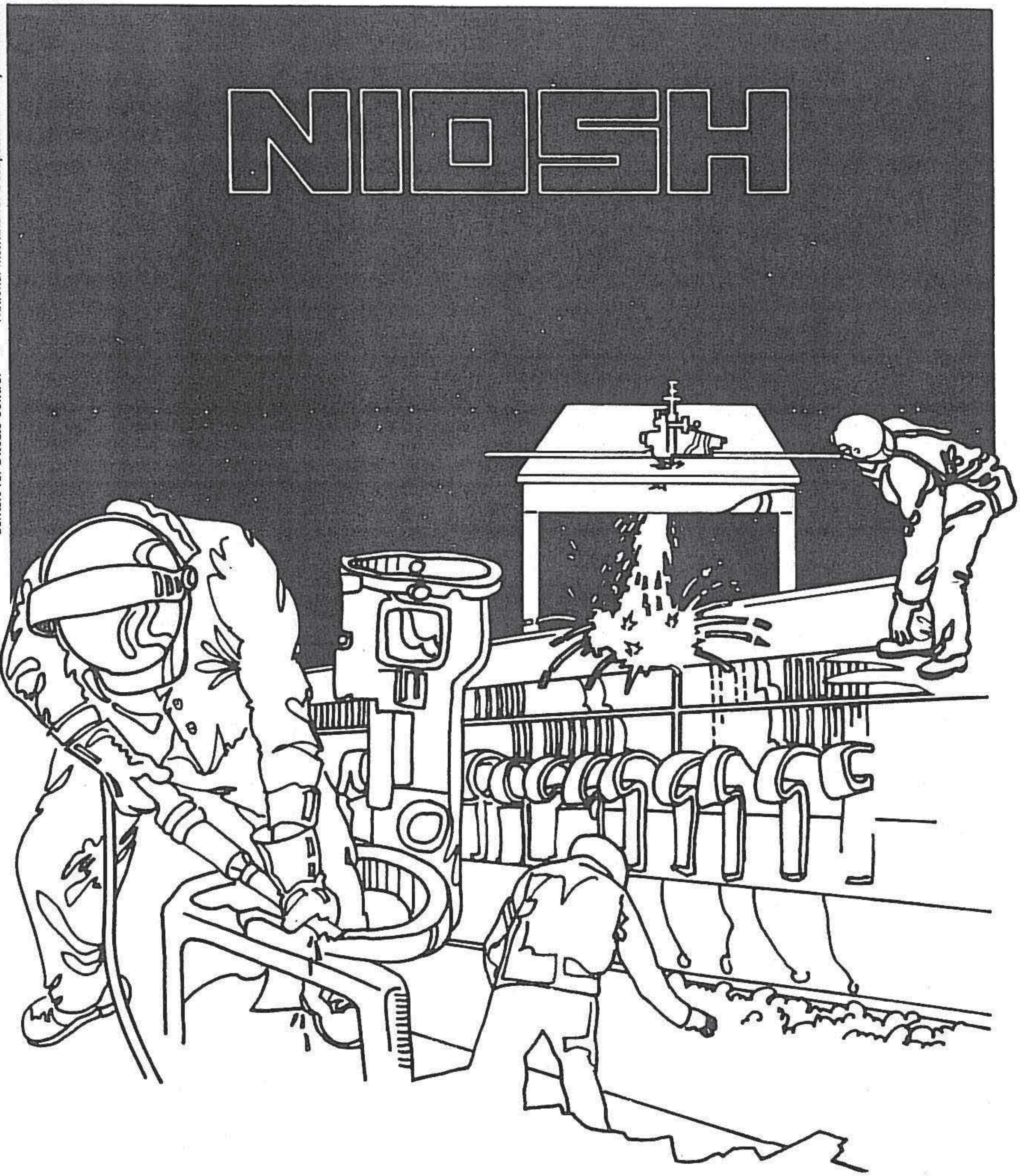
U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES ■ Publ. Service
Centers for Disease Control ■ National Institute for Occupational Safety and Health



# Health Hazard Evaluation Report

HETA 80-190-1135
AMERICAN CYANAMID COMPANY
KALAMAZOO, MICHIGAN

HETA 80-190-1135
JUNE 1982
AMERICAN CYANAMID COMPANY
KALAMAZOO, MICHIGAN

NIOSH INVESTIGATORS:
James D. McGlothlin, I.H.
Paul Schulte, M.S.
Harold Van Wagenen

## I. SUMMARY

On June 2, 1980, the National Institute for Occupational Safety and Health (NIOSH) received a request from the Oil, Chemical, and Atomic Workers International Union, Local 7-220, for a Health Hazard Evaluation of the American Cyanamid Company, Kalamazoo, Michigan. The request was generated because of employee concern about potential exposure to formaldehyde, epichlorohydrin, dimethylamine, ammonia, hydrochloric acid, styrene, maleic anhydride acrylamide, sulfuric acid, and bis (chloromethyl) ether, and the reportedly high rate of permanent disabilities and mortality before retirement. This plant manufactures specialty chemicals and flocculants for paper and water treatment plants.

On September 17, 1980, an initial environmental and epidemiologic investigation was conducted. A walk-through survey, observation of work practices, unstructured employee interviews, chemical inventory, and review of industrial hygiene measurements made by company officials, were performed. Special attention was paid to the design of local exhaust ventilation for reactor vessels, drumming stations, and pre-mix tanks used to manufacture flocculants.

On January 6-7, 1981, NIOSH conducted an environmental and control technology survey. NIOSH obtained personal and area air samples for acrylamide, dimethylamine, formaldehyde, bis (chloromethyl) ether, hydrochloric acid, epichlorohydrin, and sulfuric acid.Between the first and second NIOSH survey, one of the plant buildings suffered a major toluene explosion and fire, completely shutting down production and use of maleic anhydride, styrene, ammonia, and toluene. The company has no immediate plans to rebuild the damaged facility; therefore, no sampling for these compounds was performed.

NIOSH investigators found low levels of dimethylamine (range: nondetectable (N.D.) to 0.63 milligrams per cubic meter of air ($mg/M^3$) (OSHA Permissible Exposure Limit (PEL) is 18.0 $mg/M^3$, Limit of Detection (LOD) 0.01 $mg/M^3$); hydrochloric acid (range: N.D. to 0.14 $mg/M^3$) (PEL 7.0 $mg/M^3$, LOD 20 ug/sample), and sulfuric acid (range: 0.03 $mg/M^3$ to 0.38 $mg/M^3$) (PEL 1.0 $mg/M^3$, LOD 5.0 ug/sample). Acrylamide, bis (chloromethyl) ether, and epichlorohydrin were not detected. Formaldehyde, however, was detected in concentrations from 0.04 $mg/M^3$ to 1.91 $mg/M^3$, the latter being a personal (11-minute) short-term sample; NIOSH recommends the lowest feasible limit for formaldehyde. Exposures to all other chemicals detected were within recommended limits.

The control technology assessment of batch process equipment, including local and general exhaust ventilation, was determined to be substandard in the specialty chemical building. Chemical leaks from seals and fittings in several of the reactor kettles appeared to be the most common source of peak exposure during initial batch mixing.

The epidemiologic study consisted of reviewing long term disability insurance claim records and employee work histories. Results indicate no abnormal pattern of disabilities by type but the overall rate was four times the rate for Social Security disabilities in Michigan. Occupational causes for these rate differences were not evident.

Based on observation of work practices, employee interviews, and professional judgement, NIOSH concluded that a potential health hazard from overexposure to formaldehyde and dimethylamine as a result of equipment malfunction, and leaky reactor vessel agitator seals and fittings may exist at the American Cyanamid Company. Plans for improvements in plant ventilation are in progress. However, during the interim, steps should be taken to reduce short-term peak exposures to various chemicals. Recommendations to accomplish this are found in Section VIII of this report. Rates of long term disabilities were approximately 4 times greater than Michigan Social Security disability rates but there is no indication of an occupationally related cause.

KEYWORDS: SIC 2810 (Chemical Manufacturers), formaldehyde, dimethylamine, bis (chloromethyl) ether, hydrochloric acid, epichlorohydrin, sulfuric acid.

## II. INTRODUCTION

On July 2, 1980, NIOSH received a request from the Oil, Chemical, and Atomic Workers International Union (Local 7-220) to perform a Health Hazard Evaluation at the American Cyanamid plant in Kalamazoo, Michigan. The request mentioned exposure to several specialty chemicals including formaldehyde, epichlorohydrin, dimethylamine, sulfuric acid, bis (chloromethyl) ether, hydrochloric acid, acrylamide, styrene, anhydrous ammonia, toluene, and maleic anhydride during the manufacture of paper resins, liquid plastics, flocculants, and Alum (a wastewater flocculant). The request also mentioned poor maintenance of equipment, inadequate ventilation, a high rate of worker disability, and reported premature death rates among its workers.

An initial survey was conducted by NIOSH on September 17, 1980, and a follow-up on January 6-7, 1981. NIOSH industrial hygienists, an epidemiologist, and an engineer participated in the evaluation.

NIOSH distributed Interim Report #1 for this investigation in December 1980, which contained recommendations to improve environmental monitoring, ventilation, and reduce employee exposure to batch process chemicals.

## III. BACKGROUND

The American Cyanamid plant in Kalamazoo, Michigan, has been manufacturing chemicals for the past 40 years. Specialty chemicals (current production 3.0 million pounds per month) have been manufactured for the last 25 years, and flocculants for the past 5 years. The primary products are flocculants for paper and water treatment. There are 43 workers in production, 11 in maintenance, and approximately 14 salaried workers. Industrial hygiene measurements are made at least twice per year, ventilation measurements once per month, and personal protective equipment such as boots, gloves, safety glasses, coveralls, hard hats, and respirators are supplied by the company.

### A. Plant Production

The plant chemical processing (entirely by batch operation) is conducted in three separate buildings. The three types of chemical products and their processes are briefly discussed below.

#### 1. Organic Flocculants:

Polyamine and polyacrylamide products are manufactured in a modern, well-designed installation which was built in 1975. Chemical feed stocks, of various degrees of hazard, are epichlorohydrin, dimethylamine, ethylene diamine, hydrochloric acid, acrylamide monomer, isopropyl alcohol, ammonium persulfate, and formaldehyde. Major chemicals are handled in bulk from outside storage tanks, while minor ingredients are handled by drum. Various chemicals are added to large mixing kettles according to formulation via pipe transfer systems. When the batch is made it is transferred via pipe system to railroad tank cars, trucks, or 55 gallon drums.

2. Alum:

Alum is batch processed from company mined bauxite, sulfuric acid, and water in a wooden tank installation. Various amounts of bauxite and sulfuric acid, and water are added to large wooden kettles; the liquid is agitated with stirring rods; then the product is transferred to railroad or truck tank cars by pipe.

3. Specialty Chemicals:

In the remaining operable building, melamine formaldehyde resin products are being produced. The hazardous chemicals employed include formaldehyde, melamine powder, acrylamide monomer, hydrochloric acid, and sodium hydroxide solution. The basic problem with this department's batch chemical processing equipment from the occupational exposure standpoint is that it was initially designed and installed some 20 to 30 years prior for an entirely different line of chemical products. Minimum changes had been made to accommodate production of the current melamine formaldehyde resins. However, ventilation controls were not upgraded with these changes. The manufacturing process is similar to speciality chemicals where kettles and pipe transfer of chemicals from storage tanks are extensively used.

Employee exposure to chemicals are predominantly from leaks in pipe lines, and transfer junctions, and leaks from seals and fittings around kettle agitators. Also, high chemical exposure from inadvertent spills of chemicals or emergency repair of process equipment during a batch process cycle.

## IV. METHODS AND MATERIALS

### A. Environmental

No environmental samples were taken during the initial survey. However, company industrial hygiene data were shared with NIOSH investigators to evaluate employee exposure to chemicals used at this plant.

Company data showed that short-term Drager tube measurements were performed for the following chemical contaminants: acrylamide, ammonia, dimethylamine, epichlorohydrin, formaldehyde, isopropanol, styrene, and toluene. Except for occasional excursions above the Threshold Limit Values (TLV's) for ammonia, dimethylamine, and formaldehyde, most measurements showed employee exposures to these chemicals to be below Occupational Safety and Health Administration (OSHA) standards.

Work practices were observed, and OSHA 200 forms were examined.

Personal and general area air samples were collected on January 6-7, 1981, to evaluate workers' exposure to chemicals used in the organic flocculants, Alum, and specialty chemicals buildings. Between the first and second NIOSH survey, a major toluene explosion and fire, caused by overheating of a large reaction vessel, destroyed one of the specialty chemical buildings. Because of the explosion, environmental sampling for maleic anhydride, styrene, toluene, and ammonia could not be performed. The company has no immediate plans to construct a new building for the manufacture or use of these chemicals. However, sulfuric acid, formaldehyde, hydrochloric acid, bis (chloromethyl) ether, dimethylamine, and epichlorohydrin were sampled in the organic flocculants and other specialty chemical buildings.

1. Air Sampling:

The personal sampler was attached on the lapel of the employee in order to collect an air sample representative of his breathing-zone. Area samplers were positioned at specific locations in the working environment and generally within a distance of 0.5 to 3 feet from the workers' breathing-zones; see summary of sampling and analytical methodology listed below. Each of the sampling data tables (Tables I-IV) includes information denoting the types of samples collected and their location.

2. Environmental Controls:

Most chemicals listed were generally controlled by local exhaust ventilation. Since production was by batch process and performed almost exclusively in reaction kettles, design of ventilation hoods was usually custom made for each vessel. Schematics of some of these hoods are shown in Figure 1. Ventilation measurements were performed by NIOSH on some of these hoods using a Kurz (model 441) Air Velometer.

B. Medical

All Long Term Disability (LTD) claims for the Kalamazoo plant, filed in the period 1976-82, were retrieved from the insurance carrier of American Cyanamid and evaluated. The incidence rates for disability cases were derived and compared with incidence rates for Social Security disabilities for the State of Michigan (1969-71 and 1976). Mortality information could not be evaluated adequately due to the small number of deaths which would have led to the formation of unstable death rates. Such rates are not useful for evaluation.

## V. EVALUATION CRITERIA

### A. Environmental Standards

To assess the concentrations of air contaminants found in the place of employment, three primary sources of criteria were used: (1) NIOSH criteria for recommended standards for occupational exposure to substances (criteria documents); (2) recommended and proposed threshold limit values (TLV's) and their supporting documentation as set forth by the American Conference of Governmental Industrial Hygienists (ACGIH) (1980); and (3) occupational health standards as promulgated by the U.S. Department of Labor (OSHA) (29 CFR 1910.1000).

The following table includes Environmental criteria Limits, sources of criteria, and primary effects data for each substance evaluated.

| Substance | NIOSH Recommended Criteria | ACGIH TLV | OSHA Standard | Primary Health Effects |
|---|---|---|---|---|
| Acrylamide | 0.3 mg/$M^3$[a] | 0.3 mg/$M^3$ | 0.3 mg/$M^3$ | Affects central and peripheral nervous system, irritates eyes, skin. |
| Dimethylamine | ----- | 18.0 mg/$M^3$ | 18.0 mg/$M^3$ | Irritates eyes, throat, lung edema, skin irritation |
| Formaldehyde | lowest feasible limit (1) | 2.0 ppm[b] | 3.0 ppm<br>5.0 ppm-ceiling[2]<br>10.0 ppm-peak[3] | Irritates eyes, nose, throat, pulmonary irritation vomiting, may cause cancer |
| Bis (chloromethyl) ether | Lowest feasible limit | 0.001 ppm | Lowest feasible limit | May cause cancer Avoid all contact |
| Hydrochloric Acid | ----- | 7.0 mg/$M^3$ (ceiling) | 7.0 mg/$M^3$ (ceiling) | May cause ulcers of nose; cough, burn throat, eyes; severe skin irritant |
| Epichlorohydrin | 2 mg/$M^3$ (19.0 mg/$M^3$-15-min. ceiling) | 10.0 mg/$M^3$ | 19.0 mg/$M^3$ | May cause nausea, vomiting, abdominal pain; irritates eyes and skin with deep pain |
| Sulfuric Acid | 1.0 mg/$M^3$ (10-hr. time-weighted avg.) | 1.0 mg/$M^3$ | 1.0 mg/$M^3$ | Irritates eyes, nose throat; pulmonary edema; burns skin, eyes, corrodes teeth |

---

a. $mg/M^3$ = milligrams of substance per cubic meter of air.
b. ppm = parts per million parts of air.
1. Formaldehyde: Current Intelligence Bulletin #34, April 1981 - listed as suspected human carcinogen.
2. Ceiling Level - exposure not to exceed this level after 15 minutes of exposure.
3. Peak Level - exposure never to exceed this level.

---

B. Toxicological

Formaldehyde:

Formaldehyde is a colorless, flammable gas with a strong, pungent odor. Occupational exposure may cause severe irritation to the mucous membranes of the respiratory tract and eyes. Systemic intoxication is unlikely because of its intense irritation. If workers are exposed to high concentrations, coughing, difficulty breathing, and pulmonary edema may occur.[1] Evidence of the carcinogenicity of formaldehyde was first reported on October 8, 1979. Preliminary data from an inhalation study of rats and mice indicated that for exposures of 15 ppm for 6 hours/day, 5 days/week for 16 months, formaldehyde caused cancer in rats.[2] The type of cancer is squamous cell carcinoma of the nasal turbinates. Because formaldehyde has induced a rare form of cancer in rats and mice, NIOSH has recommended that, as a prudent public health measure, occupational exposure be kept to the lowest feasible limit.

VI. RESULTS AND DISCUSSION

A. Environmental

All personal and general area samples for acrylamide, bis (chloromethyl) ether, and epichlorohydrin were below the limits of detection on the days NIOSH sampled. Dimethylamine was detected in 6 of 8 samples, ranging from 0.23 $mg/M^3$ (chemical operator) to 0.63 $mg/M^3$ (general area at operator's desk). The mean concentration was 0.34 $mg/M^3$ (Table II). None of these samples exceeded the environmental criterion for this compound (OSHA-18.0 $mg/M^3$).

Formaldehyde was detected in 8 of 8 samples in the specialty chemical building, and ranged from 0.03 ppm to 1.6 ppm. The mean concentration was 0.33 ppm (Table III). The 1.6 ppm was a short-term personal sample collected from a specialty chemical operator.

Hydrochloric acid was detected in 2 of 4 samples, both were general area samples taken in specialty chemicals, and were reported at 0.09 $mg/M^3$ at the pH bench, and 0.14 $mg/M^3$ at the quench tank (Table IV); neither hydrochloric acid sample exceeded the PEL of 7.0 $mg/M^3$. Bis (chloromethyl) ether, which may chemically form from the reaction of formaldehyde and hydrochloric acid, was not detected in any of the NIOSH samples (n=6).[1] The limit of detection for BCME is 0.01 ug/sample. It was hypothesized that addition of water simultaneously to the formaldehyde and hydrochloric acid batch process probably hydrolizes any potential bis (chloromethyl) ether formation to levels below the limit of detection. This may be a significant finding since ingredients for potential BCME (i.e., formaldehyde and hydrochloric acid added together) formation are present.

Sulfuric acid was detected in 7 of 7 samples in the Alum building (Table V). Concentrations ranged from 0.03 mg/M$^3$ above the settling tank, to 0.38 mg/M$^3$ for one of the chemical operators. The mean concentration was 0.16 mg/M$^3$. None of these samples exceeded the environmental criteria of 1.0 mg/M$^3$ (10-hour time-weighted average [TWA]) for this compound.

Although the samples collected by NIOSH were below environmental criteria, there were instances during this investigation where sharp, irritating odors were detected by NIOSH environmental investigators. Odors would be most strong during the initial charging of chemicals, such as dimethylamine and formaldehyde, into a reactor vessel. These odors, however, would diminish within a few minutes because of local exhaust ventilation. Leaks in seals and fittings around the reactor vessel drive shaft or agitator appear to be the source of these odors. Control of emissions from seals and fittings in chemical process industries have improved in recent years through engineering controls. Single and double mechanical seals have proven to be effective in controlling fugitive emissions.

Ventilation measurements taken during chemical operations at various hoods show average face velocities generally exceeded 100 feet per minute (fpm). These rates are summarized below by chemical reactor vessel, its number, and average face velocity at hood entrance.

| Chemical Reactor Vessel | Vessel Number | x=Face Velocity (fpm) |
|---|---|---|
| B-Polyamine | 120-001B | 174 |
| A-Polyamine | 120-001A | 136 |
| PRX-Reactor | 120-006 | 125 |
| Drum Station | ----- | 205 |
| Specialty Chemical Reactor | RE3-1 | 181* |

*Note: Ventilation was very good at bottom (x=400-600 fpm); however, rates decreased to 50-100 fpm at top - suggesting chemical dust buildup near the top of exhaust.

Substandard ventilation does exist at some reactor vessels (see Appendix 2) in the plant. American Cyanamid management is aware of these deficiencies and has forwarded their recommended ventilation modifications to headquarters for corporate approval.

B. Medical

The LTD records of new claims for the period 1976-82 were evaluated. Eligibility for disability was based on inability to perform one's Cyanamid job, are less than 65, and with one month of full-time employment. A total of 12 records were supplied by Cyanamid's insurance carrier. These represent all claims filed during the specified period. Table VI shows the disability diagnosis and the year first disabled for each case. Of the twelve disability cases filed, eleven were male. Due to the paucity of female cases only the male cases were analyzed.

The average age of the disability cases was 53 years (range: 31 to 64 years). Four of the cases had job titles of reactor operator, 4 maintenance, 1 fork lift driver, 1 laboratory technician, and 1 manager. The mean time between year first employed and the year first disabled was 18.5 years; the median was 21.5 years (range 1-34 years). No apparent pattern was observed in the disability diagnoses.

The rates of long term disability for males for the years 1976-1980 averaged 4.0% per year. These rates are based on very small but relatively constant numbers: 1976, 3/63 (4.7%); 1977, 3/64 (4.6%); 1978, 0/43 (0.0%); 1979, 4/45 (8.8%); 1980 1/49 (2.0%).

To evaluate these data disability claims for Michigan from the Social Security Administration were used as reference. The most available data was for the period 1969-71 and 1976. During that period the mean disability rate was 0.58% for males. The specific disability rates for males were: 1969 (11,198/2,095,000 = 0.53%), 1970 (11894/2,155,000 = 0.55%), 1971 (14,941/2,228,000 = 0.67%), and 1976 (13,100/2,308,115 = 0.56%). The mean age for the 1969-71 series was 52.2 years.

The criteria for eligibility for coverage in the Social Security and the Cyanamid disability programs is not exactly the same. For Social Security, workers must have worked in covered employment for 5 of the 10 years preceding the onset of disability. The Cyanamid program initiates eligibility after one-month of full-time employment. Consequently for comparative purposes it is necessary to adjust the rates for Cyanamid by removing all disability cases with less than 5 years employment. Of the 11 male disability cases only 8 meet the coverage eligibility requirements. The adjusted disability rate (yearly average) for Cyanamid is then 2.4%.

The Social Security system disability requirements are more severe than the Cyanamid requirements. To be eligible for Social Security disability a worker must be unable to engage in any substantial gainful activity because of a medically determinable physical or mental impairment that has lasted or can be expected to last for at least twelve months or result in death. Cyanamid has a two tier approach. In the first two years, a worker is eligible for LTD after being totally disabled (with respect to one's current job) for 26 weeks and under the regular care of a physician. Beyond two years LTD eligibility is based on the inability to perform any job for which a person is reasonably qualified on the basis of education, training, and experience.

Of the 8 cases that met the coverage eligibility only cases with at least two years of disability were used in the comparison because these would be chosen with criteria similar to those of the Social Security system. Five of the 8 cases were identified: four had more than two years disability and 1 had a disability leading to death. Because of the adjustment for two years of disability the only calender years that could be evaluated were those more than two years prior to February 1, 1982. Hence only LTD rates for the years 1976-79 were evaluated. The adjusted rates were as follows: 1976, 2/62 (3.2); 1977, 2/63 (3.2%); 1978, 0/43 (0%); 1979, 1/41 (2.4%). The average of these rates is 2.2%. These adjustments have resulted in destablizing the Cyanamid LTD rates making them less useful for comparative purposes. Still, the ratio of the Cyanamid LTD rates (1976-79) to those of Social Security claimants in Michigan (1969-71 and 76) is 2.2/.58=3.79. Hence the rate of long term disabilities at the American Cyanamid plant is approximately four times greater than the Michigan rate for males.

## VII. CONCLUSIONS

The level of control technology effectiveness in minimizing occupational exposure appeared to vary considerably from department to department. The main positive engineering control feature was operation of a number of well-designed and sturdy local exhaust ventilation units installed on reactor vessel sampling stations, drum handling stations, certain major transfer or recirculation pump sites, and pre-mix tanks. However, there were a number of process equipment units on which both local and general exhaust ventilation were either nonexistent or ineffective (particularly in the specialty chemical department).

Deficiencies in monitoring equipment, work practices, and personal protective equipment were observed and suggestions for improvement outlined in section VIII.

An investigation of disability retirement records showed that the incidence rate in the plant during 1976-80 was approximately four times greater than the incidence rate of Social Security disabilities in Michigan for a comparable period. There is nothing to indicate the cause of the disabilities. The failure to find either a common pattern of diagnoses or an earlier age of onset than for the reference group reduces the liklihood that occupational factors could account for this excess.

A number of methodologic factors might be considered as artificial causes of the apparent difference between Cyanamid and Social Security disability rates. The number cases from the Cyanamid plant is small and hence the annual rates are not very stable. However the rates are relatively constant on a yearly basis and exceed the Social Security rate in 3 out of 4 years reviewed. The eligibility requirements for the two series of cases are not precisely the same but the Cyanamid rates have been adjusted down to account for most of the difference in criteria. The use of Social Security rates from 1969-71 and for 1976 to compare with Cyanamid disability rates from 1976-80 may appear to have a slight temporal bias but there is no indication that the Social Security rates in 1969-71 are much different than the Social Security disability rates for 1976-80.

Differences in age distributions between the two groups might contribute to the rate difference but it is more likely that the Social Security rates would be influenced by older people with higher disability rates. This should also tend to minimize the difference between the two groups. Generally these confounding factors do not seem strong enough to account for magnitude of the rate differences. The failure to identify a common pattern of disability diagnoses or to identify confounding factors provides no answer why the Cyanamid disability rates appear to be increased.

## VIII. RECOMMENDATIONS

### A. Organic Flocculants:

1. Improve packing around mixing vane shafts in the reactor vessels. Since transfer of intermediates may pose a problem of fugitive emissions from worn drive shaft seals, a maintenance system for repacking glands should be instituted, or replaced with recommended mechanical seals (Figures 1 and 2).

2. Organic vapor respirators should be provided to workers until engineering controls are completed.

### B. Specialty Chemicals:

1. Repair water float cutoff valve for the quench tank. Excess formaldehyde exposure may have resulted from residual vapors caused by overfilling the quench tank the day before.

2. Institute a maintenance program that will prevent plugging of the local exhaust ventilation system from a buildup of chemical dust poured into the reactor vessel.

3. Improve ventilation at the quench tank. (Vapors generated during quenching are not thoroughly captured by the current system.)

### C. Alum Building:

1. Inspect and replace corroded settling tank covers.

2. Make observation portals above the settling tanks as small as possible to improve capture velocity of existing ventilation.

D. Plantwide:

1. Management should develop a system for workers reporting fugitive emissions from reactor vessels. Industrial hygiene sampling, even if scheduled, may not detect elevated chemical emissions for days.

2. Continuous organic vapor monitoring is the best state-of-the-art hygiene practice for monitoring and alerting management to fugitive emissions. NIOSH highly recommends their use, especially in batch chemical process industries.

3. Ventilation modifications for reactor vessels (Appendix 2) at the American Cyanamid Kalamazoo plant and controls, should be installed as soon as possible.

4. Work practices should include staying away from (as best possible) seals and fittings of reactor kettles during transfer of chemical intermediates, and good personal hygiene, after contact with any chemicals in batch operation.

5. Respiratory protection should be provided as an interim measure to workers in the reactor kettle area until chemical leaks from seals and fittings are properly secured.

## IX. REFERENCES


1. Occupational Diseases, A Guide to Their Recognition (Revised 1977). DHEW (NIOSH) Publication No. 77-181.

2. Current Intelligence Bulletin #34, Formaldehyde: Evidence of Carcinogenicity. DHHS (NIOSH), April 15, 1981.

3. Control of Emissions from Seals and Fittings in Chemical Process Industries: National Institute for Occupational Safety and Health Technical Report (DHHS (NIOSH) Publication No. 81-118), 1981.

4. Patrick, David R. Synthetic Organic Chemical Manufacturing Industry Standards Development Program. U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, March 1979.

5. Occupational Characteristics of Disabled Workers: National Institute for Occupational Safety and Health Research Report (DHHS (NIOSH) Publication No. 80-145), 1980.

## X. AUTHORSHIP AND ACKNOWLEDGEMENTS


| | |
|---|---|
| Evaluation Conducted and Report Prepared By: | James D. McGlothlin, M.S., M.P.H.<br>Industrial Hygienist<br>Industrial Hygiene Section |
| | Paul Schulte, M.S.<br>Epidemiologist<br>Medical Section |
| | Harold Van Wagenen<br>Chemical Engineer<br>Division of Physical Sciences and Engineering |
| Environmental Assistance: | Andrew D. Lucas<br>Industrial Hygienist<br>Industrial Hygiene Section |
| Originating Office: | Hazard Evaluations and Technical Assistance Branch<br>Division of Surveillance, Hazard Evaluations, and Field Studies<br>Cincinnati, Ohio |
| Report Typed By: | Betty L. Widener<br>Clerk-Typist<br>Industrial Hygiene Section |


## XI. DISTRIBUTION AND AVAILABILITY OF REPORT

Copies of this report are currently available upon request from NIOSH, Division of Standards Development and Technology Transfer, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days, the report will be available through the National Technical Information Service (NTIS), 5285 Port Royal, Springfield, Virginia 22161. Information regarding its availability through NTIS can be obtained from NIOSH Publications Office at the Cincinnati address. Copies of this report have been sent to:

1. American Cyanamid Company, Kalamazoo, Michigan
2. Oil, Chemical, and Atomic Workers International Union, Local 7-220
3. NIOSH, Region V
4. OSHA, Region V

For the purpose of informing the 43 affected employees, a copy of this report shall be promptly posted in a prominent place place accessible to the employees for a period of 30 calendar days.

TABLE I

Sampling and Analytical Methodology

American Cyanamid
Kalamazoo, Michigan
HETA 80-190

| Chemical | # of Samples Sample Type/ | Flow Rate (lpm)* | Location | Sampling Medium/ Analysis | Detection Limit |
|---|---|---|---|---|---|
| Acrylamide | 4 G.A.** 3 P*** | 1.0 | Specialty Chemicals | Impinger/$H_2O$/gas chromatography[a] | 17 ug/sample |
| Dimethylamine | 5 G.A. 2 P | 0.2 | Organic Flocculants | Silica gel/gas chromatography[a] | 0.01 mg/sample |
| Formaldehyde | 5 G.A. 3 P | 0.2 | Specialty Chemicals | Impinger/sodium bisulfite/NIOSH Method P & CAM 125[1] | 2.0 ug/sample |
| Bis (chloro-methyl) ether | 3 G.A. 2 P | 1.0 | Specialty Chemicals | Impinger/sodium trichlorophenoxide/ gas chromatograph[a] | 0.01 ug/sample |
| Hydrochloric Acid | 3 G.A. 1 P | 0.2 | Specialty Chemicals | Impinger/sodium acetate/ion specific electrode/ NIOSH Method P & CAM S-246 | 20 ug/sample |
| Epichlorohydrin | 5 G.A. 2 P | 0.2 | Organic Flocculants | Charcoal/gas chromatography/ NIOSH Method P & CAM S-118[a] | 0.01 mg/sample |
| Sulfuric Acid | 4 G.A. 3 P | 1.0 | Alum | Filter/ion chromatography/ NIOSH Method P & CAM 268 | 5.0 ug/sample |

* lpm = liters per minute
** G.A. = general area sample
*** P = personal sample
a. See Appendix 1 for laboratory analyses, details, and modifications.
1. NIOSH Manual of Analytical Methods, Second Edition. DHEW (NIOSH) Publication No. 77-157, 1977.

TABLE II
Organic Flocculants

American Cyanamid
Kalamazoo, Michigan
HETA 80-190

January 6-7, 1981

| Sample Location | Sample Type | Sampling Period | Sample Volume (liters) | Dimethylamine (mg/M$^3$) |
|---|---|---|---|---|
| January 6, 1981 | | | | |
| Operator's Desk | G.A.* | 16:35-22:17 | 64.0 | 0.63 |
| Reactor Vessel 120-006 | G.A. | 16:39-22:17 | 63.0 | 0.48 |
| Reactor Vessels | P** | 16:42-22:17 | 65.0 | 0.31 |
| Above Drumming Station | G.A. | 17:33-22:17 | 56.0 | N.D.[a] |
| January 7, 1981 | | | | |
| Reactor Vessels | P | 10:17-14:14 | 43.0 | 0.23 |
| Reactor Vessels | P | 10:25-14:22 | 42.0 | N.D. |
| React Vessel 120-006 | G.A. | 10:51-14:12 | 38.0 | 0.54 |
| Dimethylamine Pump | G.A. | 11:02-14:16 | 37.0 | 0.54 |
| Environmental Criteria (OSHA): | | | | 18.0 |

* G.A. = General area sample
** P = Personal sample
a. N.D. = Nondetectable

TABLE III

Specialty Chemicals

American Cyanamid
Kalamazoo, Michigan
HETA 80-190

January 6-7, 1981

| Sample Location | Sample Type | Sampling Period | Sample Volume (liters) | Formaldehyde (ppm) |
|---|---|---|---|---|
| January 6, 1981 | | | | |
| Reactor Vessel E120-003 | P* | 10:39-10:50 | 11.0 | 1.6 (1.9 $mg/M^3$)+ |
| Reactor Vessel E120-003 | G.A.** | 16:47-22:17 | 330 | 0.05 |
| January 7, 1981 | | | | |
| Quench Tank | P | 9:39-13:55 | 256 | 0.11 |
| Quench Tank | G.A. | 9:16-14:40 | 324 | 0.30 |
| Operator's Desk | G.A. | 9:21-14:44 | 323 | 0.43 |
| Weigh Tank | G.A. | 10:47-15:17 | 270 | 0.06 |
| Weigh Tank | P | 10:44-12:47 | 123 | 0.04 |
| Near Reactor Vessel E120-003 | G.A. | 11:13-14:17 | 184 | 0.03 |
| Environmental Criterion: | | | | Lowest feasible limit |

*  P = Personal sample
**G.A. = General area sample
+$mg/M^3$ = milligrams of substance per cubic meter of air)

TABLE IV
Specialty Chemical
American Cyanamid
Kalamazoo, Michigan
HETA 80-190

January 6-7, 1981

| Sample Location | Sample Type | Sampling Period | Sample Volume (liters) | Hydrochloric Acid (mg/M$^3$) |
|---|---|---|---|---|
| January 6, 1981 | | | | |
| Above Quench Tank | G.A.* | 9:17-9:40 | 332 | N.D.[a] |
| January 7, 1981 | | | | |
| Reactor Vessel E120-003 | P | 9:46-14:42 | 23 | N.D. |
| Outside Quench Tank | G.A. | 9:16-14:40 | 324 | 0.14 |
| pH Bench, 3rd Floor | G.A. | 9:21-14:21 | 325 | 0.09 |
| Environmental Criteria (OSHA): | | | | 7.0 |

TABLE V

Alum Building

January 6-7, 1981

| Sample Location | Sample Type | Sampling Period | Sample Volume (liters) | Sulfuric Acid (mg/M$^3$) |
|---|---|---|---|---|
| January 6, 1981 | | | | |
| Above Settling Tank | G.A. | 18:05-22:45 | 280 | 0.03 |
| Next to Digester | G.A. | 18:04-22:45 | 280 | 0.03 |
| January 7, 1981 | | | | |
| Tank Loading Dock (Acid Resale) | P | 8:45-9:41 | 53 | 0.09 |
| Near Digester | P | 9:33-12:52 | 199 | 0.33 |
| Near Digester | G.A. | 9:31-14:34 | 303 | 0.06 |
| Alum Tank Operator | P | 12:54-14:29 | 95 | 0.38 |
| Alum Tank #4 | G.A. | 11:02-14:16 | 94 | 0.20 |
| Environmental Criteria (NIOSH): | | | | 1.0 |

* G.A. = General area sample
** P = Personal sample
a. N.D. = Nondetectable

TABLE VI

LONG TERM DISABILITY CLAIMS FILED (1976-82)

American Cyanamid
Kalamazoo, Michigan
HETA 80-190

January 6-7, 1981

| DISABILITY DIAGNOSES | YEAR FIRST DISABLED |
|---|---|
| Multiple sclerosis | 1979 |
| Back and leg pain | 1980 |
| Peptic ulcer-duodenal | 1976 |
| Myocardial Infarction | 1979 |
| Gastritis/duodenal ulcer | 1980 |
| Rhuematic heart disease | 1977 |
| Arthritis | 1976 |
| Histoplasmoma/breathing difficulty | 1977 |
| Degenerative disc disease | 1976 |
| Kidney cancer | 1979 |
| Esophagitis/Chronic obstructive pulmonary disease | 1979 |
| Emphysema, hypertension, chronic prostatitis urinary tract infection | 1977 |

# APPENDIX 1

## Acrylamide

Analysis of seven (7), 15-ml impinger samples for acrylamide. These samples were analyzed by gas chromatography using a nitrogen-phosphorus detector.

Seven impinger samples were submitted for analysis of acrylamide. These samples were processed in accordance with the OSHA Method Number 21 for acrylamide, with modifications. The modifications were made because of the collection matrix which was $H_2O$ in the impingers submitted. The modifications were in the selection of columns and the temperature program of the gas chromatograph. No peaks were detected on any of the samples. The detection limit for acrylamide is about 0.00113 mg/ml. Since the sample was collected in 15 ml of $H_2O$, the limit of detection was 17 ug/sample.

## Dimethylamine

The eight silica gel tube samples were analyzed for dimethylamine by NIOSH P & CAM Method No. 221 (modified). The A and B portions of the samples were separately desorbed with 1 ml of 0.4 N HCl in 80% methanol. One-half (1/2) ml of each sample solution was then made basic with 1/2 ml of 0.5 N NaOH in 80% methanol containing triethylamine as an internal standard. The sample solutions were subsequently analyzed by gas chromatography using a Hewlett-Packard 5731A GC equipped with a nitrogen/phosphorous detector. A glass column (6' length x 1/4" diameter) was used packed with 4% Carbowax 20M + 0.8% KOH on 60/80 mesh Carbopack B. The oven temperature was programmed from 70°C to 170°C at a rate of 8°C per minute. The limit of detection was 0.01 mg analyte per sample tube for this analysis.

## Bis (chloromethyl) ether

Each of the impinger samples were analyzed according to NIOSH Method P & CAM 220 (modified) using a Tracor MT 222 gas chromatograph with an electron capture detector. A 6' x 1/4" (4 mm i.d.) glass column packed with 3% QF-1/3% OV-17 on 100/120 mesh Gas Chrom Q was used isothermally at 170°C with a gas flow rate of 30 ml per minute, using 5% methane in argon as the carrier gas.

The samples and blank for BCME detection contained more interferring peaks than did the standards and blank generated internally. This may have been due to the impurities of the 2,4,6-trichlorophenol in the impinger solution. The internal standards and blank were made up with an impinger solution which contained recrystallized 2,4,6-trichlorophenol. This was a recommendation taken from an article by Marsha L. Langhorst, Richard G. Melcher, and George J. Kallos entitled Reactive Adsorbent Derivative Collection and Gas Chromatographic Determination of Chloromethyl Methyl Ether in Air located in the American Industrial Hygiene Association Journal 42, January 1981, pages 47-55.

The limit of detection was 0.01 ug/sample or 0.5 ppm (v/v) assuming a 4-liter air volume for bis (chloromethyl) ether in impingers.

## Epichlorohydrin

Epidhlorohydrin samples were analyzed by gas chromatography according to NIOSH Method S-118 with modifications.

The A and B sections of the samples were separately desorbed in 1 ml of carbon disulfide containing 1 ul/ml toluene as internal standard. The analysis was performed using a Hewlett-Packard 5731A gas chromatograph equipped with a flame ionization detector. A 20' x 1/8" stainless steel column packed with 5% FFAP on 40/60 Chromosorb T at an isothermal oven termperature of 120°C. The limit of detection for epichlorohydrin was 0.01 mg.

## Sulfuric Acid

These seven filter samples labeled with the indicated laboratory numbers were analyzed for sulfuric acid via ion chromatography. NIOSH Method P & CAM 268 was followed in preparing the standards, samples, and blanks. To enhance the sensitivity of the method, three procedural modifications were adopted: (1) an additional anion separator column was placed in series with the separator column described in the method; (2) a slightly weaker eluant, 3.0 mm $NaHCO_3$/2.4 mm $Na_2CO_3$, was used; and (3) a series of standards covering the analytical range 0.6 to 40 ug/ml $SO_4$ was prepared. Results are reported in micrograms sulfuric acid per filter. A limit of detection of 5 ug $H_2SO_4$/filter is estimated.

APPENDIX 2

Organic Flocculants Department
American Cyanamid Kalamazoo, Michigan
Process Area Ventilation Modifications

1. Replace 3" duct from reactor vessel 120-006 sample head with 4". Approximately 30', 6 elbows, 1-30' entry to 12" duct.

2. Replace slot hood on reactor vessel 120-003 agitator with 5" round hood with 2" flange. Replace 3" duct with 5". Approximately 5', 2 elbows, 1-45° elbow, 1-30° entry to 7" duct.

3. Replace 3" duct from reactor vessel 120-001B sample hood with 3 1/2". Approximately 4 1/2', 5 elbows, 1-45° entry to 8" duct.

4. Replace 3" duct from reactor vessel 120-001A sample hood with 3 1/2". Approximately 18', 1 elbow, 3-45° elbows, 1-45° entry to 11" duct.

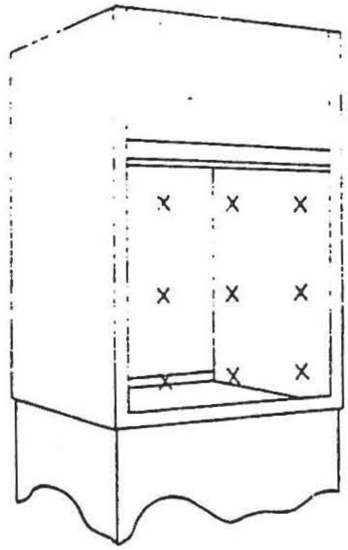
5. Build two new hoods for reactor vessel 130-006 pump per sketch. Duct the two hood together with 5" duct. Approximately 3 1/2', 1-90° elbow, 1-45° elbow each. After the two join, run 6 1/2" duct to main. Approximately 16', 1-90° elbow, 2-45° elbows, 1-45° entry to 11" duct.

6. Replace 8" duct with 11" duct on 1st floor. Approximately 8', 1 elbow.

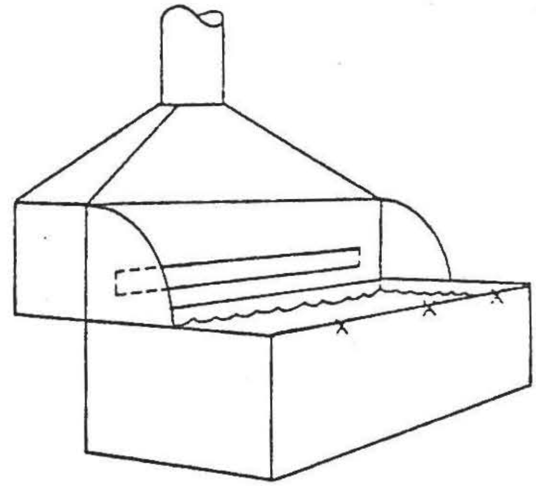
Duct work to be aluminum, hel-arc welded.

Work to be done according to Cyanamid Standard Specification No. GS-150.

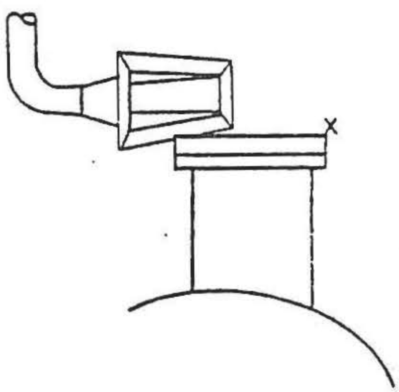
HE 80-190
FIGURE 1



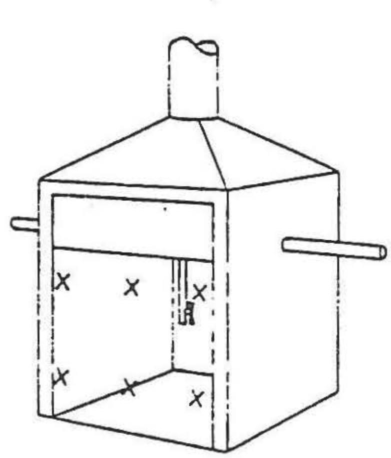
A. Laboratory Bench Hood



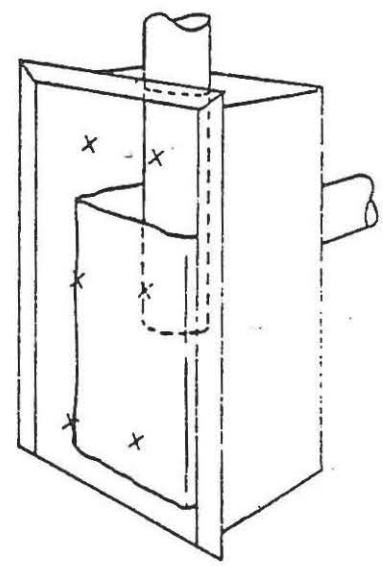
B. Wash Tank With Slot Hood



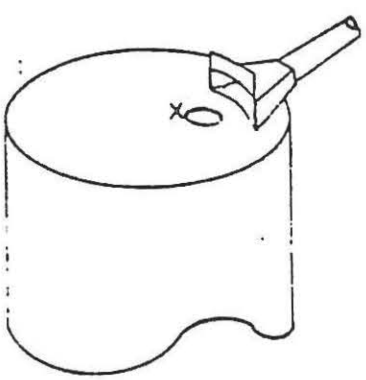
C. Dip Sticking Port With
Slot Hood



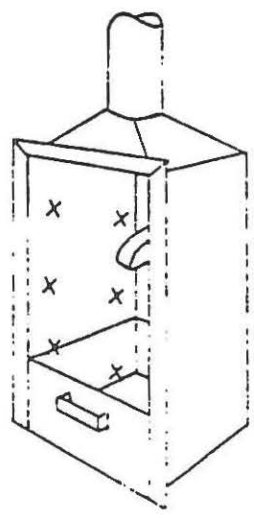
D. Sampling Station Hood



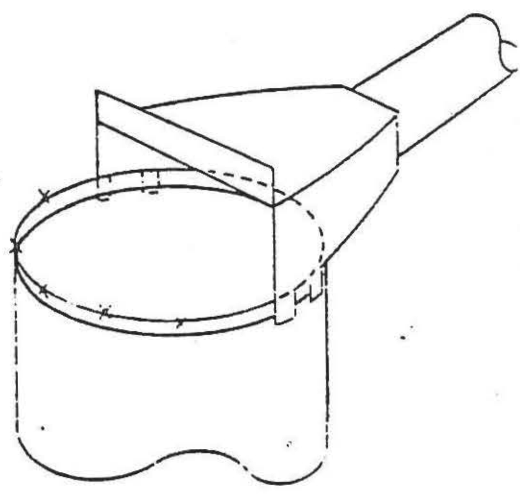
E. Bag Packing Hood
(Open Bags)



F. Flanged Slot Hood
For Drum Filling



G. Valve Bag Packer
Hood.



H. Hood For Open Tank

X's Indicate Locations Where Specified

FIGURE 2

American Cyanamid
Kalamazoo, Michigan
. HE 80-190

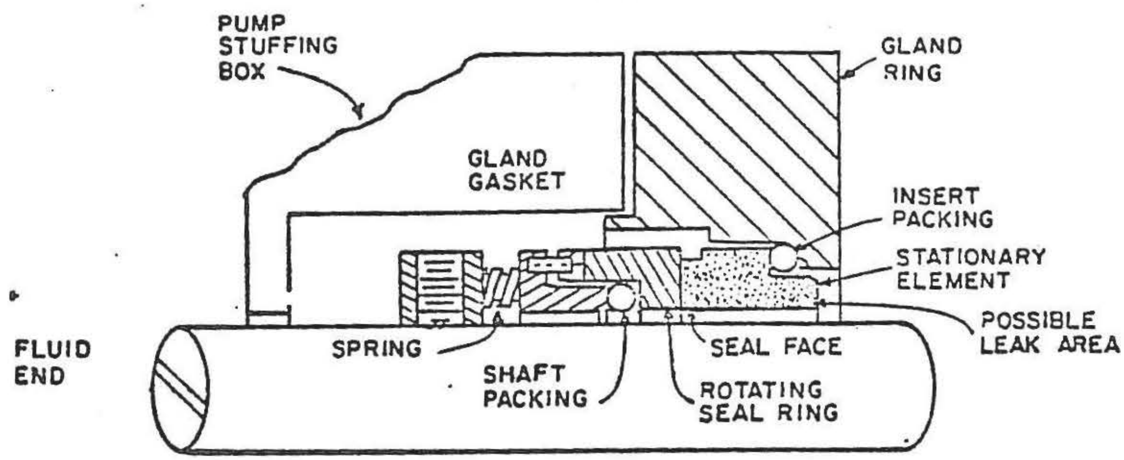



Diagram of a Basic Single Mechanical Seal
(Better)

---

FIGURE 3

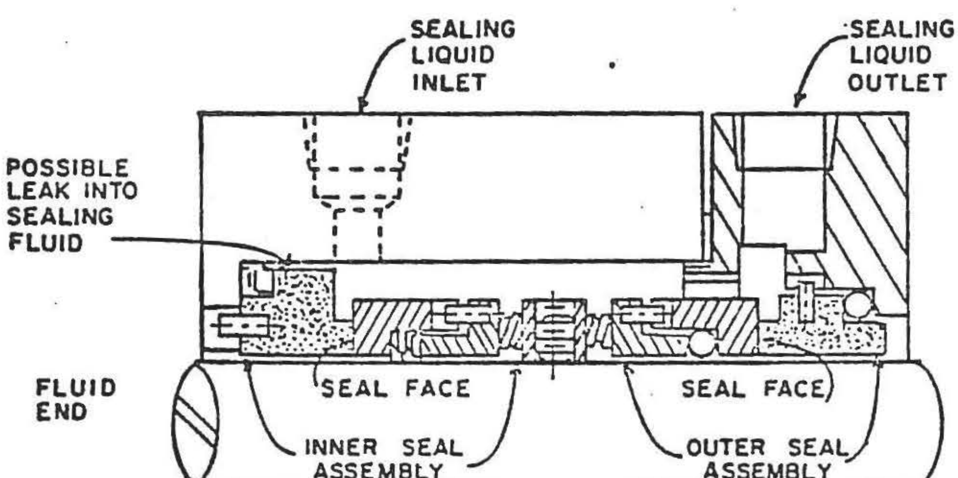



Diagram of a Double Mechanical Seal (back to back)

(Best)

Figures 1 and 2 reprinted with permission from EPA, Reference 4.