WALK THROUGH INDUSTRIAL HYGIENE SURVEY

DOW CHEMICAL, USA
Michigan Division
Midland, Michigan 48640

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Industrial Hygiene Section
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PURPOSE:	To conduct a walk-through survey of the acrylamide and polyacrylamide production facilities of the Dow Chemical Company, Michigan Division, as part of an industrywide assessment of extent and degree of worker exposure to these substances, and to gather information needed to be used in a feasibility assessment for epidemiologic research.
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STANDARD INDUSTRIAL CLASSIFICATION OF PLANT:	2869 - Industrial Organic Chemicals, not classified elsewhere 2899 - Chemicals and Chemical Preparations, not elsewhere classified

ABSTRACT

On May 17-18, 1984, a site visit to Dow Chemical Company, Michigan Division, Midland, Michigan was conducted to gather information regarding the production of acrylamide and polyacrylamide, to estimate the number of potentially exposed workers to these compounds, and to determine the necessity of conducting an indepth industrial hygiene study at this site. Dow has produced aqueous acrylamide monomer in a facility designated Separan I and dry and aqueous polymer in a facility designated Separan II since the mid-1950s. An aqueous-oil polymer emulsion has been produced since the early 1980s in a facility designated Separan III. Dow has never produced a dry monomer. The industrial hygiene program in these production areas also has existed since the mid-1950s. The method currently used by Dow to sample for acrylamide is a solid sorbent tube connected to a small, battery operated pump. The current NIOSH method employs a solid sorbent tube preceeded by a 37 mm cellulose filter. The current analysis method of High Performance Liquid Chromatography and Ultra Violet detection is used by both parties.

Based on the information gathered during this site visit it was decided that Dow Chemical Company should be included in the study and an indepth industrial hygiene study would be necessary (see Conclusion and Recommendation Section). This survey will be conducted at a later date.

Industrial hygiene sampling was not conducted during this walk-through survey.

INTRODUCTION

The National Institute for Occupational Safety and Health (NIOSH), Division of Surveillance, Hazard Evaluations and Field Studies (DSHEFS), Industrywide Studies Branch (IWSB), Industrial Hygiene Section (IHS) conducted a walk-through survey of Dow Chemical Company, Michigan Division, Midland, Michigan on May 17-18, 1984, to gather information relating to the production of acrylamide and polyacrylamide, estimate the number of workers potentially exposed, and to determine the necessity of conducting an indepth industrial hygiene study. In addition, information will be gathered in order to assess the feasibility and need for further epidemiologic studies. Dow Chemical produces acrylamide at its Separan I facility. Various forms of polyacrylamide are produced in facilities designated Separan II and III. This survey was conducted in accordance with Code of Federal Regulations, Title 42, Part 85a and Public Law 91-596, Section 22.

Since commercial production of acrylamide, a known neurotoxin, began in 1952, there have been at least 48 industrywide reported cases of acrylamide poisoning. All of these cases have involved exposure to acrylamide monomer from either acrylamide and polyacrylamide manufacture or acrylamide monomer grouting (1-9). Acrylamide exposure can occur by ingestion, inhalation of vapors or aerosols, or by dermal absorption. Dermal absorption is a major route of exposure because acrylamide is very soluble in water and can easily penetrate the skin. The initial symptoms presented following dermal exposure are numbness, tingling, and coldness in the hands and feet followed by excessive sweating and erythema. Muscular weakness, peripheral neuropathy, absent deep tendon reflexes, severe atoxia, weight loss, fatigue, sleepiness, and lethargy may also occur (10,11).

There is a lack of adequate exposure data in the reported cases of human acrylamide intoxication, therefore, it is not possible to relate toxic effects of the chemical to a known dose. In addition, there are no epidemiological studies that might serve as the basis for determining such a relationship. Acrylamide toxicity testing on animals for neurotoxic effects has been used to establish current occupational exposure limits. The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) for airborne acrylamide is 0.3 mg/m^3 (0.1 ppm) as an eight-hour time-weighted average (TWA). This corresponds to an approximate dose of 0.05 mg/kg/day of acrylamide in a 70 kg worker who is breathing 10 m^3 of air in eight hours.

A minimal amount of information is available to State and Federal regulatory agencies, regarding the concentrations of acrylamide to which workers are exposed. In 1976, limited air sampling data was obtained from one acrylamide manufacturing plant. The data, reported as eight-hour TWA, showed personal breathing zone concentrations of airborne acrylamide ranging from 0.1 to 3.6 mg/m^3(10).

Until recently there have been no completed studies evaluating the carcinogenicity of acrylamide. In 1983, the Environmental Protection Agency (EPA) received a Toxic Substance Control Act section 8(e) notice of a two-year feeding study which indicated that acrylamide was a positive animal carcinogen. This study was conducted jointly by several acrylamide manufactures, including Dow Chemical. The histopathology data indicated that neoplasms in female rats were increased at the 2.0 mg/kg/day dose level for the following sites: central nervous system (brain and spinal cord), mamary gland, clitoral gland, uterous, oral cavity, pituitary gland, and thyroid gland. These results were statistically significant when compared to control animals. Since the OSHA PEL for acrylamide is based solely on its neurotoxic effects, there was concern that this level may not provide an adequate margin of safety for a carcinogenic risk (12). This walk through was conducted therefore, as part of a larger study of all acrylamide manufacturers, to gather information regarding extent and degree of worker exposure to acrylamide and polyacrylamide as an effort to adequately assess this risk. In addition, the information gathered will be used to assess the feasibility and need for conducting epidemiologic research.

DESCRIPTION OF FACILITY

The Dow Chemical Company, Michigan Division was founded in 1897, in Midland, Michigan. The entire site covers approximately 4,500 acres and employs about 4,500 persons. There are 80 production plants, three of which are involved in the production of acrylamide monomer or polymer. These three production facilities are designated Separan I, II and III. Dow had an estimated annual production capacity of 50 million pounds of acrylamide in 1981, and 100 million pounds in 1984.[13,14]

Separan I produces acrylamide monomer in an aqueous solution. The monomer is transported to Separan II or III where it is used to produce various forms of polymer. The monomer has been produced by Dow at this facility since the mid-1950s. Dry monomer has never been commercially produced by Dow.

Acrylamide polymer in a dry and aqueous form, has been produced in Separan II since the mid-1950s. There were two Separan II facilities prior to the early 1980s, during which time one of the facilities was closed and demolished. Separan II is located some distance from Separan I and III. The polymer is used in water clarification, waste water treatment, enhanced oil and mineral separation and mineral enrichment. It is marketed under the following trade names: Pusher, Separan and Purifloc.

Acrylamide monomer is converted to a polymer in a water and oil emulsion, in Separan III. This facility, which is adjacent to Separan I, has been on line since 1981. This emulsion is used in various applications such as waste water treatment, mining, and enhanced oil recovery. It is marketed under the following trade names: Pusher and Separan.

Each Separan facility has a lunch area which is separated from the production area. The workers are provided with work uniforms which are changed daily. Each worker is provided a separate locker for street clothes and protective equipment. In addition, there are designated smoking and non-smoking areas; adherence to an area designation is enforced.

DESCRIPTION OF WORKFORCE

The current workforce involved in the production of acrylamide or polyacrylamide is about 55 persons, with an additional 35 persons involved in peripheral jobs such as shipping. The production employees may have a direct exposure, while those employees involved in peripheral jobs may have only have a potential for exposure.

The majority of the workforce is male. The number of workers per shift is generally the same, however, there maybe slightly more workers on the day shift. A list of job titles and an explanation of duties maybe found in Table I. All three facilities operate three production shifts year-round beginning about 8:00 a.m., 4:00 p.m. and 12:00 a.m. The entire facility was unionized in 1942 by the United Mine Workers. In 1972, the United Steel Workers, Local 12075, became the collective bargaining representative. There is no scheduled rotation of Separan workers between Separan facilities and between other production areas within the Division, because each Separan facility has an individual senority roster.

House cleaning associated with a particular job and job task is the responsibility of the individual production worker. Each facility has maintenance personnel assigned on a full-time basis to handle all general clean-up and repair. Craftsmen are assigned to a facility on an as-needed basis.

Personnel records are located at Midland, Michigan, and are maintained on all terminated employees for 75 years. The records of current and terminated employees contain name, social security number, date of birth, last known address, starting and termination dates, and job history. The above information must be obtained from several different forms, however, which are contained within an individual employee's record.

DESCRIPTION OF PROCESS

The Michigan Division of the Dow Chemical Company produces aqueous acrylamide monomer in a facility designated Separan I. Dry acrylamide monomer has never been produced for commercial use. The monomer is then transfered to facilities designated Separan II or Separan III. In Separan II, the monomer is polymerized and dried. The monomer may also be polymerized in a batch processes to form aqueous liquid polymer. In Separan III, the monomer is also polymerized, but a water-oil emulsion is formed. This process description will be divided into three sections reflecting these three production areas. Each production facility has an elaborate in-line sample collection system for acrylamide. The systems include remote and scrubber vented sample boxes, vacuum bottle collection and hand-held pumps with remote collection hoses. With the exception of the

hand-held pump, each sampling site is under negative pressure and is completely enclosed. Once a sample collection bottle is placed inside the site, it is filled automatically.

Separan I (see Figure I)
Acrylonitrile (ACN), one of the raw materials used in the production of acrylamide, is received in rail road tank cars and is then transferred via a pipe to storage tanks. The ACN is pumped from the storage tanks into a reaction tank which contains a metal catalyst. Water is added to the reaction tank where the reaction occurs. Polymerization of acrylamide is prevented in the storage tank by bubbling air through it. The reaction tanks are located in an area which is open at the top and bottom to allow for appropriate air movement around the tanks. As the reaction is completed, the contents of the tank are passed through various vessels where the liquid is concentrated and any unreacted ACN is removed. As the entire process is a closed-loop system, any unreacted ACN is recycled back to the reaction tank. The acrylamide monomer is sent to temperature controlled storage tanks, or is sent via truck or rail car to Separan II, or via pipe line to Separan III. Raw material (ACN) receiving and finished product (monomer) shipping areas utilize the same truck area. Occasionally, a small amount may be drummed and sent to a customer as a sample.

This facility has an extensive continuous gas chromatographic area monitoring system for the detection of ACN leaks. There are numerous sampling points located throughout the process area, especially near potential leak sources. In addition, there are several points along the building drainage system in the production area.

Separan II (see Figure II)
Separan II is physically located some distance from Separan I, therefore the acrylamide monomer solution must be transported to the storage area for this site via trucks or rail cars. The majority of monomer is sent by truck. Once the monomer leaves the Separan II storage area, it is passed through a filter to remove any polymer that may have formed. The filtered solution is sent to the reaction vessel where the monomer is polymerized. The monomer content of the polymer will vary widely depending on the final product, however, the monomer content is always less than 1000 ppm. From the reaction vessel, the polymer is sent to a holding tank. The polymer is then bulk loaded as an aqueous solution in rail cars, or it is sent through a continuous dryer, a grinder, and a series of screens. The polymer emerges from the screens as a granule. The dry, ground polymer may either be sent to silo storage or shipping. The polymer granular may be shipped by bulk rail car or packaged in 50 pound bags. The bags, which are filled by an automated bagging system, are palletized, wrapped in heat-shrunk plastic, and may be sent to the warehouse for storage before shipping.

Separan III (see Figure III)
The acrylamide monomer solution travels from Separan I to the Separan III storage area via an overhead pipe line. From the storage area, the monomer is sampled for quality control specifications and is passed through a filter to remove any polymer before it is sent to the mixing vessel. In this vessel, various process parameters are controlled before the solution is sent to the reaction vessel. In the reaction vessel, a heavy weight oil is

added and the monomer is polymerized. The resulting emulsion is sent through a filter where any solids are removed and incinerated. The filtered liquid is sent to a temperature controlled storage area. The final product is shipped in bulk trucks or rail cars. Occasionally, a small quantity may be drummed and sent to a customer as a sample.

DESCRIPTION OF ENGINEERING CONTROLS

There have been several engineering controls added to all three facilities over the last several years which would minimize worker exposure to acrylamide. The controls which would have the greatest impact on employee exposure are:

1. An elaborate in-line sample collection system for acrylamide is used to collect quality control samples. Each sampling site is completely enclosed and is under negative pressure, thus reducing potential exposure to acrylamide monomer. These sampling sites are vented remotely to a scrubber.

2. The entire production and storage areas have been diked to contain any spills.

3. General ventilation has been increased in all areas.

Modifications relating to a specific facility are:

Separan I
There is an extensive leak detection monitoring system for ACN in the general area and drainage system. Since ACN historically has been considered to be much more toxic than acrylamide, control of exposure to ACN has also limited exposure to acrylamide.

Separan II
1. There is an automatic bagging system which reduces the amount of time an employee spends in the bagging area.
2. A central vacuum system has been installed which alleviates sweeping. The vacuumed dust is either recycled or incinerated.

DESCRIPTION OF MEDICAL, INDUSTRIAL HYGIENE AND SAFETY PROGRAMS

Medical
Dow Chemical Company maintains a full-time medical department. The department is staffed by a variety of health professionals such as physicians, nurses, and medical technicians. The department is equipped to handle all routine care and minor emergencies. A pre-employment physical is given and a voluntary biennial physical is offered to every employee. The supervision of each production plant encourages all employees to monitor their own hands for peeling. If peeling is found, the employee is sent to the medical department for evaluation.

In addition, an employee's hands may be checked periodically for peeling as part of the plant's industrial hygiene program.

Industrial Hygiene and Safety

A concerted effort has been made by Dow Chemical Company to reduce employee exposure to acrylamide. There is a very large staff devoted full-time to industrial hygiene and safety for the entire Michigan division. In addition, an industrial hygienist is assigned to the acrylamide and polyacrylamide facilities. The company has monitored for acrylamide since 1955. Prior to 1978, the industrial hygiene samples consisted of airborne area and wipe test sampling. Data collected after 1978, has been augmented with personal breathing zone samples. The data revealed that the overall exposure to airborne acrylamide has decreased with time. Personal breathing zone samples representing a particular job such as packager, generally have been below the current PEL of 0.3 mg/m^3 TWA-8 hour. Short term monitoring data of a specific job task required of a packager such as loading or unloading, however, were generally higher. This indicates that while certain job tasks may give high short term exposures to acrylamide, the overall job has a lower eight hour TWA. It should be noted that the reported incidence of breakthrough in these air samples is extremely small. While breakthrough may be attributed to many factors such as retention volume of absorbate, sample time and velocity of air flow through the tube; it is generally a function of humidity, presence of other contaminants and/or concentration of the contaminant of interest. Based on the data, it is not possible to determine the reason for breakthrough in this case, however, breakthrough in general and this data set in specific is not considered to be a major concern in sampling for acrylamide.

Dow has used three different sample collection methods and four different sample analysis methods since data was first collected in 1955. The current sampling method employees a solid sorbent sampling tube connected to a small, battery operated pump. The sample is analyzed by High Performance Liquid Chromatography (HPLC) and Ultra Violet Detection (UV).

There is an extensive training program for all new employees which emphasizes the appropriate handling and clean-up of acrylamide. The neurological effects and carcinogenic potential of acrylamide are stressed not only to the employees, but to all vistors. Employees are also alerted to the symptoms of acrylamide exposure, and are directed to report all presentation of symptoms to their supervisor. Employees are instructed in various emergency procedures such as handling a spill or evacuation of the building. Safety equipment such as hard hats, glasses, and shoes are required for all employees and vistors. There are separate lockers for street clothes and protective equipment. Each employee has a daily change of uniforms. There are designated smoking and non-smoking areas and the adherence to these designations is enforced. There is also a lunchroom separated from the production area. Each process area has a sign-in sheet which must be signed by all vistors upon entering or leaving the area.

EVALUATION CRITERIA

The recommended levels or applicable standards used in this report as related to toxic substances are (1) NIOSH recommended levels, (2) Federal Occupational Standards as promulgated and enforced by the Occupational Safety and Health Administration (OSHA), U.S. Department of Labor (29 CFR 1910, 1000) Permissible Exposure Limits (PEL) and, (3) American Conference of Government Industrial Hygienists (ACGIH) Threshold Limit Values (TLVs).(10,15,16)

Listed below are the recommended levels or applicable standards for acrylamide:

NIOSH Recommended Level	OSHA PEL	ACGIH TLV
0.3 mg/m^3 10 hr TWA	0.3 mg/m^3 8 hr TWA	0.3 mg/m^3 8 hr TWA

CONCLUSIONS AND RECOMMENDATIONS

Dow Chemical Company is suitable for inclusion in the industrywide study of worker exposure to acrylamide because it manufactures acrylamide (an aqueous monomer) and polyacrylamide (an aqueous and aqueous-oil emulsion). The company has a well established medical and industrial hygiene program, with industrial hygiene data of airborne acrylamide levels from 1955. The current Dow method used to sample for acrylamide consists of a solid sorbent tube connected to a small, battery operated pump. The sample is analyzed by HPLC-UV. The current NIOSH method for collection of airborne acrylamide uses a solid sorbent tube preceeded by a 37 mm cellulose filter. The analytical method used is currently the same one used by Dow.

An indepth industrial hygiene study should be conducted at Dow Chemical Company for the following reasons: 1) the differences in the sample collection methods used by Dow and NIOSH, make direct comparison of data collected by NIOSH industrial hygienists at other companies and data collected by Dow at this facility impossible. 2) Dow Chemical produces an aqueous-oil polymer emulsion. This type of polyacrylamide product is unique to Dow. 3) Dow has one of the larger potentially exposed worker population in this study.

FIGURE I

SEPARAN I
ACRYLAMIDE MONOMER PRODUCTION
DOW CHEMICAL COMPANY
PROCESS FLOW DIAGRAM

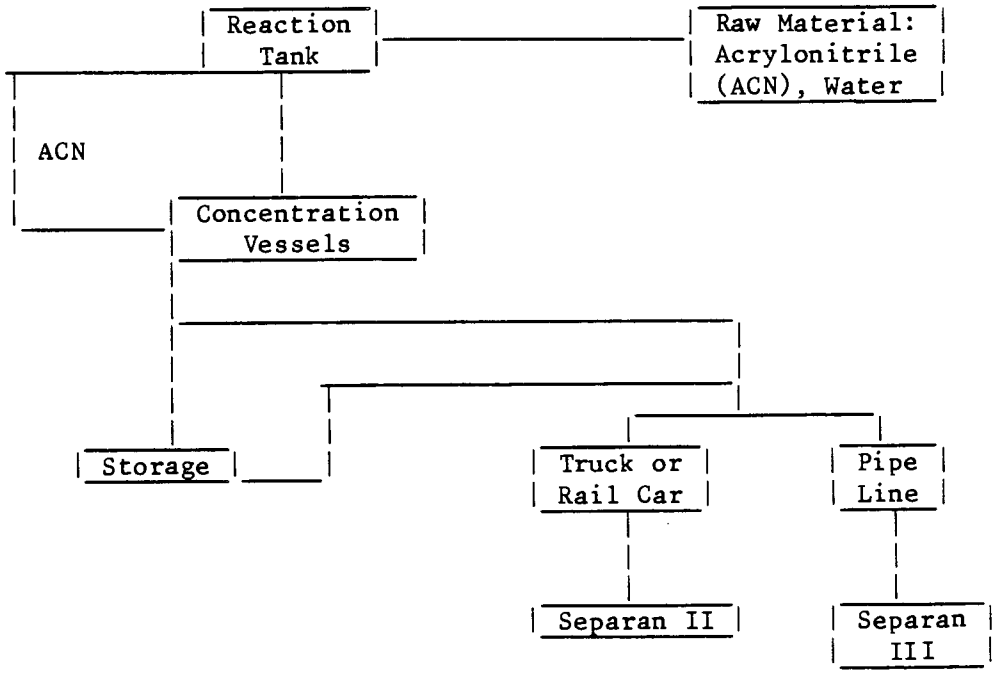

FIGURE II

SEPARAN II
POLYMER, AQUEOUS SOLUTION OR POWDER
DOW CHEMICAL COMPANY
PROCESS FLOW DIAGRAM

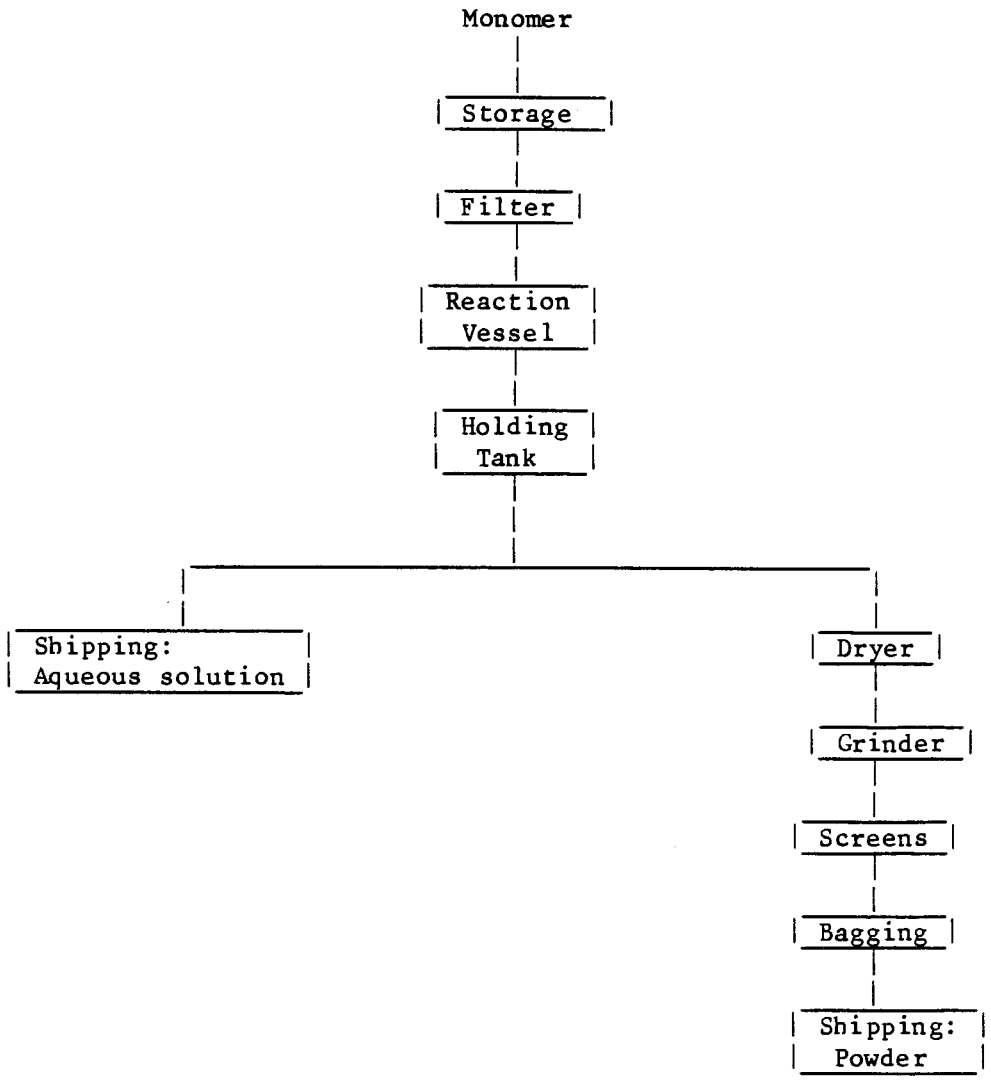

FIGURE III

SEPARAN III
POLYMER, WATER-OIL EMULSION
DOW CHEMICAL COMPANY
PROCESS FLOW DIAGRAM

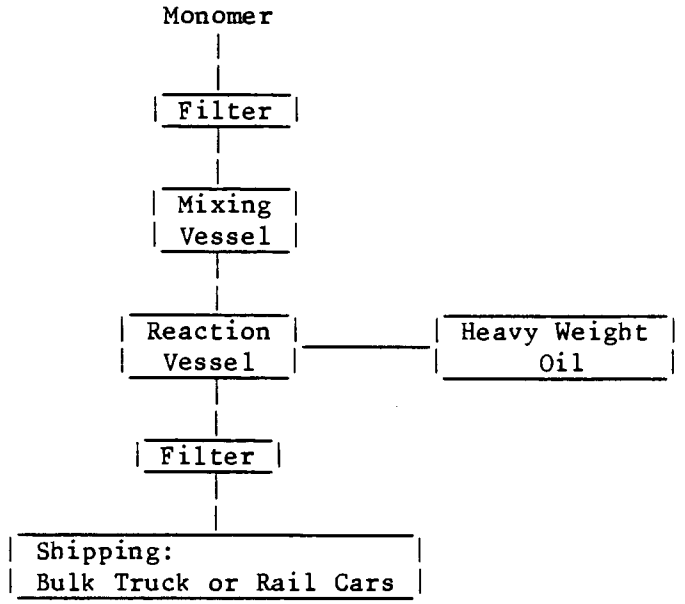

TABLE I

JOB TITLES AND DESCRIPTION OF DUTIES
SEPARAN I, II, III
DOW CHEMICAL COMPANY*

JOB TITLE	DESCRIPTION OF DUTIES
Supervision	Production personnel responsible for managing plant operations. Consists of supervisors, foreman and engineers.
Office Staff	Personnel responsible for nonproduction activites who spent little time in production areas. Consists of secretaries and clerks.
Operators	Personnel responsible for conducting plant operations.
Packagers	Personnel responsible for final product packaging, storage and shipping.
Maintenance Personnel	Responsible for day-to-day cleanup and repair operations. Consists of janitors, mechanics and utility personnel.
Laboratory	Personnel responsible for lab operations (quality assurance) with little time spent in production areas.

* This table was reproduced from information supplied by Dow Chemical Company.

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APPENDIX I*

The following codes are applicable to all three Separan facilities.

CATEGORY	- CODE	- EXPLANATION
Year	-	Time period when data was collected.
Descripion	Job Title	See Table I
	Process Sampling	Process sample collection using dip techniques, sampling boxes and sidestream sampling.
	Maintenance Operations	Specific job tasks involving cleaning and repairs such as filter changes and washing and cleaning operations.
	Process Operations	Day-to-day production operations such as loading reactors.
	Load/Unload Operations	Loading or unloading of trailers, tank cars, rail cars, etc.
	Production Areas	General areas in the plant where production operations occurred.
	Point Source Areas	Specific point sources where acrylamide or mixtures were used.
	Non-Production Areas	Plant area isolated from day-to-day process operations (lunchroom, locker room, control room).
	Maintenance Activities	Areas in the plant where a specific maintenance task was performed.
Data	See Attached	

* This appendix was reproduced from information provided by Dow Chemical Company.

APPENDIX I

CATEGORY	- CODE	- EXPLANATION
No. of Samples	--	Total number of samples collected for the Description and Data category.
Range	--	Low to high acrylamide concentrations.
Mean(arithmetic)	--	Average acrylamide concentration. NOTE: non-detectable values were not included in the mean and standard deviation calculations.
Std. Dev.	--	Standard deviation of the mean acrylamide concentration.
Sampling	See Attached.	
Analysis	See Attached.	