product pumps
D. Drumming facilities

Control Techniques

A. Vapor recovery system
B. Enclosed filter and hold tank
C. Peristaltic product pumps
D. Local exhaust ventilation



Potentially Hazardous Chemicals Involved

Agent	PEL	Chemical and Physical Properties		Health Hazard: Route of Entry	Health Hazard: Effect
Acrylonitrile	2 ppm	M.P.	$-117^{\circ}F$	Inhalation	Irritant
		B.P.	$171^{\circ}F$	Absorption	Narcotic
		V.P.	83 mm	Ingestion	
		solubility	7.1%	Contact	

Figure 1. Acrylic Emulsion Process

During the reaction cycle the mixture is agitated. To minimize leakage around the agitator shaft, a Glascote, teflon-impregnated, white asbestos packing gland with lantern ring is used. Local exhaust ventilation at the reactor remove any vapors escaping the seal. At the end of the reaction cycle, a chemical scavenger is added to the reactor to reduce the amount of residual acrylonitrile left in the mixture. Produce specifications are for a maximum residual acrylonitrile concentration of 1 percent, but the product can be scavenged to a concentration of 0.1 percent acrylonitrile. The batch is then dumped from the reactor to the next stage of the process. After each batch is dumped, the reactor interior is cleaned with an aqueous caustic solution. In the past, workers used to enter the vessel and clean it manually, causing exposure to residual acrylonitrile monomer With caustic cleaning the vessel remains sealed and workers are not exposed.

The company made an effort to try and replace acrylonitrile as one of the raw materials for this product some years ago. When they were unable to make a product with the desired properties this effort was abandoned.

The water emulsion is then pumped through an enclosed filter to remove coagulants formed during the reaction. To prevent worker exposure to acrylonitrile, a special filter and hold tank assembly is used (Chapter III). The filtered emulsion is then pumped to a mixing tank where further ingredients are added to give the product the required properties. The enclosed mixing tank is not normally a source of exposure. From the mixing tank, the finished emulsion is pumped to the drum filling area and packaged in 55-gallon drums. The original product pumps were a source of operational and worker exposure problems. The solution to this problem is discussed in Chapter III. To further minimize worker exposure at this point, added engineering controls were installed (see Chapter III).

III. CONTROL TECHNIQUES

VAPOR RECOVERY AT UNLOADING FACILITIES

Acrylonitrile raw material is stored in underground vessels after delivery to the site in tank trucks. When a load comes in, the truck is hooked up to a vapor recovery system to prevent any escape of vapors into the workplace (Figure 2).

A line from the bottom of the tank truck is hooked to the suction side of an unloading pump. The pump discharges into the underground storage tank. A line from the vapor space of the storage tank is connected back to the top of the tank truck, making a closed system of the tank truck and storage tank. As liquid acrylonitrile is pumped into the storage tank, vapor is displaced back into the tank truck. No vapor enter the workplace during unloading except when lines are disconnected.

REACTION PRODUCT FILTRATION

During the reaction cycle, solids form in the water emulsion. To remove these solids the, emulsion is pumped through a SWECO shaker filter. The filter is operated batchwise, with a cycle time of 60 minutes. The totally enclosed filter operates at ambient pressure and temperature. Liquid effluent from the filter is piped to a 55-gallon drum hold tank. The drum is now closed on top with a float apparatus indicating the liquid level in the drum. When the drum fills, the operator turns on a pump to empty the drum into another mix tank for the next phase of the process. In the past, the hold tank drum was open and the operator looked to see when he had to pump it empty. Concentrations of acrylonitrile in air around the filtering operation have been reduced substantially since the installation of this engineering control as shown by the data in Table 1.

After a batch is filtered, solids are discharged from the filter into another drum. During the entire filtering operation, operators wear a Type C pressure demand airline respirator to further limit their exposure to acrylonitrile.

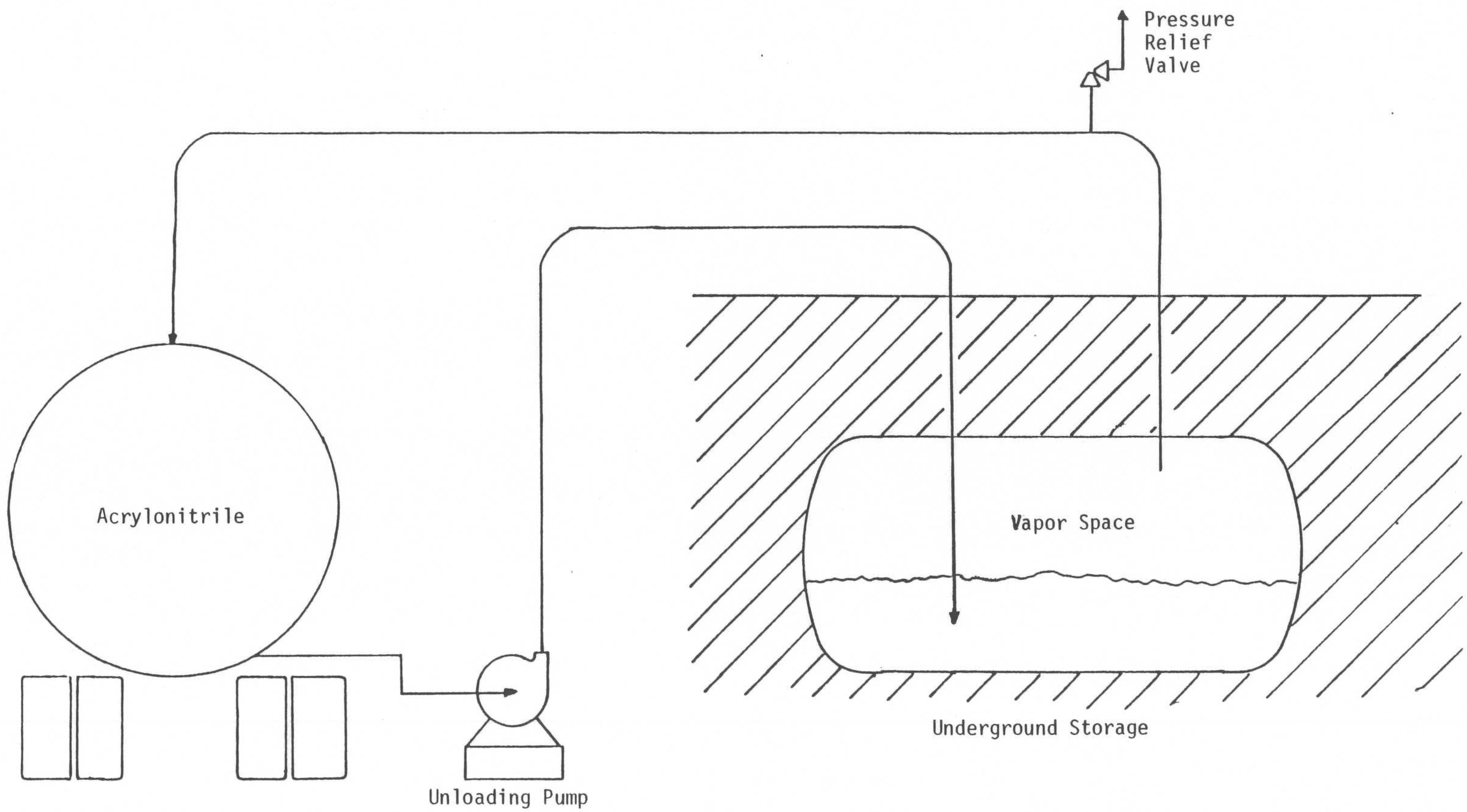


Figure 2. Vapor Recovery at Raw Material Unloading

TABLE 1

EMULSION FILTRATION DATA
AIRBORNE ACRYLONITRILE LEVELS (ppm)
(READ ACROSS)

BEFORE ENGINEERING CONTROLS

130	4	4.2	2	19.5	61
82	65	19	33	22	48
6	15	28	1	115	17
22	59	5	19		

38.3
20.2

AFTER ENGINEERING CONTROLS

3	4	5	1	1	3
24*	5	21*	4	1	11
1	2	2.4	2.4	12	3.5
15*	6.5	2	4	3	7
4	1	4	2	0.7	1
4	3	10	6	2	8
1	0.8	0.3	6.9	1.4	5.4
6.7					

4.9
3.8

*Engineering controls not properly used.

Note: This data has a lognormal distribution.
DuPont Data

PRODUCT PUMPS

In the past, the plant used centrifugal pumps to transfer the product acrylic emulsion from the mixing tank to the drumming facilities. These pumps had a history of problems caused by the nature of the liquid product. The liquid became very viscous when heated or subject to shear stress and the pumps would seize up. Maintenance personnel would have to open the pumps to get them back in operation and this presented an increased potential for exposure to residual acrylonitrile in the product. To eliminate this problem, the company installed new Waukesha, Bredel peristaltic pumps, Model Numbers SP/40 and SP/50. The pumps operate at ambient temperature and approximately 20 psig discharge pressure. The liquid product only comes in contact with the inside surfaces of the natural rubber hose component of the peristaltic pump. In this pump, the liquid is not subject to the temperature and shear stresses that a centrifugal pump imposes; hence, does not become viscous and cause the pump to seize. Maintenance on the peristaltic pumps in much less than was required for the original centrifugal pumps.

DRUMMING FACILITIES

Liquid acrylic emulsion product is shipped from the plant in 55-gallon drums. The drumming area has local exhaust ventilation to minimize worker exposure to acrylonitrile. Workers, performing the drumming, wear Type C pressure demand airline respirators to further protect themselves from inhalation exposure. In the past, local exhaust ventilation was not used in the drumming area. Since the installation of this engineering control, airborne concentrations of acrylonitrile in the drumming area have been reduced markedly (Table 3).

PERSONAL PROTECTIVE EQUIPMENT

In addition to the airline respirators required when performing certain tasks, workers wear neoprene or butyl rubber gloves during some operations to prevent dermal exposure to acrylonitrile. As shown by the data below (Table 2), butyl rubber has a lower permeation rate but neoprene is thought to have a longer breakthrough time.

Table 2. Permeation rates for acrylonitrile in contact with butyl rubber and neoprene materials used for gloves.

	Neoprene	Butyl Rubber
Thickness	30 mils	15 mils
Breakthrough Time	>15 minutes	>15 minutes
Permeation Rate	5 $\mu g/min/cm^2$	0.01 $\mu g/min/cm^2$

Note that this is laboratory data and does not necessarily match plant operation usage. Most acrylonitrile exposure at this plant is from final product in which the acrylonitrile concentration is 1% or less.

TABLE 3

EMULSION DRUM FILLING DATA
AIRBORNE ACRYLONITRILE LEVELS (ppm)
(READ ACROSS)

BEFORE ENGINEERING CONTROLS

3	1	2	1.5	7	5.5
1.5	2	2	5	3	0.1
1.5	2.5	3	2.6	2	0.6*
0.2*	3	1	1	1.5	0.8*
2.4					

2.2

AFTER ENGINEERING CONTROLS

0.1	0.4	0.9	0.5	0.9	1.2
2.2	0.6	1.1	0.5	1.1	0.4
0.6	0.6	0.2	0.3	0.8	0.4
0.3	0.8	0.3	0.1	0.1	0.3
0.3	2	0.3	0.1	0.4*	0.7
2.2	0.3	1.1	2.2	2.2	0.5
1.1	0.2	0.1	0.1		

0.71

* None detected. This is the limit of detection.

Note: This data has a lognormal distribution.
DuPont Data.

WORK PRACTICES

The company has a very effective work practices program to help prevent exposure to acrylonitrile and other hazards. The considerations that make the program effective are:

- o Training of operators and maintenance personnel -- operators are trained for each operation and task they will encounter during plant operation. It is the Foreman's responsibility to make certain the person being trained fully understands the job procedures, modes of release of chemical substances and potential hazards involved, and control techniques to be used.

- o Documented training material for each job classification.

- o Plant safety standards that address:

  - health hazards of chemicals
  - mode of emission of chemicals
  - control technique to be used

- o Management follow-up and monitoring to ensure consistent application of work practices by the various plant operators. Monitoring for organic vapors is done using a DuPont personal dosimeter, model Protec GAA.

An example of a plant safety training guide is shown in Figure 3.

#902

JOB SAFETY TRAINING GUIDE

PLANT: CHICAGO
DEPT.: F&F
AREA : POLYMER

DATE: 3/22/76
SUPERSEDING DATE: 4/12/73
BY: D. W. Kuhns

SUBJECT: OPERATION OF "LECTON" REACTORS

I. INTRODUCTION

The purpose of this Guide is to outline the steps to safely operate the "Lecton" reactors. (Also see Standard Practice #909).

II. DETAIL

A. DO

1. Wear protective safety equipment as specified when handling emulsion raw materials.
2. Use the proper procedure for handling toxic monomers and ammonium hydroxide, and know what to do in case of accidental exposure. (Refer to JST 905)
3. Insure that the condenser and reactor vents are operable before each batch, and regulations involving the present system are understood. Rupture disk should be inspected quarterly.
4. Check the condenser every Monday by feeding water from the top and record on weekly start up log (OV-11)
5. Use circulating water on the condenser during manufacture of the batch. Switch to City water only if the tower is down for repair and use only until normal tower cooling can be resumed.
6. Manufacture batches according to batch card instructions and refer any process problems to the Foreman or Supervisor immediately.
7. Use caution when working on damp floors.
8. Be sure ventilating system is running.

B. DON'T

1. Enter any vessel without complete vessel entry permit procedure and approvals, (Std. Prac. # 211).
2. Handle any materials in the area without knowing "S" classification.
3. Leave the area unattended while a batch is in process in the reactors.
4. Process any batches if ventilation, refrigeration or vent system is substandard.

Reason for Revision: To revise items 2, 3, 4, and eliminate 6 under DO. Revise item 3 under DON'T.

Approvals: Author: DW Kuhns Safety Suprv.: J. P. Kau...

Prod. Supt.: ... Plant Mgr.: ...

Figure 3. Example of Job Safety Training Guide