

Epichlorohydrin
Manufacture and Use
Industrial Hygiene Survey

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Abstract

Five epichlorohydrin facilities were selected for industrial hygiene survey studies, two of which were both manufacturers and users and three were users only. Walk-through industrial hygiene surveys were conducted at each plant site, preliminary information collected and plant reports prepared. Detailed industrial hygiene surveys were then made to conduct personal and area sampling in these plants over periods of three shifts. Results of these completed industrial hygiene surveys were then reported individually.

This report consolidates the findings of these studies conducted in the five plants. The report includes the air sampling data collected, summary tables of worker exposure levels to epichlorohydrin and associated solvents or process materials, evaluation of exposure level measurements, exposure controls efforts, and recommendations.

Chemical operators represent the job type that has the greatest exposure to epichlorohydrin in the manufacturing and resin manufacturing processes. Epichlorohydrin manufacturing processes indicate exposures ranging from non-detectable to 2.1 ppm for epichlorohydrin and from non-detectable to 8.9 ppm allyl chloride for 20 samples in 2 plants. The five resin processing plants representing 39 samples showed exposures to chemical operators ranging from non-detectable to 0.83 ppm for epichlorohydrin.

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INTRODUCTION

AUTHORITY

NIOSH has been granted the authority and responsibility under the "Occupational Safety and Health Act of 1970" to conduct field research studies in industry, evaluate findings and report on these findings (1). Section 20(a)7 of this Act states that NIOSH shall conduct and publish industrywide studies of the effects of chronic or low-level exposure to industrial materials, processes, and stresses on the potential for illness, disease or loss of functional capacity in aging adults. Section 20(c) provides the authority to enter into contracts, agreements, or other arrangements with appropriate public agencies or private organizations for the purpose of conducting studies relating to responsibilities under the Act. For this purpose NIOSH established a contractual agreement with Tracor Jitco, Inc. to perform an industrywide study of worker exposure to epichlorohydrin.

PURPOSES OF THE STUDY

There are many chemicals used in industry for which there are insufficient data and experience to determine the extent of worker exposure and the long term biological effects on exposed workers. Additionally, there is a need to determine the effectiveness of control measures presently in use by industry, and to identify work practices and other control methods which would limit worker exposures.

The primary purposes of the industrial hygiene study are to determine worker exposure to epichlorohydrin and to document existing engineering controls, work practices, administrative controls, and biological and environmental sampling requirements and control procedures being used by the companies. Individual walk-through and complete industrial hygiene survey reports were prepared for each plant and submitted to NIOSH, company management, the national and local union, and the NIOSH and OSHA regional office.

LIMITATIONS OF STUDY

The industrial hygiene surveys represent singular evaluations of worker exposures to epichlorohydrin and do not reflect possible variations in exposure due to seasonal or operational changes. An attempt was made to evaluate exposures for each job type as encountered during all work shifts. These studies were made during periods of normal production. Encountering a highly unusual exposure situation during a sampling period of several shifts was remote; therefore, the resulting exposure measurements are considered to represent those that are associated with the usual and normal operating conditions.

Generally, the samples also do not reflect exposures during maintenance operations. Routine maintenance is often accomplished at specified times during the year. On these occasions, safety procedures which are designed to minimize exposure are followed. On-stream maintenance or repair work is common and may result in significant short term exposure unless safe work procedures are followed. When maintenance operations were encountered during the sampling period, exposure measurements were made and so identified. Whenever there were potential significant exposures to other process materials associated with epichlorohydrin work areas these were also evaluated.

CRITERIA FOR EVALUATIONS

The permissible concentration for epichlorohydrin is 5 ppm or 19 mg/m³ as a TWA exposure level (2). The CRITERIA FOR A RECOMMENDED STANDARD . . . OCCUPATIONAL EXPOSURE TO EPICHLOROXYDRIN published by NIOSH, September, 1976, recommends a permissible concentration for epichlorohydrin of 0.5 ppm (1.9 mg/m³) as a TWA with a ceiling concentration of 5 ppm (19 mg/m³) for a 15 minute period during the work shift (4). The permissible concentrations (2,3) for the associated process chemicals and solvents are as follows:

Allyl chloride	1 ppm or 3 mg/m ³
MEK	200 ppm or 590 mg/m ³
MIBK	100 ppm or 410 mg/m ³
Acetone	1000 ppm or 2400 mg/m ³
Methylene chloride	200 ppm or 720 mg/m ³
Toluene	100 ppm or 375 mg/m ³
Xylene	100 ppm or 435 mg/m ³
Methyl cellosolve	25 ppm or 80 mg/m ³

Effects of Exposure to Epichlorohydrin

The acute effects on humans of over exposure to epichlorohydrin are irritation of eyes and throat, facial swelling, nausea, vomiting, headache, dyspnea, coma and possible death; skin exposure can result in severe burning and eczema, as well as systemic poisoning by absorption through the skin. A more complete discussion of exposure effects is contained in the NIOSH criteria document (4).

STUDY DESCRIPTION

TYPES OF PLANTS, PROCESSES AND OPERATIONS SURVEYED

Five plants were surveyed for this report. Two plants were both manufacturers and users of epichlorohydrin, and three plants were users only. These plants were selected for study because they were considered to be the best suited to conduct future mortality studies. The surveys were conducted between February and August, 1976. Exposures to epichlorohydrin and associated process solvents were evaluated.

Plant Descriptions

Plants A and B are manufacturers and users of epichlorohydrin located in the southwest U.S. Both are of conventional open structure chemical process design. Practically all products are synthesized from petroleum products and/or sea water.

Plant A was built shortly after World War II and presently comprises over 1,000 acres housing a multiplicity of chemical manufacturing plants. The production complex is broken into blocks, and with a few exceptions, each block houses a distinct manufacturing facility. Allyl chloride, the starting base from which epichlorohydrin is synthesized, is produced in one block and delivered to glycerine production by pipe line. Epoxy resins are manufactured in an epoxy unit which is located about 1 mile from glycerine production. Epichlorohydrin is pumped from glycerine production and stored in closed tanks.

Plant A has been producing epichlorohydrin since 1956. The plant was designed to minimize worker exposure to epichlorohydrin and other process chemicals and there have been no substantial design changes since the plant has been on stream. However, there have been constant programs for equipment updating and increased use of automatic control equipment as new technology became available. The plant has a design capacity of 260 million pounds of epichlorohydrin per year. The greater portion of the epichlorohydrin produced is for captive use in the production of glycerine and epoxy resins; some of the production is shipped for customer use in tank cars, tank trucks, or drums.

Plant B, a petrorefining and petrochemical manufacturing operation, began production of epichlorohydrin at this site in 1945. The glycerine plant is located in the petrochemical manufacturing area and employs about 10% of the manufacturing plant work force. Epichlorohydrin is manufactured in the glycerine plant, used directly for glycerine manufacture, piped to storage for shipment, or piped to the epoxy manufacturing plant which is located in the complex but about ½ mile to the east. Plant B is comparable to Plant A in size.

Glycerine plant production of epichlorohydrin began in 1948. The process has undergone some changes during this period primarily in the manner of reacting the internal process ingredients. Initially the glycerine plant production of epichlorohydrin was used primarily for glycerine production. While the demand for glycerine and glycerine production has diminished, the use of epichlorohydrin for epoxy resin production has increased. To meet the demand for epoxy resin production some epichlorohydrin is delivered by barge to this plant B site from another plant site. Plants C, D, and E are epichlorohydrin users.

Plant C, located in the southcentral U.S., was purchased in 1965 for the manufacture of a number of different resins and coatings, including the epoxy resins. Epoxy resins are manufactured in an enclosed four-story building in which other processing also takes place. This building, though enclosed, has window openings on all floors and has good natural ventilation. Mechanical ventilation is also provided on each floor by a 36" wall exhaust fan. A central process control room housing the process monitoring equipment is located on the west side of the third floor. This control room is enclosed and generally isolated from the processing area. The chemical operators monitor the reaction parameters and maintain the processing records in this control room. Storage and weigh tanks are located on the fourth floor. The main epoxy storage tank and pumping equipment is located out-of-doors adjacent to a railroad siding. Recycled wet-epichlorohydrin is stored in receiving tanks located in an isolated room in a nearby building.

Production of epoxy resins actually began at the Plant C site about 1952. In the early days of manufacturing, epichlorohydrin was received in drums and had to be poured, as needed, into the weigh tanks or into the feed lines to the reaction vessels. Although the basic batch process has remained the same, epichlorohydrin exposures have been substantially reduced as the result of converting the open pour technique to a closed pipeline system. Processing variables are modified to obtain the resin properties desired by customers, producing both liquid and solid resins. Production of resin increased from the late 1950's until 1975 when market demand slumped and production declined; production was expected to resume an upward trend. The plant consumes several million pounds of epichlorohydrin per year.

Plant D, located in the southern U.S., is engaged in the processing of crude tall oil and the manufacture of products for the pulp and paper industry. Epichlorohydrin is used in Plant D only in a semi-enclosed two-story resin production building that is centrally located within the plant complex of buildings, processing equipment, and storage facilities. The resin building has adequate natural ventilation with two 30" diameter openings located in the roof, and doors and windows normally open. There is also a 9' x 6' opening in the east wall of the 2nd level kettle area with a 36" pedestal fan located adjacent to this wall opening directing air toward the kettle area. A 7' x 3' door on the west wall also provides natural outside air flow into the 2nd level kettle area. Natural ventilation inflow from the two openings measured 6150 CFM to the 2nd level operator's work station-kettle area at the time of the survey. The ground floor has open walls and is normally unoccupied except during inspections or for use as a passageway.

The processing equipment involved at plant D is minimal, primarily several totally enclosed reaction vessels and associated storage, mixing, and weigh tanks, and pumps and associated piping systems. The operator's primary work station is located at the top of the reaction kettle (2nd level-kettle room) where the process controls and a viewing port in the kettle are located. Epichlorohydrin is received in tank trucks and transferred to a storage tank located several hundred yards from the resin production facility, adjacent to a railroad track and roadway. The epichlorohydrin is pumped from storage to the production area as needed for the batch process operations.

Use of epichlorohydrin in Plant D in the production of wet strength resins for use by the paper industry has been continuous since 1952 using essentially the same processing methods and equipment. Plant D is comparatively smaller than the other plants surveyed. It is one of several small resin producing plants operated by this company.

Plant E's former epichlorohydrin production plant, the epoxy resin manufacturing plant, and the dyestuffs manufacturing plant are all located in a large, wooded, 1250 acre site in the eastern U.S. Epoxy production is conducted in a large, enclosed three-story building; production occupies all three floors of over one-half the building. The remaining portion of the building is used for storage and other chemical processing. The building is one of a number of similar size and design located in the complex. The batch process reaction vessels (kettles) and ancillary equipment, i.e., process pipes and vent lines, pumps, and control equipment, occupy most of the epoxy production area. The first level contains resin filters, the resin flaker machinery, and drum/bag filling stations.

The Plant E epichlorohydrin production facility, no longer operative, is located approximately 200 yards from the epoxy resin building. It is of conventional open structure chemical processing design with an adjacent enclosed process control room where the chemical operators monitored the process.

Plant E produced epichlorohydrin from 1960-1966; the production level was regulated by the demand in epoxy resin production. The plant was capable of producing 35 million pounds per year of epichlorohydrin, all captive to resin manufacture.

Epoxy resins have been produced continuously at Plant E since 1958. Past production figures were not obtained. However, this plant is a major producer of epoxy resins and current production is about 25 million pounds per year.

Process Description

Epichlorohydrin Manufacture:

At plant A, allyl chloride, chlorine, and water are fed to a reactor which yields a mixture of 70% 1,3-dichlorohydrin and 30% 1,2-dichlorohydrin. These products are washed with a cold dilute alkali solution to remove hydrochloric acid and to yield an impure epichlorohydrin. The impure epichlorohydrin is steam distilled to produce crude epichlorohydrin; in the process the light

ends are removed and flared. Crude epichlorohydrin is distilled in a fractionating column to produce epichlorohydrin of 99+% purity. The residue from the distillation column are the heavy ends (Figure 1).

Epichlorohydrin is produced in Plant B by the same general process as in Plant A. Allyl chloride is made by chlorination of propylene. Glycerine is made by hydrolysis of epichlorohydrin. All processing is enclosed in process equipment and piping systems. See the epichlorohydrin process flow sheet (Figure 2). Propylene is purified in several stages of finishing columns and then reacted with chlorine to produce the allyl chloride which is finished for feed to the epichlorohydrin production area and to storage for shipment. Allyl chloride, chlorine, and water are fed to a dynamic reactor which forms dichlorohydrin and HCL. Introduction of caustic (NaOH) and heat results in the production of epichlorohydrin and a salt (NaCl) brine. A portion of the epichlorohydrin is subject to high temperature hydrolysis (heat and Na_2CO_3) to form the crude glycerine. The glycerine is finished in an adjacent glycerine production area. Products and feed materials are stored at the tank farm; intermediate and finished product/by-product transfers also take place at the tank farm.

Epoxy Resin Manufacture:

Plant A employs two processes for producing epoxy resins: Continuous and batch. In the continuous process, epichlorohydrin is condensed with bisphenol A to form a liquid epoxy resin. The entire system is closed. Excess epichlorohydrin is stripped from the reacted mixture and returned to the storage tank. In the batch method, various epoxy resins are made in kettles by condensation of epichlorohydrin and other substances to form a novalac resin. All kettles are sealed and discharged into a closed system. Excess epichlorohydrin is stripped from the mixture and returned to the storage tank. Solvents used in the production of resins include toluene, methyl ethyl ketone, and methyl isobutyl ketone. Resins are pumped to the resin finishing area also located in the epoxy production area. Most of the workers employed in this area are concerned with resin finishing and shipping. When the resin reaches the finishing area it contains no free epichlorohydrin. (See the generalized epoxy resin manufacture flow sheet - Figure 3.)

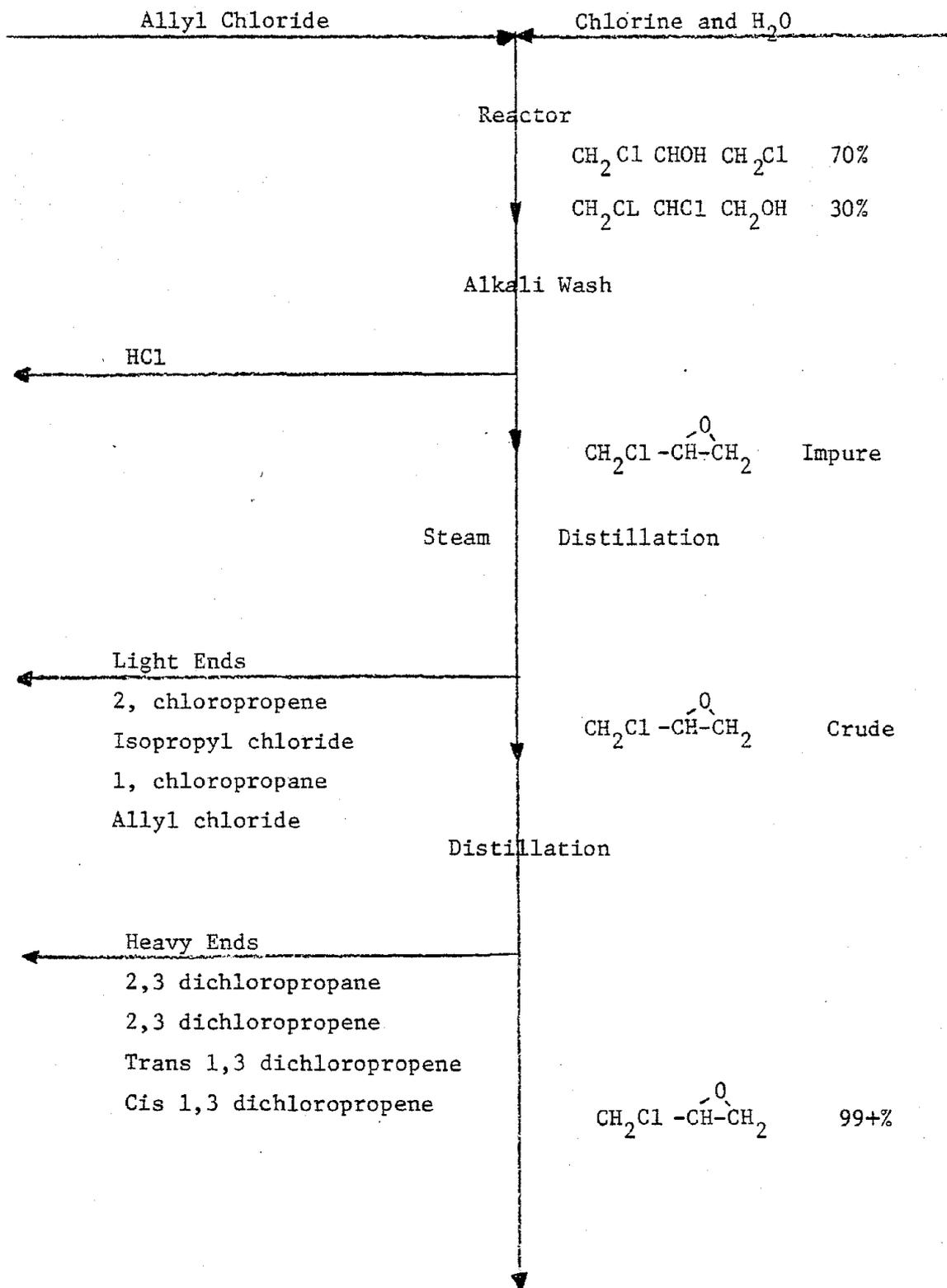


Figure 1
 Flow Diagram for Manufacture of Epichlorohydrin
 Plant A

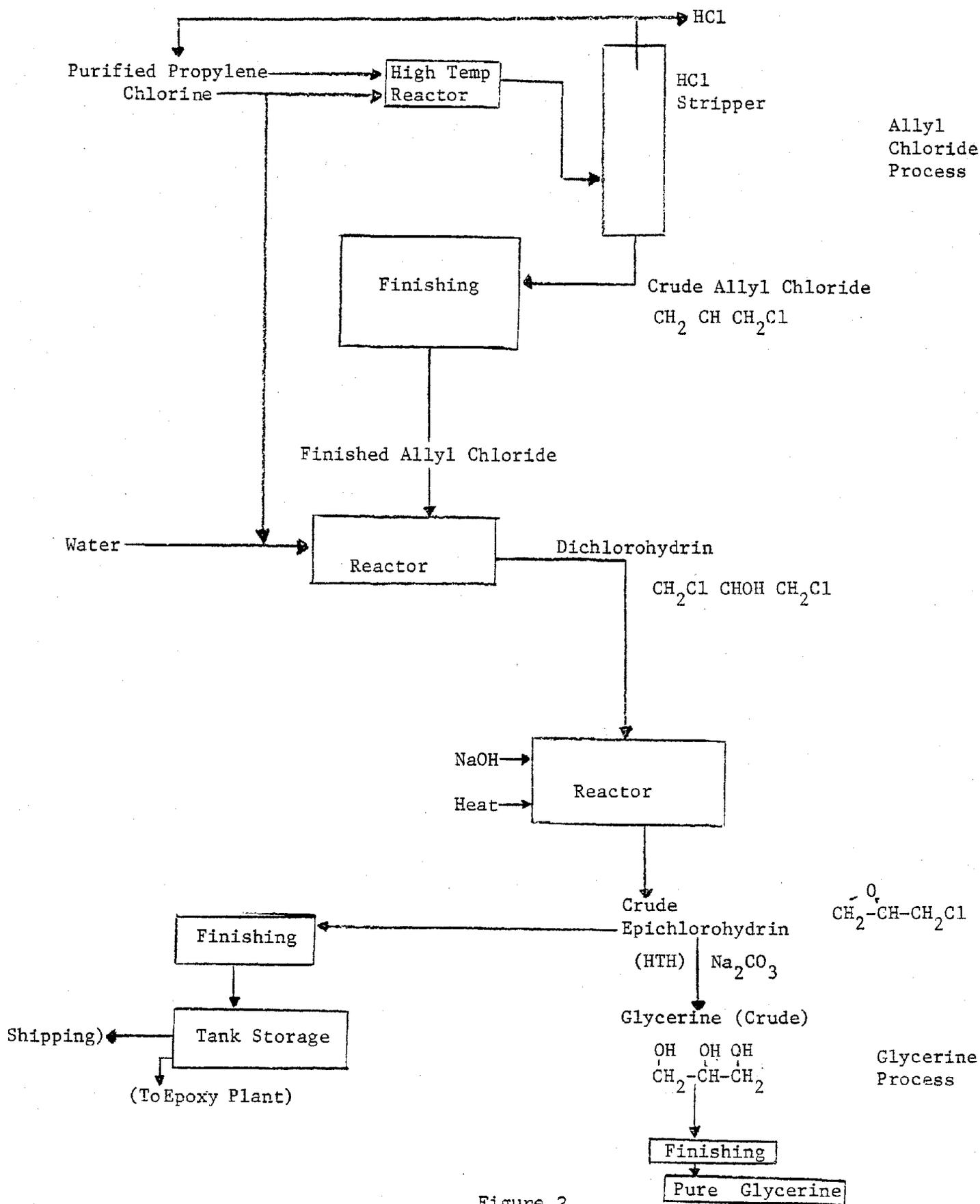
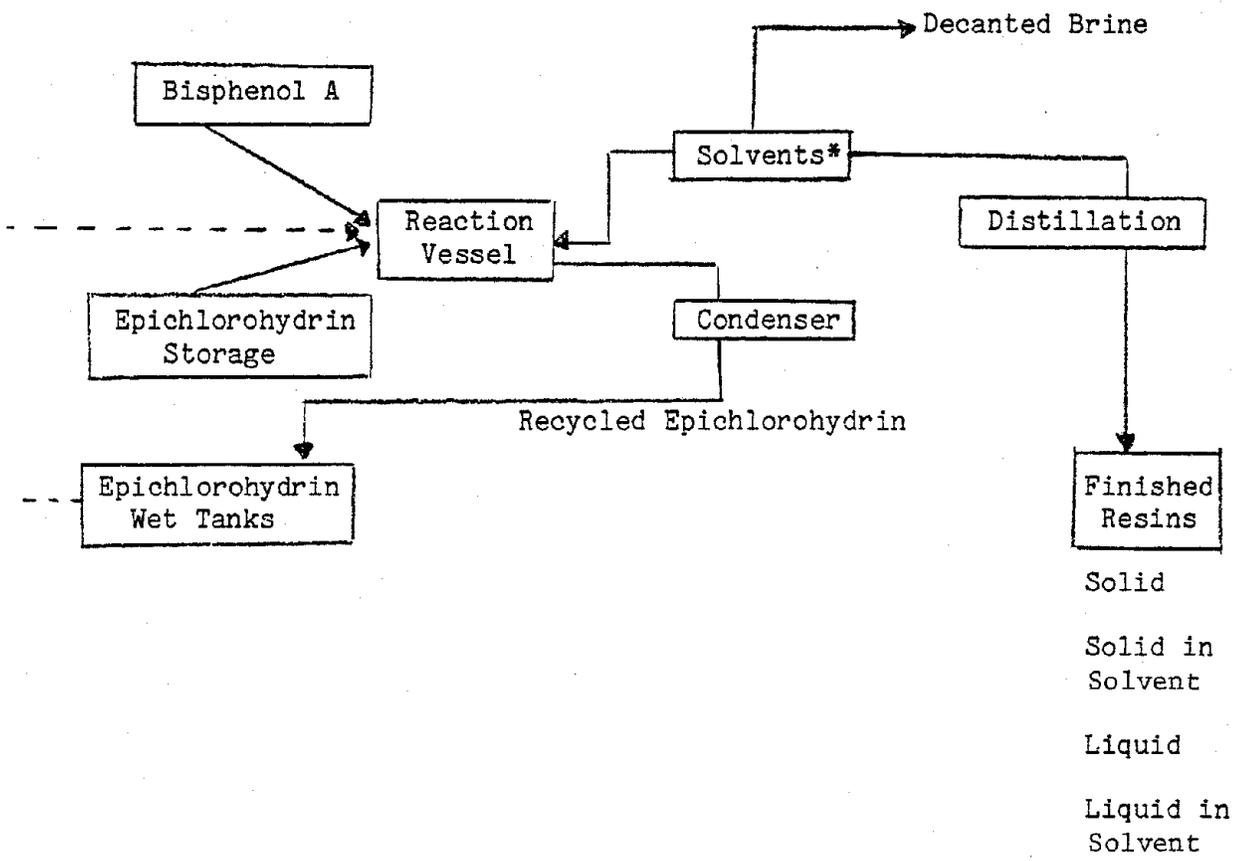


Figure 2

Flow Diagram for Manufacture of Epichlorohydrin with Allyl Chloride and Glycerine Process Plant B



* Solvents include low boiling ketones such as MEK, MIBK, acetone, and xylene, toluene, methyl cellosolve, and methylene chloride.

Figure 3
General Process Flow Sheet

The epoxy resin manufacturing operations of Plant B involve reacting epichlorohydrin and bisphenol A and caustic as in Figure 3. When the desired reaction is complete, the aqueous brine is removed and the resin transferred to finishing where, depending on the process, solid, solid-in-solvent, liquid, or liquid-in-solvent product is produced. The various processing and/or solvent steps include the use of low boiling ketones such as MIBK and acetone.

At Plant C, epichlorohydrin is received in railroad tank cars and stored in an outdoor storage tank. It is pumped, as needed, from storage to weigh tanks located on the fourth floor of the epoxy resin building. Weighed batches then flow by gravity to the reactors (kettles) where they condense with the bisphenol A (or other reactant) exothermally (Figure 3). All feed materials are charged to the reaction vessel through piped connections. The reaction vessel has a water jacket which allows control of the temperature and reaction rate. The kettles are totally enclosed and operate at near atmospheric pressure until after the reaction is complete and then air pressure is applied to the reaction kettle to draw off the supernatant water-brine. The reaction mixture is neutralized with acid and solvent is added. The resin-in-solvent is filtered and the solvent may then be distilled off and recycled. The resin produced is a reactive epoxy compound varying in molecular weight according to the reactant used and the degree of polymerization; it, therefore, may be liquid (perhaps a very viscous liquid) or solid. The liquid resins are shipped in railroad tank cars; the solid resins are shipped in bags.

Some resin process recipes require the raw material epichlorohydrin; others allow use of the recycled (wet) epichlorohydrin.

Plant D produces several polyamide resins, which are sold to the paper industry to provide wet-strength characteristics to paper products (6).

Epichlorohydrin, polyamine, adipic acid, water, and sulfuric acid are the raw materials involved. Polyamine and adipic acid are reacted in an enclosed reaction vessel and fed to a second enclosed reaction vessel, diluted with water to a prescribed solid content, and then reacted with the epichlorohydrin which flows from an enclosed weigh tank through a continuous piping system. Sulfuric acid and a large volume of dilution water are added to the resin solution which is then cooled and pumped to tank cars, tank trucks, or drums for shipping. The resin forming reaction effectively complexes all of the epichlorohydrin and the resin solution contains no free, i.e., unreacted, epichlorohydrin.

At Plant E, epichlorohydrin was manufactured by the conventional continuous process. All epichlorohydrin produced was for captive use in the production of epoxy resins. Thus, operations were sporadic and production varied according to resin processing demands.

The basic resin manufactured at Plant E is the product of a controlled reaction (condensation) of epichlorohydrin and bisphenol A under alkaline conditions in a batch process (closed systems). Depending upon the particular resin being produced, reactants and/or solvents may be introduced to modify the resin properties and the viscosity of the liquified resin products. A variety of reactants are used in the production of various resins. Solvents

used include methyl ethyl ketone, methyl isobutyl ketone, acetone, toluene, and xylene. Epichlorohydrin is received in railroad tank cars and is pumped to storage and to the process. The reactants used, dependent upon customer and production requirements, include, in addition to bisphenol A, tetrabromo bisphenol A, o-cresol, paraformaldehyde, caustic soda, oxalic acid, and p-tertiary butyl phenol.

Operations Surveyed

The industrial hygiene study of the Plant A epichlorohydrin facility was conducted between July 11 and 15, 1976. During this period, air samples were collected to evaluate exposures to epichlorohydrin, allyl chloride, and benzene. Benzene was a potential low-level contaminant originating from an adjacent production area and not a by-product of the epichlorohydrin process.

In Plant A epoxy production the two operators concerned with the formulation of resins were sampled. These are the only two jobs in the plant that have a potential exposure to epichlorohydrin except in unusual situations such as during repair or replacement of process equipment.

During the industrial hygiene study at Plant B, conducted August 8-12, 1976, air samples were collected to evaluate the worker exposures to epichlorohydrin in the epoxy resin plant and to epichlorohydrin and allyl chloride in the glycerine production plant. In addition, the solvents MIBK, MEK, and acetone which are used in the epoxy resin production plant were evaluated.

Air samples were collected at Plants C (February 24-25, 1976), D (June 17, 1976), and E (May 10-13, 1976) to evaluate exposure to epichlorohydrin in the epoxy resin production areas. In addition, exposures to process solvents were evaluated at Plant E.

WORKER JOB DESCRIPTIONS AND JOB TITLES

Both Plants A and B employ 50-60 persons in epichlorohydrin production; the work force includes production workers (operators), supervisory personnel, and maintenance personnel. All plants surveyed employ 30-50 persons, primarily chemical operators, in epoxy production.

Epichlorohydrin Production

Glycerine production in Plant A employs 50 persons including supervisory staff, engineering, laboratory, and production workers. Although all employees in the Plant A glycerine unit may have an occasional exposure, production workers have the greatest potential for exposure to epichlorohydrin. All supervisory and technical staff are housed in the administrative area which is air conditioned. The control room, immediately adjacent to the administrative area, is also air conditioned. Other workers include: Production foreman, shift foreman, operators, maintenance, and packaging. Production foremen are housed in the administrative area and act as assistants to the superintendent; they supervise production and coordinate activities of the shift foremen. Shift foremen have supervisory responsibility for production and maintenance. They are housed in the control room, but, depending on operational problems, may spend from 50% to 100% of their work shift in the production area.

There are two classes of operators in Plant A: Control A and Control C. Control A is the senior operator and is responsible for monitoring control instruments and making necessary adjustments to maintain production. Normally an operator spends more than 80% of the work shift in the control room. Each Control A Operator will inspect the production area at least twice during the shift and will investigate or correct operational problems in the production area.

The Control C Operator spends about 50% of the work shift in the production area; one of his major duties is the collecting and analysis of the process samples. During the sampling operation he is required to wear an organic vapor respirator. At the time of the study, automatic sampling and analysis equipment was being installed to relieve the Control C Operator of the sampling responsibility. During the study there was an Operator C trainee for two work shifts. The trainee performed the same duties as the Control C Operator.

Plant A maintenance personnel are primarily mechanics and pipe-fitters. Maintenance of electronic instruments and electrical equipment is provided by other units of the division. Maintenance personnel serve the entire block, thus, exposure to epichlorohydrin is a function of the time spent in repairing and servicing epichlorohydrin units.

There is one Head Packaging Operator and four general operators in Plant A. The Head Packaging Operator spends most of his time in supervisory and administrative duties; the four general operators are responsible for loading epichlorohydrin into railroad tank cars, tank trucks, and drums. In addition, they maintain the warehouse and load trucks with filled drums.

Plant B glycerine operating personnel are employed around the-clock with about five men required per operator job. Supervisory personnel such as the shift foreman and the maintenance foreman are employed each shift. In addition, about ten maintenance personnel are assigned to the glycerine area. The total work force amounts to some 60 employees during normal production periods; however, this number varies considerably. For instance, a large complement of maintenance workers, perhaps 150, may be employed in the plant during a turnaround period.

The job types in Plant B glycerine production that may have significant exposures to epichlorohydrin because of the nature and location of the work, include G100 operators whose duties include process control of propylene and allyl chloride purification associated with the manufacture of crude and finished allyl chloride, G300 operators whose duties include process control of epichlorohydrin manufacture including chlorine, water and allyl chloride to dichlorohydrin to epichlorohydrin, C Plant operators whose duties include process control of epichlorohydrin crude to finished columns, HTH operator whose duties include process control of recycled wet epichlorohydrin and neutralizing with HCl to produce glycerine, Shift Foremen who supervise process operations, Maintenance Foremen who supervise maintenance (day shift only). Plant B glycerine operations are normally automated, and monitored and

operated from control rooms. Thus, most of the operating time is spent in the control rooms. However, the operators make frequent routine inspections of the process in the production areas or may conduct sampling or on-stream maintenance as required. Maintenance preparation is conducted by the operators and supervised by the shift foreman. Major maintenance work proceeds under the supervision of the maintenance foreman.

Epoxy Resin Production

During normal operations there are two operators in the epoxy resin areas of Plant A: Control B Operator who controls the batch operations and Control C Operator who controls the continuous operation. The two operators spend about 80% of the work shift in the control room and about 20% in the production area. The shift foreman spends most of his time in the resin finishing area; his office is separate from the control room.

Nine operators per shift, or about 45 operators, are employed at Plant B in the manufacture of the epoxy resins. In addition, three shift supervisors are employed per shift; a maintenance supervisor is employed on the day shift. Thus, about 60 employees work routinely in the epoxy plant area. The job types with potentially significant exposures to epichlorohydrin include 2A Kettle Operators whose duties include process control of manufacture of a solid epoxy resin, 3A Kettle Operators whose duties include process control of the manufacture of a liquid epoxy resin, 3A Utility Kettle Operators whose duties include process control in manufacture of liquid epoxy resin, Resin Train Operators whose duties include process control of liquid epoxy resins, Feed and Recovery Operators whose duties include process control in liquid epoxy resin manufacture of feed materials and recycling or recovery, and Shift Foremen who supervise the epoxy resin processes. In each of the process areas of Plant B, a control room houses the process monitoring instrumentation. The operators are in the control room a large part of each shift.

Plant C employs 30-40 persons in epoxy production. It is estimated that there may be 30-50 current employees who have some extended work experience in epoxy resin production. The work force is and has been quite stable. The employees include 260 hourly wage personnel; about one-half of these have worked in epoxy resin production. Internal movement is the rule since every man is expected to be able to do the various jobs in the department. Supervisors are expected to be able to supervise other departments so they rotate jobs between departments. Job openings are filled by bid and seniority/priority so men routinely move to more personally suitable jobs.

At Plant D, the process using epichlorohydrin employs from 2-5 resin operators and a supervisor over 3 shifts. Service and maintenance personnel have only occasional exposure to epichlorohydrin. The employee promotional scheme allows a chemical operator to advance by transferring to different operating jobs in the various departments in the plant. Therefore, a number of employees of this plant have had experience as an operator in resin production; the span of employment of any individual in resin production has, however, been of relatively short duration. It is estimated that 50 workers have been employed in the production of resins since 1952; since 1962, 22 workers have had assignments to this production area. Prior to 1962, records show only a general "operators" classification and do not identify the production area.

In Plant E, four chemical operators and one foreman were employed per shift during the years of epichlorohydrin production. It is estimated that about 50 workers were employed as operators or foremen in the epichlorohydrin plant during the period 1960-1966.

Presently, about 60 persons are employed in Plant E epoxy resin production. Identification of past employees can be obtained from seniority lists (1966-1975) and from old pay records and the personnel files. Availability of the older records (seniority and pay) was not clearly shown at the time of the plant survey, nor could a total number of employees who have worked in this department be provided at this time. However, it has been estimated that 200-250 might be expected to be identified if a search is done.

OBSERVATIONS AT WORK SITES

All of the plants surveyed have a medical program for employees and all provide pre-employment and annual medical examinations. Plants A and B have in-plant industrial hygiene programs which provide air sampling and analyses on a routine basis. Plant C secures industrial hygiene service on a contract basis and Plant D has no formal in-plant industrial hygiene service, but receives service from the corporate medical department which includes industrial hygiene. Plant E has detailed a production chemist to initiate a program of air sampling and analyses.

No long-term records of past exposures were maintained by any of the plants surveyed. Plant A began a sampling program in 1974 and Plant B in 1975. The remainder of the plants have only been collecting limited data since 1976.

The potential for respiratory and skin exposure exists in all of the plants, however, safety precautions are generally taken in all of the plants to prevent contact with the process chemicals. It was noted that workmen recognize the danger of contact with epichlorohydrin and generally avoid contact with all process chemicals. Also, when a leak develops, prompt corrective action is taken.

Medical Programs

The Plant A medical department is located immediately outside the plant area and is adjacent to a community hospital and health center. All major occupational accident and illness victims are hospitalized in the community hospital. The basic medical staff consists of a medical director, three staff physicians, and a research biologist; 14 staff nurses cover all production shifts. The medical department performs the usual function of an occupational medical service including pre-placement, termination, and periodic medical examinations. It is also very active in preventive health maintenance and in the epidemiologic and toxicologic investigations relative to the recognition and prevention of occupational illness and injury.

All Plant A workers assigned to allyl chloride, epichlorohydrin, and resin production receive a pre- and post-employment medical examination consisting of the following:

- Blood and urine analysis
- General physical examination and health history
- Chest X-ray
- Pulmonary function-FVC and FEV₁
- Electrocardiogram
- Vision test

These same workers are also examined on the following routine schedule:

Blood and urine	Annually
General physical examination	Over 40 years of age-every two
Pulmonary Function	years; under 40 years of age
Chest X-ray	every four years
Electrocardiogram	Over 40 years of age only-every
Vision	two years

At Plant B the medical program is closely allied with the company safety and health program. The medical program was only recently instituted; thus, complete records of exposure levels and medical findings, including occupational disease detection and reporting is not available. The company management has apparently provided long range support to the medical program and to the health and safety program and is expanding these programs to provide good medical services and improved preventive health and safety programs. An example of the efforts being made to determine the worker health experience as related to long term exposures to materials in the work environment is the ongoing epichlorohydrin study being conducted by Plant B.

The in-plant medical department of Plant C is staffed by a nurse who is on duty during the day at a first aid dispensary. A contract physician provides pre-employment physicals and may be called upon to provide medical services for job-related injuries. Injured workmen may be taken directly to a nearby hospital for treatment.

A local physician performs pre-employment and annual physical examinations for all employees of Plant D, and serves as the plant physician; he is on-site approximately 2 hours one day per week. The physician and a predecessor have provided this service for many years. Plant employees' medical records are maintained in the physician's office.

The Plant E medical department currently has two part-time contract physicians, a nursing staff, and an X-ray technician providing medical services to the facility. Pre-employment physical examinations are done. Annual blood and urine tests and chest X-rays, as well as special tests related to specific manufacturing operations, are done for production workers. A complete physical examination is available to all on a voluntary basis once every 1-3 years. A medical clinic is maintained at the plant site. A record is kept of all visits by personnel to the medical department and of all medical findings and treatments.

Industrial Hygiene Programs

Industrial hygiene in Plant A is a function of the Environmental Health Department which was organized in 1973. The Department, which serves the entire plant complex, is directed by a senior industrial hygienist who is assisted by three staff industrial hygienists. Between 1956 and 1973, industrial hygiene personnel were on the staff of the medical or safety department.

In addition to service provided by the department, each major production unit of Plant A has an environmental chemist on its staff who provides certain industrial hygiene services to the unit including area and personnel monitoring and sampling analyses. The environmental chemist is responsible to the superintendent of the production unit but works closely with the Environmental Health Department. The environmental chemist assigned full time to the glycerine unit is required to monitor all production areas once per month. Other monitoring is conducted as required when leaks are suspected or when equipment is being repaired or placed on-stream. Each worker is monitored each two years using the charcoal adsorption procedure. All substances adsorbed by the charcoal are determined. Based on these values, each worker is assigned an exposure index determined by dividing the TWA by the TLV for each substance and summing these values. If the index is over 1, corrective measures are taken; workers with an index between 0.5 and 1.0 are monitored each year. Exposure records are kept by the glycerine unit and the Environmental Health Department. If the worker transfers to another production area his exposure record goes with him.

The Plant A Environmental Health Department personnel serve as consultants and advisors to plant superintendents by providing advice on hazards and controls, and recommending monitoring programs. Additionally the Department performs special services and independent audits. All exposure data are reported to the Environmental Health Department. A system is presently being developed to maintain these records on an ADP system. The Department has a chemical laboratory but most of the analytical work is performed by the Central Research Laboratory.

The industrial hygiene program at Plant B has been continuously active since 1974; an industrial hygienist was employed at that time. An industrial hygiene graduate student assists during the summer months. The industrial hygienist reports to the plant manager of Safety and Industrial Hygiene as do a number of persons who are primarily concerned with maintenance of safe working conditions and who assist in inspecting, defining, and controlling the associated potential health hazards within the complex. The corporate manager, Safety and Health-Manufacturing, has overall responsibility for the Industrial Hygiene and Safety program.

The Plant C industrial hygiene program consists of annual industrial hygiene surveys conducted by National Loss Control Service Corp. (NATLSCO), periodic sampling by the Corporate Industrial Hygienist, and in-plant monitoring and area grab sampling by the Plant Safety Manager. Samples are analyzed by NATLSCO.

Plant D does not have an active industrial hygiene program on site. Industrial hygiene service may be provided by the corporation's medical department which includes an industrial hygiene staff.

No formal in-plant industrial hygiene program has previously existed at Plant E either. Some air sampling in the plant was done in the early 1970's. Currently, a production chemist has been detailed to initiate a program of air sampling and analyses as a part of an effort to develop an industrial hygiene program for the total plant.

Past Exposures

Exposure data for Plant A has been collected for epichlorohydrin and allyl chloride since the sampling program began in 1974. Even before this date, however, industrial hygiene services were provided by the central staff of the division and corporate headquarters. Exposure records are currently maintained by the Environmental Health Department as well as by the individual operating units. Examples of summary data collected from 1973 to 1975 are contained in Appendix A.

Exposure data for Plant B personnel has been collected for epichlorohydrin and allyl chloride since the sampling program was started in 1975. Some source samples were collected earlier in 1974. These records are maintained by the industrial hygiene program.

Worker exposure data to epichlorohydrin at Plant C has not been collected. Some air sampling has been done by plant personnel, but no detectable levels were found. It is possible that the levels of exposure on a time weighted average basis are very low since the chemical operators spend a considerable portion of their work-time in the semi-isolated control room located on the 3rd floor, and process chemicals are well controlled.

Most Plant C workmen have multiple exposures since several materials are used in every process. Also, since many have worked, at one time or another, in various process areas, their exposure history would be complex.

No exposure records are available for Plant D because exposures had not been determined before 1976. Constancy of the process parameters and the current air sampling could provide valid estimates of retrospective exposures for the operators in the production area. Plant D reported 8 air samples collected during 1976 in the resin production area showed results ranging from 0.07 to 0.36 ppm epichlorohydrin. This data is summarized in Appendix A.

Limited plant data on current air concentrations of epichlorohydrin in the epoxy area of Plant E show the levels to be less than 2.5 ppm and, under some conditions of limited ventilation, to be less than 5 ppm. No records exist on past exposure levels to epichlorohydrin or other materials. Processes and facilities have been essentially constant for epoxy resin production and thus exposure levels to epichlorohydrin have probably remained about the same since 1958.

Workers in the former epichlorohydrin production area of Plant E, in addition to being exposed to epichlorohydrin, would also have had some exposure to allyl chloride and trichloropropane, i.e., during the period 1960-1966.

Potential Exposures

In the glycerine unit of Plant A there are potential respiratory and skin exposures to a variety of chemical substances including allyl chloride, epichlorohydrin, and glycerine. Benzene is a low level area contaminant which originates in another production area. The light and heavy ends resulting from the production of epichlorohydrin are handled in such a manner that exposure to these substances would only result if an unusual emergency occurred. In the event of an emergency, there are potential exposures to chlorine or hydrochloric acid gas.

During normal operations in epoxy production of Plant A only the operators engaged in the formulation of epoxy resins are exposed to epichlorohydrin. Here the exposure is largely respiratory, but occasionally the operators may have skin contact with epichlorohydrin. There is also the possibility of skin contact with phenol, but extensive safety precautions are taken to prevent any contact with this material. Methyl ethyl ketone and toluene are also present as area contaminants. Methylene chloride is used to remove spilled resins; this procedure presents a limited hazard through skin contact with the solvent or inhalation of fumes.

Potential respiratory and skin exposure to a number of organic solvents, raw materials, and products in the production of epichlorohydrin, allyl chloride, glycerine, and epoxy resins were also noted at Plant B. These materials include allyl chloride and epichlorohydrin in the glycerine plant, and epichlorohydrin and low boiling ketones such as MIBK, MEK, and acetone in the epoxy resin plant. Since the processes are essentially totally enclosed and out of doors, the primary operator exposures are related to the inadvertent low leakage level (plant general air concentrations) or to the occasional relatively larger leaks which occur occasionally when gaskets at pipe flanges or pump seals fail. Also the use of solvent for maintenance or cleaning presents potential exposure to the solvent vapors.

Plant C uses over 600 raw materials; 97 of these are identified to workmen in a "pink sheet operating procedure" as having some hazard potential. Computer batch cards (instructions of ingredients to be used in production) identify the hazardous materials to be used by the operators in each process operation. Each hazardous raw material identified on the batch card is further described in the "Handbook of Dangerous Chemicals"; hazards precautions, protective equipment, first aid measures, and suggestions to physicians are outlined.

Epichlorohydrin exposures in Plant C may occur from any leakage from the enclosed process. The rate of leakage under normal operating conditions would appear to be minimal since the systems are well maintained and leakage is not tolerated. Similarly, exposure to solvents (ketones) is also a function of any process leakage.

As already mentioned, natural ventilation in the resin building of Plant D is appreciable. No earlier definitive epichlorohydrin air concentration measurements have ever been made in this plant. Epichlorohydrin is delivered by tank-truck, pumped through integral and continuous piping to storage tanks and then to the weigh tank at the location of use. Epichlorohydrin might escape this system only where a pipe or connection leaks, or a leaky pump seal develops. In the transfer of epichlorohydrin to the reaction vessel, some vapor might escape into the building if the reaction vessel port were left open. Epichlorohydrin odor can be occasionally detected on the charging floor of the reaction vessel where the operator is stationed.

Plant D is initiating studies to determine worker exposures to the various materials to which their employees are exposed. Since the resin production process involves several amines, some exposures to amines may occur in the work area.

In the epoxy resin area of Plant E the chemical operators are potentially exposed to the raw materials, intermediates, and final products of resin production. In addition, other process operations are conducted within the same building and the raw materials and products of these processes may contribute other potential exposures to these operations. Currently, these other processes may contribute possible building air contamination from other process materials including diethanolamine, diethylenetriamine, amino ethyl piperazine, and aqueous hydrazine. At the time of the survey, the general plant site and the working areas showed no evidence of general air contamination. However, at one outdoor location an odor of nitrobenzene was noticed.

SAMPLING PROCEDURES AND ANALYTICAL METHODS

The sampling and analytical method used in this study was developed under a NIOSH contract specifically for use by NIOSH in conducting evaluations of atmospheres containing epichlorohydrin. Details of the method are contained in Appendix B.

In practically all cases the sample duration was a significant portion of a full working shift, i.e., representative of the 8-hour shift. In a few cases, the sampling was only for a selected portion of the work shifts. The purpose of these samples was to determine exposure for intermittent work operations which could be defined, and to evaluate the effectiveness of the control methods in use. Most samples were collected using personnel samplers which were worn by the worker, thus providing time weighted average (TWA) exposure levels. Some samples were also collected in various general working areas.

Charcoal adsorption tubes used in the study were obtained from SKC (SKC, Inc., Environmental Sciences Division, P.O. Box 55, Venetia, Pa., 15367). The air sampling pumps used were SKC Model 222-351 Personal Pump and du Pont (E.I. du Pont de Nemours & Co., Inc., Applied Technology Division, Wilmington, Delaware, 19898) Model P200 Constant Flow Sampler.

At Plant B, paired air samples were collected simultaneously on the majority of the jobs (workers) sampled and these same jobs were sampled during three different shifts over a period of four days. Sample analyses were done in three separate laboratories. Plant B personnel collected samples in bags and

analyzed by gas chromatography and microcoulometry. NIOSH samples were collected on SKC charcoal tubes and analyzed in the NIOSH laboratory. Tracor Jitco samples were also collected on SKC charcoal tubes and analyzed in the Kettering Laboratory, University of Cincinnati Medical Center. Solvent samples were analyzed according to the method described by White, et al. (6). The standard method employing the 100 mg charcoal adsorption tubes presented no difficulties in sampling or analyses. Where ventilation measurements were made, the Alnor Velometer was used.

STUDY RESULTS AND DATA ANALYSES AND EVALUATION

Summary data resulting from the analyses of air samples collected at each of the plants surveyed are presented in tables C-1 to C-10, Appendix C. These data are referred to in the subsequent evaluation of these results. This air analysis data is arranged in the following manner:

Table C1	Epichlorohydrin Mfg. - Plant A
C2	Epichlorohydrin Mfg. - Plant B
C4	Epichlorohydrin Use/Epoxy Mfg. - Plant C
C6	Epichlorohydrin Use/Epoxy Mfg. - Plant D
C7	Epichlorohydrin Use/Epoxy Mfg. - Plant E
C8	Epichlorohydrin Use/Epoxy Mfg. - Plant A
C9	Epichlorohydrin Use/Epoxy Mfg. - Plant B
C3	Epichlorohydrin Mfg. - Plant B (Consolidated Tracor Jitco and NIOSH data)
C5	Epichlorohydrin Use/Epoxy Mfg. - Plant C (Operator TWA Calculation)
C10	Epichlorohydrin Use/Epoxy Mfg. - Plant B (Consolidated Tracor Jitco and NIOSH data)

These data will be discussed first on an individual plant basis. The exposure data corresponding to the job types consolidated from plants of similar types are then discussed.

WORKER EXPOSURE TO EPICHLOROHYDRIN

Results of the study in plant A showed that the TWA exposure to epichlorohydrin in the manufacturing process ranged from non-detectable to 0.41 ppm for 14 samples (Table 1). In the manufacture of epoxy resins, a limited number of workers were exposed to epichlorohydrin. Of the six TWA samples collected, five indicated non-detectable concentrations and the sixth 0.43 ppm (Table 2).

The results of 22 air samples collected in manufacturing areas of Plant B showed TWA exposure levels for epichlorohydrin to range from non-detectable to 2.1 ppm. The results of 23 air samples collected in the resin process areas range from non-detectable to 0.83 ppm epichlorohydrin.

Results of air sampling and analysis in Plant C showed air concentrations in the various work areas of epoxy resin production to vary from non-detectable to 1.5 ppm. The TWA exposure level calculated for the chemical operators was 0.09 ppm epichlorohydrin.

Table 1

Epichlorohydrin Manufacturers

TWA Air Concentrations of Epichlorohydrin for Jobs or Areas

<u>Job Classification</u>	<u>Plant</u>	<u>Epichlorohydrin ppm</u>	<u>No. Samples</u>	<u>Range TWA</u>	<u>Median TWA</u>
CHEMICAL OPERATORS	A	.38, ND ⁺ , .23, .33 ND, .39, .41, ND	8	ND-0.41	0.28
	B	ND, 0.26, ND, 2.1 ND, ND, 1.9, 0.54 ND, 0.16, 0.34, 0.12	12	ND-2.1	0.14
All Operators	A & B	---	20	ND-2.1	0.20
SHIFT FOREMEN (PRODUCTION)	A	0.17, 0.1, 0.14	3	0.1-0.17	0.14
	B	ND, 0.31, ND	3	ND-0.31	ND
All Foremen	A & B	---	6	ND-0.31	0.13
SHIPPING CREW					
Drumming	A	0.08, 0.06	2	0.06-0.08	0.07
Tank Car Loader	A	0.28	1	0.28	0.28
	B	0.27	1	0.27	0.27
All Shipping	A & B		4	0.06-0.28	0.23
MAINTENANCE					
Pipefitters	A	ND, ND, ND	3	ND	ND
Foreman	B	0.08	1	0.08	0.08
AREAS					
Control Room	B	0.5, ND, ND, 0.37	4	ND-0.50	0.25
Glycerine Pro- duction	B	ND	1	ND	ND

⁺ Non-detectable based on sampling method and analytical limit of 0.05 ppm.

Table 2

Resin Manufacturers
TWA Air Concentrations of Epichlorohydrin by Job or Area

Job Classification	Plant	Epichlorohydrin ppm	No. Samples	Range TWA	Median TWA
Chemical Operators	C	0.09 (Calculated)	1		0.09
	B	ND*, ND, ND, ND, ND, 0.56, 0.12, 0.07, 0.34, 0.83, 0.42, 0.10, 0.52, ND, ND, ND	16	ND-0.83	0.04
	D	0.15, 0.05	2	0.05-0.15	0.10
	A	ND, ND, ND, ND, ND 0.43	6	ND-0.43	ND
	E	ND, ND, ND, ND, ND ND, ND, ND, ND, ND ND, ND, ND, ND	14	ND	
All Operators	A - E		39	ND-0.83	ND
Foreman (operating)	B	ND, ND, 0.36, 0.6, ND	5	ND-0.6	ND
	E	ND	1		ND
Foreman (maintenance)	B	ND	1		ND
All Foremen	B & E		7	ND-0.6	ND
Resin Finishing Flaker	E	ND, ND	2	ND	ND
Kettle Areas	D	0.36, ND, ND, ND, 0.42	5	ND-0.42	ND
	E	ND, ND, ND, ND, ND, ND,	6	ND	ND
	B	ND	1	ND	ND
	C	0.05, 0.07, 0.13, 0.05, 0.35, 0.59	6	0.05-0.59	0.10
Wet Tank/Pump Room	C	1.5	1	1.5	1.5

* Non detectable based on sampling method and analytical limit of 0.05 ppm except those collected at plant E where the limit of detection was 0.1 ppm.

Plant D air sampling results showed TWA exposure levels to epichlorohydrin to range from non-detectable to 0.42 ppm and at Plant E the air sampling results in the various work areas and for all chemical operators was non-detectable for epichlorohydrin.

Epichlorohydrin Manufacturers

Air samples in two epichlorohydrin manufacturing plants showed median TWA exposure levels of 0.20 ppm epichlorohydrin for chemical operators, 0.13 ppm epichlorohydrin for production foremen, and 0.03 ppm epichlorohydrin for shipping crew. These 30 TWA samples ranged from non-detectable to 2.1 ppm epichlorohydrin (Table 1).

Resin Manufacturers

Table 2 shows the TWA air concentrations of epichlorohydrin in resin manufacturing plants determined for the following job types:

All chemical operators represented by 39 TWA samples collected in five plants showed a range of TWA exposure levels of non-detectable to 0.83 ppm epichlorohydrin.

Operating foremen represented by 7 TWA samples collected in two plants showed a range of TWA exposure levels of non-detectable to 0.60 ppm epichlorohydrin and a median TWA exposure level which was non-detectable.

Resin finishing operators represented by two samples collected in one plant showed TWA exposure levels to epichlorohydrin to be non-detectable.

WORKER EXPOSURE TO OTHER ASSOCIATED PROCESS MATERIALS

Results of 14 air samples in Plant A showed that the TWA exposure to allyl chloride for all workers in the epichlorohydrin manufacturing process ranged from non-detectable to 0.68 ppm (Table 3). Calculated TWA exposure level for mixtures of epichlorohydrin and allyl chloride did not exceed the present standard; however, if the recommended standard for epichlorohydrin were promulgated some exposures to the mixture would be in excess of the exposure index. A potential for low-level exposure to benzene from other process areas also exists in the plant area, but all samples collected were at non-detectable levels (Table C1).

In the manufacture of epoxy resins at Plant A, the plant operators were exposed to methyl ethyl ketone, methylene chloride, and toluene. Although there were measureable concentrations of each, the exposure index for combinations of these substances was not exceeded.

Table 3

Epichlorohydrin Manufacturers

Air Concentrations of Allyl Chloride for Various Jobs or Areas

<u>Classification/Area</u>	<u>Plant</u>	<u>Allyl Chloride (ppm)</u>	<u>No. of Samples</u>	<u>Range TWA</u>	<u>Median TWA</u>
CHEMICAL OPERATORS	A	0.24, ND*, ND, 0.68 0.08, 0.11, 0.11, 0.26	8	ND-0.68	0.18
	B	8.9, ND, ND, ND, 0.42, ND, 0.65, ND ND, ND, ND, 0.20	12	ND-8.9	ND
Chemical Operators	A & B		20	ND-8.9	ND
LEFT FOREMEN (PRODUCTION)	A	0.30, 0.17, ND	3	ND-0.30	0.17
	B	ND, 0.20, 0.17	3	ND-0.20	0.17
Production Foremen			6	ND-0.30	0.17
TRUCK LOADING (EPICHLOROHYDRIN)	B	ND	1	ND	ND
PIPE FITTERS	A	ND, ND, ND	3	ND	ND
WELDER	B	0.17	1	0.17	0.17
LABORER					
Control Room	B	ND, ND, ND	3	ND	ND
Epichlorohydrin Production	B	0.10	1	0.1	ND

ND = Not detectable based on sampling method and analytical limit of 0.05 ppm.

The results of 21 air samples collected at Plant B epichlorohydrin manufacturing work locations showed TWA exposure levels for allyl chloride to range from non-detectable to 8.9 ppm (Table 3). The current permissible TWA exposure limit for allyl chloride (1 ppm) was exceeded for one job type during an operational repair necessitated during one shift. The operator wore a cartridge respirator during the repair period, thus reducing the actual exposure from measured potential exposure. Calculated TWA exposure levels for mixtures of epichlorohydrin and allyl chloride did not exceed the permissible limit for the mixtures except for the one instance of excursion of allyl chloride during operational repair. At Plant B in the manufacture of epoxy resins, results also showed TWA exposure levels for MIBK, acetone, and MEK to be well below the permissible TWA limits for these solvents (Table 4).

Air concentrations of process solvent were also measured in Plant C and were determined to be less than 10 ppm at all work locations (Table 4).

At Plant E, TWA air concentrations of the process solvents toluene, xylene, acetone, MEK and methyl cellosolve were determined and the results showed levels considerably below the respective permissible TWA level (Table 4). The resin producing process at Plant D used no volatile solvents.

Table 3 shows the TWA air concentrations of allyl chloride determined for the following various job types in epichlorohydrin manufacturing:

All chemical operators represented by 20 TWA samples collected in two plants showed a range of TWA exposure levels of non-detectable to 8.9 ppm allyl chloride.

All production foremen represented by 6 TWA samples collected at two plants showed a range of TWA exposure levels of non-detectable to 0.30 ppm. The median exposure levels for the two plants were both 0.17 ppm allyl chloride. Also one sample collected in one plant showed a TWA exposure level of 0.17 ppm allyl chloride for a maintenance foreman.

Table 4 shows, for resin manufacturing operations, the TWA air concentrations of various process solvents determined for the various job classifications. A variety of solvents and solvent mixtures are used. Since solvent use varies both from plant to plant and from process to process the exposure to solvents by job type are quite specific to a job location.

EXPOSURE CONTROL EFFORTS

Chemical processes in all plants surveyed are enclosed and the process structures are generally open providing considerable dilution ventilation. In several resin manufacturing plants, the processes are housed in generally open buildings; ventilation is assisted by mechanical ventilators which also provide considerable dilution of airborne materials. Plants A, B, and E employ some local exhaust ventilation. All of the plants were maintained in a safe and orderly manner and the housekeeping procedures were generally very good.

Table 4

Resin Manufacturers

TWA Air Concentrations of Process Solvents for Various Job Types

Job Classification	Plant	TWA (ppm)						
		Toluene	Xylene	Acetone	MEK	MIBK	Methyl Cellosolve	Methylene Chloride
Chemical Operators	A	6.8,1.7,0.6 0.6,1.0,6.5			ND, ND, ND, ND, ND, ND,			1.0,4.7,7.4, 3.8,4.0,10.6
	B			0.1,0.1,ND ⁺ 4.5,2.8,3.8 0.8	ND,ND,2.1 0.90	ND,5.8,ND 3.6,16.3,20.2		
	E	3.5,2.5,4.2 11.7,3.5,2.1 0.58,0.84,3.0 0.88,3.8,3.2 1.7,0.59,1.4	0.1	ND,ND,0.16, 0.23	ND			ND,ND,ND, ND,ND,ND
Foreman (operating)	B			ND	0.2,0.2	0.70		
	E	1.7			ND			ND
Maintenance Foreman	B			0.2	ND	0.80		
Product (Resin) Finishing	E	4.4,3.2		ND	ND			ND
Areas 3d fl center	E	0.49						ND
3d fl north	E			ND				
2nd kettle	E			ND				
2nd kettle west	E	3.9	0.81					
2nd kettle east	E	1.7						ND
1st floor	E	0.25						ND
Kettle areas	C							

* Present at well below 10 ppm

+ Non-detectable based on sampling method and analytical limit of 0.1 ppm.

Use of personal protective equipment and apparel varied from plant to process to job. Eye protection is worn throughout the plants. Emergency respiratory protection is available in all plants. In some plant areas where acutely toxic materials could be encountered such as chlorine in the allyl chloride production area and other adjacent areas, workers carried an emergency respirator. Generally, respirators are not worn in any of the plants except when an emergency situation is encountered, e.g., a worker must enter a contaminated or potentially contaminated area. Although no assessment could be made of the training received by workers in the need for and the use of protective equipment and apparel, it is apparent that the proper use of personal protection equipment is essential to minimize worker exposures even though the potentially acute exposure is abnormal and infrequent. It is also apparent that the greatest danger in this regard is to the inexperienced or new employee. Generally, experienced personnel respect the toxic nature of process materials and tend to avoid exposure. In several plants workmen were provided with protective clothing. In some work locations workers wore boots or shoe covers and gloves impervious to the process materials. Leather shoes are generally considered inadequate where epichlorohydrin may be encountered since the leather sole or top, if contaminated, may cause subsequent skin absorption and delayed effects. Thus contaminated leather shoes have been commonly disposed of and protective footwear worn.

Engineering Controls

In Plant A, the epichlorohydrin production unit is located out of doors and all processing is enclosed. The operation is entirely automated and monitored from a control room located on the west periphery of the block. During normal operations it is not necessary for any unit in the process to be manned. However, workers are often in the production area for routine inspection of equipment, sampling, and on-stream maintenance. Because pumps and pipe flange seals are kept tight, leakage is normally minimal. Work practices are in effect for on-stream maintenance and maintenance work is supervised by the shift foreman. For major on-site repairs the production unit is either by-passed or the process shut down. Equipment to be repaired or serviced cannot be opened until it has been declared safe by a person authorized to make this decision. Major repairs are usually made on the day shift when the environmental chemist is available to test for epichlorohydrin and other atmospheric contaminants.

Drum filling operations in Plant A are conducted out of doors. Epichlorohydrin is pumped directly from storage tanks and introduced into the drum through a retractable pipe with a cut off valve immediately above the drum. During the filling operation the drum opening is surrounded by a hinged exhaust ventilation hood (Figure 4). Exhaust is discharged to the atmosphere about 25 feet from the loading operation and about 10 feet above ground level. Immediately adjacent to the drum filling operation is an air ejector hood; in the intervals between drum loading, the wet loading pipe is directly in front of the intake to the air mover. As an additional precaution, workers wear an organic vapor respirator during the drum filling operation.

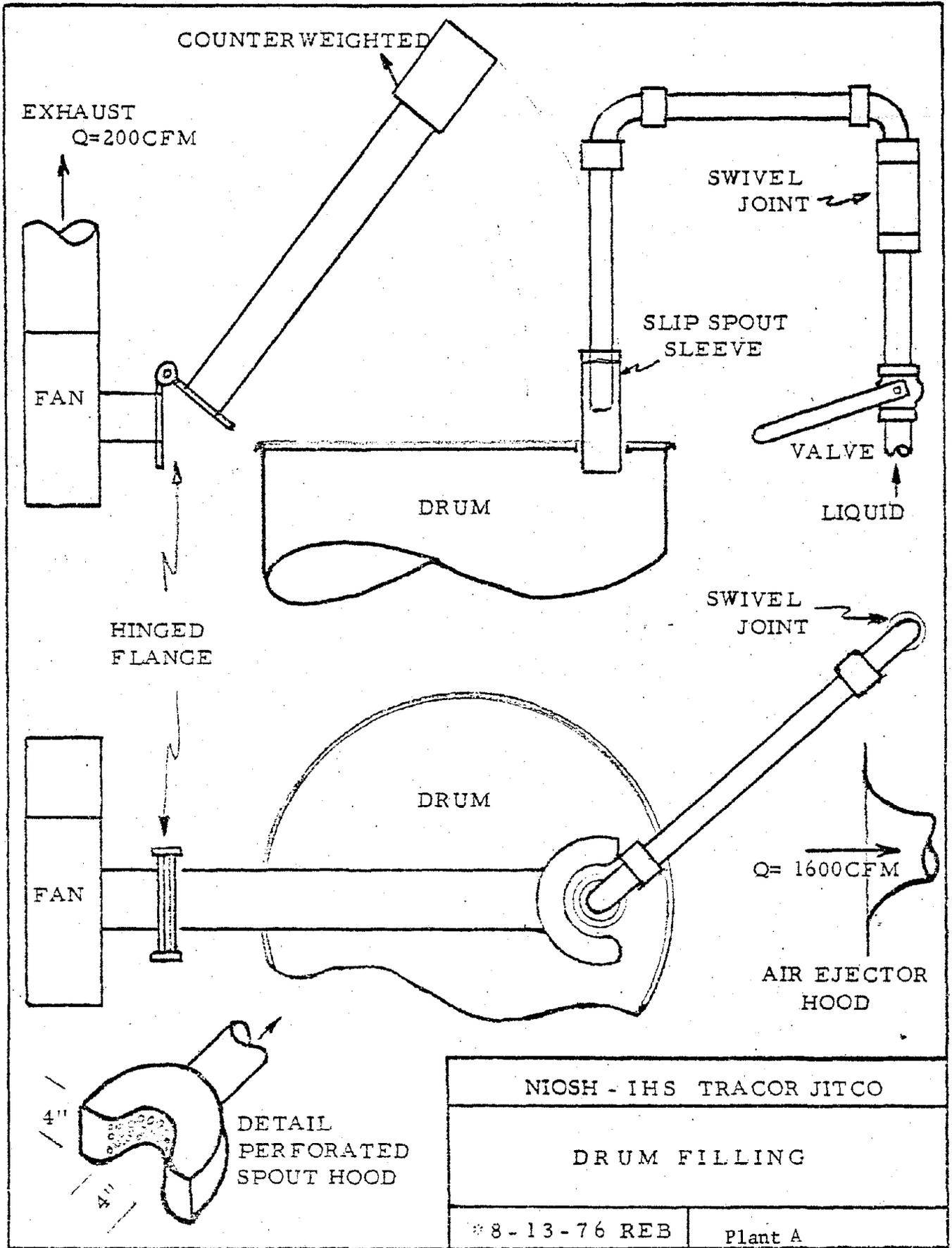


Figure 4

Some shipments are made in 10,000 gallon railroad tank cars. Each tank car is cleaned and inspected by a contractor before being received at the loading dock. A second visual inspection is made at the loading dock by removing the dome and observing the interior of the tank. Entry into the tank at the loading dock is prohibited. The tank car is top loaded and vented back to the storage tank. During the loading operation, the operator is at the control site some distance from the car. The only time that the operator may be significantly exposed to epichlorohydrin is during the disconnect procedure. Procedures for truck tank loading are similar to tank car loading. Though not observed, large shipments may be made via tanker or barge which are pre-cleaned by contract maintenance crews elsewhere and then filled by pipeline to the dock.

All Plant A epoxy resin processing equipment is located out of doors and controlled from a central air-conditioned control room. During normal operations, only the resin plant operators have a potential exposure to epichlorohydrin. When operators are in the production area they are required to wear long sleeve jackets, gloves, and eye shields, and must have an organic vapor respirator for emergency use.

The primary control in effect in Plant B is the usual one of maintaining each process in a tight, totally enclosed system, thereby minimizing the escape of epichlorohydrin and other process volatile materials into the plant environment. This effort is evident in the manufacture and use of epichlorohydrin since the product is never seen by workers, except possibly through glass ports in the reaction kettles when it is piped in as an ingredient of the epoxy resin being manufactured, or through a hood window when it is piped to the drum filling enclosure. Samples are not collected from the process stream in the epichlorohydrin manufacturing area of the glycerine plant. Pump seals and pipe flange seals are maintained tight and the leakage is, thereby, normally minimal. When a leak develops, it is promptly corrected by appropriate maintenance efforts. Most of the epichlorohydrin produced is captive to the processing needs either for glycerine production or for the manufacture of epoxy resins.

No epichlorohydrin drum filling operations were observed during the survey of Plant B. However, facilities are present to fill custom orders for epichlorohydrin and other products. The epichlorohydrin that is shipped in drums is piped from storage tanks to a central drum filling/tank car filling facility where the drums are filled and weighed in a totally enclosed, exhausted enclosure located on an open loading dock. This control system would appear to allow only minimal exposure to the operator when drums are filled. The tank car filling is done adjacent to the same loading dock. No controls external to the piping system were evident. There did not appear to be any facility for vapor return to the system.

In Plant B epoxy production, the processes are totally or semi-enclosed through the unreacted epichlorohydrin stages of the process. The second major control in effect is the open design of the process structure and all process equipment, piping, and storage facilities; this control provides maximum natural ventilation and dilution of any escaping materials if leakage occurs. The epoxy production kettles are housed in a large three-story building, which has openings to the outdoors and good natural ventilation. The reaction kettles are provided with vent lines which can be opened to the out of doors during the production cycle.

The epoxy resin production process in Plant C is enclosed in the process tanks, piping systems, weigh tanks, reaction vessels, vents to condensers, and recycle storage tanks and piping. The process is straight-forward and well understood by the operator with little likelihood of any spillage or escape of epichlorohydrin under normal operating conditions. The reactor integrity may be breached when pressure is applied since any leakage in the vessel would then allow some slight increase in leakage of reactor vessel gases. However, at this stage of the process, all epichlorohydrin should be reacted or removed. A vacuum can be applied on the reactor vessel by the operator who initiates an ejector in a vent line. The primary control in effect is the maintenance of a totally enclosed process. The pipe lines are constructed of stainless steel and little maintenance is required. The packing at pipe flanges allows some occasional leakage which is repaired immediately. Thus both process design, including the selection of the materials of construction, and appropriate and timely maintenance are important contributions to the total control effort.

Natural building ventilation in Plant D appeared to provide adequate fresh air and dilution. The primary controls which are effective in minimizing the exposure to epichlorohydrin are (1) the total enclosure of the process as well as the storage, piping, and weighing systems, especially where free epichlorohydrin is present, and (2) the utilization of relatively open processing work areas and the location of pumps, pipes, and storage in open areas. Also, when the reaction kettle port cover is removed, a steam ejector is activated in a kettle vent line. The condensate drains to a liquid waste line. This procedure prevents escape of gaseous materials from the reaction kettle when the port is opened. Close control is maintained on the temperature of the exothermic reaction mixture primarily to influence the rate of reaction and the product quality. Any overheating increases the epichlorohydrin vapor pressure producing a higher vapor concentration in the kettle and a consequent increased vapor loss to the work area. Thus, the close control of process temperature also controls exposure levels.

Epichlorohydrin production in Plant E during 1960-1966 consisted of an essentially totally enclosed process in the open air. The operators were located in an adjacent control building.

The Plant E epoxy resin processing building is extensively ventilated by natural drafts from open windows and doors during warm weather months. General dilution ventilation of eight air changes per hour of heated out-door air is mechanically provided during cold weather. In addition, some local exhaust ventilation is provided on process equipment such as the reaction kettles, resin pouring and cooling lines, and resin transfer points.

The reaction vessels and liquid lines totally enclose the liquid process materials. Leakage of liquids which may occur at some fittings and pumps requires constant surveillance and persistent maintenance as well as a special leakage collection fitting. Also available at each kettle are flexible exhaust vent lines which can be used to exhaust the kettle when the charging port is opened such as when reactant materials (dry solids) are charged into the kettle. Also, a specially designed charging funnel is placed in the reactor charging port and bags of dry material are opened and poured into the funnel. The funnel serves as an exhaust hood, having a 3 1/4" x 31 1/2" exhaust on the top of the back edge with an extension (pipe transformation) to which the flexible exhaust vent line can be attached. Under the conditions of use observed, the slot velocity varied from 400 LFM at the center, dropping to 300 LFM on each side, 6" from center, and to about 30 LFM at the ends. Thus the volume of air being exhausted was on the order of 100 CFM. For the granular type of material being charged, little or no spillage or dusting was observed. More dust production and potential exposure to bagged materials was noted to be related to the handling and disposal of the empty bags than resulted from the charging of the bulk materials; the duration of exposure, however, was brief.

Personnel Controls

In Plant A, all personnel entering the production area are required to wear long sleeve jackets, gloves, and eye shields, and must have an organic vapor respirator for emergency use. In the event of a production emergency, a warning signal is sounded and area evacuation is required.

In Plant B, several significant control measures are also effective in minimizing worker exposures to process materials. Process control rooms (where operators spend a considerable portion of their work time) are physically isolated from the processing areas; the control rooms are selectively located and are generally air-conditioned. Eye protection is provided for all workers at all times and air supplied respirators are available for use when work involves any appreciable exposure or for emergency use.

At Plant E, during epichlorohydrin production, great care was taken by all personnel to avoid contact with epichlorohydrin since its irritating nature, both skin and odor, was well known and respected. Also, protective clothing was worn by workmen if contact with epichlorohydrin was possible such as when repair or maintenance was done where leaks developed at pump seals or pipe flanges. Epoxy production operators were observed to use dust respirators when opening bags and dumping dry chemicals into the reaction kettle feed hopper and disposing of empty bags.

Housekeeping

The epoxy producing plants had difficulty preventing leakage and spillage of resin materials. These resin materials were evident throughout the resin finishing area because of accumulation and tracking by employees. Occasional cleanup of the resin from boots, floors and other work surfaces necessitated the use of solvents such as acetone and other ketones. This cleanup procedure, though effective in removing the sticky or hard resins, presents some hazard, not only respiratory, but as a potential fire hazard if not handled properly.

SUMMARY OF HAZARD EXPERIENCE

In the manufacture and use of epichlorohydrin, the industries involved and the workmen and their supervisors who are potentially exposed to this material and other associated process materials, have, through engineering controls, plant and process design and maintenance, routine and emergency work procedures, and limited environmental monitoring been successful in maintaining the time weighted average exposures of personnel to levels below present permissible levels.

Workers in this industry have experienced acute exposures to epichlorohydrin. In a few instances of accidental nature individuals have been exposed through contact and/or inhalation to high concentrations for brief periods of time resulting in acute illness requiring hospitalization or medical treatment. More commonly, individuals have been accidentally exposed to the material from a small leak or spill. In instances of skin exposure, especially prolonged due to contaminated apparel or shoes, workers have experienced skin irritation and delayed effects of the exposure described as "deep aching pain." Thus, acute exposures are potential for all workers in these industries. Serious effects may result if improper actions or procedures are followed when material spills or leaks occur, regardless of their magnitude. The acute hazard is generally appreciated by experienced personnel.

RECOMMENDATIONS

Continued and improved good industrial hygiene practices are warranted for epichlorohydrin exposure control. In line with the scope of this study the following general recommendations are made:

- (1) The plants should maintain their present control measures. Routine industrial hygiene surveillance should be continued. Where measurements indicate deficiencies, steps should be taken to effect corrective measures.
- (2) The design and installation of enclosed process systems that are leak resistant and routine maintenance of process equipment should continue to be the primary control effort. Product or material loss should be considered with regard to the potential for reduction of the losses through improved process design as well as operational maintenance procedures.
- (3) In all tank car filling operations, vapor return lines should be installed and used. Improved shaft seals, gaskets, flanges, and pumps should be considered on a replacement maintenance basis.
- (4) Respiratory protection and protective clothing should be made available and exposure and emergency conditions warrant additional protection.
- (5) Instruction of employees, especially new employees, in the toxic nature of process materials and the need for proper and timely use of protective equipment and clothing should be conducted on routine periodic basis. Training is essential to effectively minimize worker exposures. Safe work procedures and practices aimed at minimizing worker exposure should be developed, understood and followed by all employees.
- (6) Some exposures to allyl chloride were close to the permissible concentration and at present concentrations the exposure index for a mixture of allyl chloride and epichlorohydrin in epichlorohydrin manufacturing plants could be occasionally exceeded. These plants should explore methods for reducing process material losses and the consequent exposures to allyl chloride.

- (7) The use of bulk solvents for cleaning purposes in an uncontrolled or indiscriminate manner should be considered from the standpoint of the potential fire hazard as well as skin contact. Solvent vapor source points should be considered from the standpoint of the potential fire hazard, aside from the observed minimal inhalation hazard experienced by workers. Exposure periods during plant surveys were brief and thus the TWA exposure levels were found to be low.
- (8) More detailed and specific recommendations for controlling epichlorohydrin exposures are contained in the NIOSH criteria document (4).

REFERENCES

1. Public Law 91-596, Sec. 20(a)7, Occupational Safety and Health Act, 1970.
2. 29CFR Paragraph 1910.1000.
3. American Conference of Governmental Industrial Hygienists, Threshold Limit Values for 1976, ACGIH, 1976.
4. Criteria for a Recommended Standard . . . Occupational Exposure to Epichlorohydrin, September, 1976. National Institute for Occupational Safety and Health, HEW Publication No. (NIOSH) 76-206.
5. 21 CFR Paragraph 121. 2526.
6. White L.D., et al. 1970. A convenient method for the analysis of selected solvent vapors in the industrial atmosphere. Am. Ind. Hyg. Ass. J. 225-232.

APPENDIX A

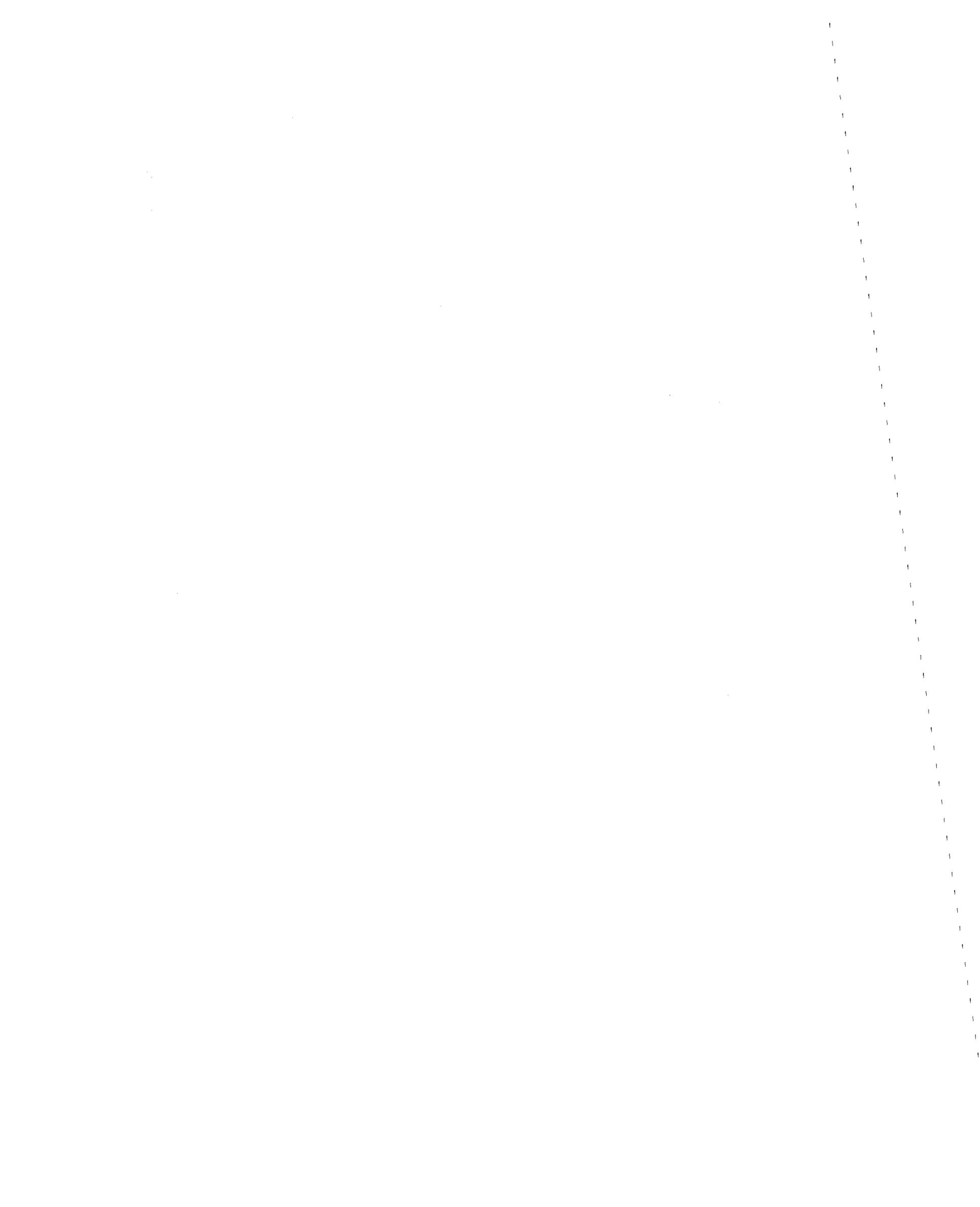


Table A-1

Plant A

EPOXY PLANT⁺
1973 AIR MONITORING

<u>JOB CLASSIFICATION</u>	<u>NUMBER OF SAMPLES</u>	<u>EPI (PPM VOLUME)</u>		
		<u>HIGH</u>	<u>LOW</u>	<u>AVG</u>
Resin Helper	1	.03	.03	.03
400 Plant Operator	1	.03	.03	.03
300 Plant Operator	1	.03	.03	.03
Control Plant Operator	1	.03	.03	.03
Grab Samples	78	13	<.60	3.17

1974 AIR MONITORING

Warehouse Operator	4	<.30	<.30	<.30
Machinist	1	<.10	<.10	<.10
Pipefitter	2	<.30	<.30	<.30
Control C Operator	3	.90	<.40	.66
2nd Class Operator BIS	1	<.10	<.10	<.10
Grab Samples	25	15	.60	2.02
Stationary Monitoring	23	1	<.10	.26

⁺Data reported by Plant A

Table A-2

Plant A

ALLYL CHLORIDE #3[†]
PERSONNEL MONITORING (1975)

<u>JOB CLASSIFICATION</u>	<u>NUMBER OF SAMPLES</u>	<u>ALLYL CHLORIDE (PPM VOLUME)</u>			<u>E P I (PPM VOLUME)</u>		
		<u>HIGH</u>	<u>LOW</u>	<u>AVG.</u>	<u>HIGH</u>	<u>LOW</u>	<u>AVG.</u>
Control "A"	6	.91	.19	.45	<.01	<.01	<.01
Control "C"	8	.94	.24	.57	<.01	<.01	<.01
Instrument	4	*4.72	.12	2.16	<.01	<.01	<.01
Lab	4	.71	.23	.40	<.01	<.01	<.01
Shift Foreman	4	*4.03	.12	1.30	<.01	<.01	<.01
Maintenance	4	*6.09	.78	3.05	<.01	<.01	<.01

NOTE: High values for allyl chloride could possibly be due to acetone interference. Analytical technique has been corrected.

* Represents potential exposure. Operators wear protective equipment during sampling operations and process upsets.

Avg. represents numerical average between high and low value, not the time weighted average.

[†]Data reported by Plant A

Table A-3

Data reported by Plant D in letter to Tracor Jitco dated May 24, 1976:

"This will confirm our recent telephone conversation in which I agreed to supply you with the results of the air sampling tests conducted at our plant. The data were reported recently in a report issued by the Analytical Division of our Research Department. The information contained herein was excerpted from this formal research report:

Nine samples of air taken from various working operations in the area of the plant were analyzed for epichlorohydrin. Concentrations ranged from 0.07 to 0.36 ppm (see table). One sample (H) analyzed 5.96 ppm, but this was not considered a reliable value because the sample size was too small (only 0.5 liters). Such small samples are not recommended for levels below 10 ppm.

Identification of the epichlorohydrin in the air samples was based on the GC peak retention times, compared with a chromatogram of a standard epichlorohydrin sample and on add-backs of the standard to the sample extracts. Addition of a small amount of n-octane as a peak-marker enabled rapid location of the epichlorohydrin.

The analytical results from the nine samples are summarized in the table below:

<u>Sample No.</u>	<u>Volume (liters)</u>	<u>Epichlorohydrin Added, ppm</u>	<u>Epichlorohydrin Found, ppm</u>	<u>Average Found, ppm</u>
A	15.1	0.20	0.37	0.14
		0.00	0.12	
		0.00	0.12	
B	26.2	0.11	0.19	0.07
		0.00	0.06	
		0.00	0.07	
C	16.6	0.18	0.29	0.09
		0.00	0.07	
D	15.6	0.20	0.28	0.10
		0.00	0.12	
E	2.4	0.00	0.12	0.12
F	15.7	0.20	0.44	0.25
		0.00	0.26	
G	14.8	0.21	0.58	0.36
		0.00	0.34	
H*	0.5*	6.30*	12.17*	5.96*
		0.00	5.30*	
		0.00	5.92*	
		0.00	6.75*	
J	2.1	0.00	0.10	0.10

*Data based on too small an air sample and are not considered reliable.

APPENDIX B

Epichlorohydrin
(1-Chloro-2,3-epoxypropane)

Analyte:	Epichlorohydrin	Method No.: S118
Matrix:	Air	Range: 11.7-43.1 mg/cu m
OSHA Standard:	5 ppm (20 mg/cu m)	Precision (\overline{CV}_T): 0.057
Procedure:	Adsorption on charcoal, desorption with carbon disulfide, GC	Validation Date: 5/9/75

1. Principle of the Method

- 1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.
- 1.2 The charcoal in the tube is transferred to a small, stoppered sample container, and the analyte is desorbed with carbon disulfide.
- 1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.
- 1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

- 2.1 This method was validated over the range of 11.7-43.1 mg/cu m at an atmospheric temperature and pressure of 23°C and 765 mm Hg, using a 20-liter sample. Under the conditions of sample size (20 liters) the probable useful range of this method is 2-60 mg/cu m at a detector sensitivity that gives nearly full deflection on the strip chart recorder for a 1-mg sample. The method is capable of measuring much smaller amounts if the desorption efficiency is adequate. Desorption efficiency must be determined over the range used.
- 2.2 The upper limit of the range of the method is dependent on the adsorptive capacity of the charcoal tube. This capacity varies with the concentrations of epichlorohydrin and other substances in the air. The first section of the charcoal tube was found to hold at least 2 mg of epichlorohydrin when a test atmosphere

containing 43.1 mg/cu m of epichlorohydrin in air was sampled at 0.185 liter per minute for 240 minutes; at that time the concentration of epichlorohydrin in the effluent was less than 5% of that in the influent. (The charcoal tube consists of two sections of activated charcoal separated by a section of urethane foam. See Section 6.2). If a particular atmosphere is suspected of containing a large amount of contaminant, a smaller sampling volume should be taken.

3. Interference

- 3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped efficiently. Preliminary experiments using toluene indicate that high humidity severely decreases the breakthrough volume.
- 3.2 When two or more compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample.
- 3.3 It must be emphasized that any compound which has the same retention time as the analyte at the operating conditions described in this method is an interference. Retention time data on a single column cannot be considered proof of chemical identity.
- 3.4 If the possibility of interference exists, separation conditions (column packing, temperature, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

- 4.1 The Coefficient of Variation (CV_T) for the total analytical and sampling method in the range of 11.7-43.1 mg/cu m was 0.057. This value corresponds to a 1.1 mg/cu m standard deviation at the OSHA standard level. Statistical information and details of the validation and experimental test procedures can be found in Reference 11.2.
- 4.2 On the average the concentrations obtained at the OSHA standard level using the overall sampling and analytical method were 0.7% lower than the "true" concentrations for a limited number of laboratory experiments. Any difference between the "found" and "true" concentrations may not represent a bias in the sampling and analytical method, but rather a random variation from the experimentally determined "true" concentration. Therefore, no recovery correction should be applied to the final result.

5. Advantages and Disadvantages of the Method

- 5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method.

The method can also be used for the simultaneous analysis of two or more substances suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

- 5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal tube exceeds 25% of that found on the front section, the possibility of sample loss exists.
- 5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

- 6.1 A calibrated personal sampling pump whose flow can be determined within $\pm 5\%$ at the recommended flow rate. (Reference 11.3)
- 6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The adsorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in front of the adsorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 liter per minute.
- 6.3 Gas chromatograph equipped with a flame ionization detector.
- 6.4 Column (10-ft x 1/8-in stainless steel) packed with 10% FFAP on 80/100 mesh, acid washed DMCS Chromosorb W.
- 6.5 An electronic integrator or some other suitable method for measuring peak areas.
- 6.6 Two-milliliter sample containers with glass stoppers or Teflon-lined caps. If an automatic sample injector is used, the associated vials may be used.
- 6.7 Microliter syringes: 10-microliter, and other convenient sizes for making standards.
- 6.8 Pipets: 1.0-ml delivery pipets.

6.9 Volumetric flasks: 10-ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Chromatographic quality carbon disulfide.

7.2 Epichlorohydrin, reagent grade.

7.3 Purified nitrogen.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

8. Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, break the ends of the tube to provide an opening at least one-half the internal diameter of the tube (2 mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be placed in a vertical direction during sampling to minimize channeling through the charcoal.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 A sample size of 20 liters is recommended. Sample at a flow of 0.20 liter per minute or less. The flow rate should be known with an accuracy of at least +5%.

8.3.6 The temperature and pressure of the atmosphere being sampled should be recorded. If pressure reading is not available, record the elevation.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

no air is sampled through the tube
be labeled as a blank.

- 8.3.9 Capped tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping.
- 8.3.10 A sample of the bulk material should be submitted to the laboratory in a glass container with a Teflon-lined cap. This sample should not be transported in the same container as the charcoal tubes.

8.4 Analysis of Samples

- 8.4.1 Preparation of Samples. In preparation for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 2-ml stoppered sample container. The separating section of foam is removed and discarded; the second section is transferred to another stoppered container. These two sections are analyzed separately. Samples should be analyzed within one week after collection.
- 8.4.2 Desorption of Samples. Prior to analysis, 1.0 ml of carbon disulfide is pipetted into each sample container. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Desorption should be done for 30 minutes. Tests indicate that this is adequate if the sample is agitated occasionally during this period. If an automatic sample injector is used, the sample vials should be capped as soon as the solvent is added to minimize volatilization.
- 8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:
1. 50 ml/min (60 psig) nitrogen carrier gas flow
 2. 65 ml/min (24 psig) hydrogen gas flow to detector
 3. 500 ml/min (50 psig) air flow to detector
 4. 175°C injector temperature
 5. 215°C manifold temperature (detector)
 6. 120°C column temperature
- 8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blow back or distillation

within the syringe needle, one should employ the solvent flush injection technique. The 10-microliter syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 microliter to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-microliter aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back 1.2 microliters to minimize evaporation of the sample from the tip of the needle. Observe that the sample occupies 4.9-5.0 microliters in the barrel of the syringe. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected. An automatic sample injector can be used if it is shown to give reproducibility at least as good as the solvent flush method.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process, provided the same batch of charcoal is used.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 2.5 in, 4-mm I.D. glass tube, flame sealed at one end. This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped with Parafilm. A known amount of hexane solution containing 94.5 mg/ml is injected directly into the charcoal with a microliter syringe, and the tube is capped with more Parafilm. When using an automatic sample injector, the sample injector vials, capped with Teflon-faced septa, may be used in place of the glass tubes.

The amount injected is equivalent to that present in a 20-liter air sample at the selected level. Six tubes at each of three levels (0.5X, 1X, and 2X of the standard) are prepared in this manner and allowed to stand for at least overnight to assure complete adsorption of the analyte onto the charcoal. These tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.4.

Two or three standards are prepared by injecting the same volume of compound into 1.0 ml of carbon disulfide with the same syringe used in the preparation of the samples. These are analyzed with the samples.

The desorption efficiency (D.E.) equals the average weight in mg recovered from the tube divided by the weight in mg added to the tube, or

$$\text{D.E.} = \frac{\text{Average Weight recovered (mg)}}{\text{Weight added (mg)}}$$

The desorption efficiency is dependent on the amount of analyte collected on the charcoal. Plot the desorption efficiency versus weight of analyte found. This curve is used in Section 10.4 to correct for adsorption losses.

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/1.0 ml carbon disulfide, because samples are desorbed in this amount of carbon disulfide. The density of the analyte is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/1.0 ml versus peak area. Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

10. Calculations

10.1 Read the weight, in mg, corresponding to each peak area from the standard curve. No volume corrections are needed, because the standard curve is based on mg/1.0 ml carbon disulfide and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{mg} = \text{mg sample} - \text{mg blank}$$

where:

$$\text{mg sample} = \text{mg found in front section of sample tube}$$

$$\text{mg blank} = \text{mg found in front section of blank tube}$$

A similar procedure is followed for the backup sections.

10.3 Add the weights found in the front and backup sections to get the total weight in the sample.

10.4 Read the desorption efficiency from the curve (see Section 8.5.2) for the amount found in the front section. Divide the total weight by this desorption efficiency to obtain the corrected mg/sample.

$$\text{Corrected mg/sample} = \frac{\text{Total weight}}{\text{D.E.}}$$

10.5 The concentration of the analyte in the air sampled can be expressed in mg/cu m.

$$\text{mg/cu m} = \frac{\text{Corrected mg (Section 10.4)} \times 1000 \text{ (liter/cu m)}}{\text{Air volume sampled (liter)}}$$

10.6 Another method of expressing concentration is ppm.

$$\text{ppm} = \text{mg/cu m} \times \frac{24.45}{\text{M.W.}} \times \frac{760}{\text{P}} \times \frac{\text{T} + 273}{298}$$

where:

P	=	pressure (mm Hg) of air sampled
T	=	temperature (°C) of air sampled
24.45	=	molar volume (liter/mole) at 25°C and 760 mm Hg
M.W.	=	molecular weight (g/mole) of analyte
760	=	standard pressure (mm Hg)
298	=	standard temperature (°K)

11. References

11.1 White, L.D. et al, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

11.2 Documentation of NIOSH Validation Tests, NIOSH Contract No. CDC-99-74-45.

11.3 Final Report, NIOSH Contract HSM-99-71-31, "Personal Sampler Pump for Charcoal Tubes," September 15, 1972.

stance

Epichlorohydrin (1-Chloro-2,3-epoxypropane)

Standard

8-hour time-weighted average: 5 ppm (20 mg/cu m)

Reference: 29 CFR 1910.93

Analytical Method

A known volume of air is drawn through a charcoal tube to trap the epichlorohydrin vapors present. The analyte is desorbed from the charcoal tube with carbon disulfide, and the sample is separated and analyzed using a gas chromatograph with a flame ionization detector. The method has been validated over the range of 11.7-43.1 mg/cu m for a 20-liter sample at 23°C and 765 mm Hg atmospheric temperature and pressure.

Sampling Equipment

A calibrated personal sampling pump whose flow can be determined accurately, $\pm 5\%$, over the range of 0.05 to 0.20 liter per minute, plus charcoal tube containing two sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam.

Sample Size

A sample size of 20 liters is recommended. Sample at a flow of 0.20 liter per minute or less.

Sampling Procedure

1. Immediately before sampling, the ends of the tube should be broken so as to provide an opening approximately one-half the internal diameter of the tube.
2. The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump. The charcoal tube should be placed in a vertical position during sampling to avoid channeling and subsequent premature breakthrough of epichlorohydrin.
3. Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.
4. Set the flow rate as accurately as possible using the manufacturer's

directions. Record the temperature and pressure of the atmosphere being sampled. If the pressure reading is not available, record the elevation. If the pump is a low flow rate pump, set the approximate flow rate and record the initial and final counter reading. The sample volume is obtained by multiplying the number of counter strokes times the cc/stroke factor.

5. The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Masking tape is the only suitable substitute for sealing the tubes. Under no circumstances should rubber caps be used.
6. One charcoal tube should be handled in the same manner as the sample tubes (break, seal, and transport), except for the taking of an air sample. This tube should be labeled as a blank.

Special Consideration

1. Where two or more compounds are known or suspected to be present in the air, such information, including their suspected identities should be transmitted with the sample.
2. Due to the high resistance of the charcoal tube, this sampling method places a heavy load on the sampling pump. Therefore, no more than eight hours of sampling should be done without fully recharging the battery.
3. If high humidity or water mist is present, breakthrough volume can be severely reduced. If condensation of water occurs in the tube, the substance will not be trapped quantitatively.
4. The desorption efficiency of charcoal varies from batch to batch. Therefore, all the tubes used to collect a set of samples should contain charcoal from the same batch. Several unused charcoal tubes should accompany the samples. Information on the batch number of the charcoal must be supplied.

Bulk Samples

A bulk sample of the suspected compound should be submitted to the laboratory in a glass container with a Teflon-lined cap. Label of the bulk sample should match air samples for identification purposes.

Shipping Instructions

Capped charcoal tubes should be packed tightly and padded before they are shipped to minimize tube breakage during shipping. Never transport, mail, or ship the bulk sample in the same container as the sample or blank tube.

Reference

Epichlorohydrin, NIOSH Method No. S118.

Backup Data Report

Substance: Epichlorohydrin, No. S118
OSHA Standard: 5 ppm (20 mg/cu m)
Chemical used Epichlorohydrin, Lot #325814
for validation: J.T. Baker Chemical Company

Procedure

The procedure followed for validation of the method for collecting and analyzing concentrations of epichlorohydrin in air is described in NIOSH Method S118, which has been adapted from P&CAM 127. Desorption efficiency tests were done at 0.5, 1, and 2 times the OSHA standard by spiking 100 mg portions of charcoal with the appropriate amounts of liquid epichlorohydrin to represent 20-liter air samples. Spiking and desorption tests were done in the 2-ml vials used with the Varian Model 8000 automatic sample injector. The use of the automatic sample injector is described in the attachment to this report. Samples of epichlorohydrin in air were generated and collected on activated coconut charcoal, Lot 105, supplied by SKC, Inc., Pittsburgh, Pa. The desorbed samples were analyzed by gas chromatography, and the amount measured was corrected for desorption efficiency (D.E.). The "found" concentrations of epichlorohydrin in air were determined by dividing the corrected mg found by the sample volume (critical orifice flow rate for that sample X 109.3 minutes). The "true" concentrations of epichlorohydrin in the generated samples were determined by comparison with a "bag" standard, using a total hydrocarbon analyzer to monitor the generated vapor concentration as described in Reference No. 1.

Modification

There was only one major modification to P&CAM 127 which was in the preparation of the samples for desorption efficiency tests. A hexane solution of epichlorohydrin containing 94.5 mg/ml was used to apply the analyte to the charcoal. This was done so it would not be necessary to inject less than 2 microliters at the 0.5X level.

Generation

Samples of epichlorohydrin in air were generated by the procedure described in the attachment to this report. The generator conditions used are given in the following table:

Generator Conditions for Epichlorohydrin

Nitrogen flow rate	0.172 liters/minute at 23°C
Dilution air flow rate	65.9 liters/minute at 23°C
Bath temperature	0°C

S118-1

B-11.

the generated vapor concentrations (Reference No. 1). Samples were collected for 109.3 minutes at a rate of approximately 0.2 liter per minute (individual critical orifices vary slightly in flow rate).

Breakthrough

A test for breakthrough of the front section of the charcoal tubes was conducted as described in the Backup Data Report for cyclohexene (Reference No. 1). Less than 5% of the generated concentration of 43.1 mg/cu m was present in the effluent after 4 hours. Sampling was done at a rate of 0.185 liter per minute, indicating a capacity of at least 2 mg of epichlorohydrin in the charcoal tube.

Discussion

A time study on the storage stability of epichlorohydrin on charcoal Lot 105 was made. Tests were done at 1X the OSHA standard level by spiking 0.378 mg of epichlorohydrin onto 100 mg of charcoal Lot 105. Two samples each of epichlorohydrin on charcoal were allowed to stand for a time period of 23, 95, and 143 hours before sample analysis. The results are summarized in Table 1.

Table 1

<u>Time on Charcoal before Analysis</u> <u>(hours)</u>	<u>mg</u> <u>taken</u>	<u>mg</u> <u>found</u>	<u>D.E.</u>
143	0.378	0.321	0.849
143	0.378	0.331	0.876
95	0.378	0.328	0.868
95	0.378	0.333	0.881
23	0.378	0.341	0.902
23	0.378	0.345	0.913

From the above results it appears that epichlorohydrin is stable on charcoal for 143 hours.

Precision and Accuracy

The statistical procedures used are described in Reference No. 4.

$$\overline{CV}_1 = 0.031$$

$$\overline{CV}_2 = 0.025$$

$$\overline{CV}_T = 0.057$$

The average recovery at the OSHA standard level was 99.3%. However, there was no apparent bias in any of the steps of the sampling and analysis procedures that were not recognized by appropriate corrections. Therefore, any variation from 100% recovery may have been related to difficulties in generating the atmosphere containing the analyte at a given concentration rather than a true bias in the method. This being the case, \overline{CV}_T is a measure of accuracy as well as precision of the sampling and analytical method.

APPENDIX C



Table C1

TWA Exposure Levels for Jobs

Plant A Epichlorohydrin Manufacturing

Job	Shift	Type or Duration of Sample	Epichlorohydrin (ppm)	Allyl Chloride (ppm)	Benzene (ppm)
Control A Operator	1	TWA	0.38	0.24	N.D.
Control A Operator	2	TWA	N.D.*	N.D.	N.D.
Control A Operator	3	TWA	0.23	N.D.	N.D.
Control C Operator	1	TWA	0.33	0.68	N.D.
Control C Operator	2	TWA	N.D.	0.08	N.D.
Control C Operator	3	TWA	0.39	0.11	N.D.
Control C Trainee	1	TWA	0.41	0.11	N.D.
Control C Trainee	2	TWA	N.D.	0.26	
Shift Foreman	1	TWA	0.17	0.30	
Shift Foreman	2	TWA	0.10	0.17	
Shift Foreman	3	TWA	0.14	N.D.	
Pipefitter 1	1	5 Hours	N.D.	N.D.	
Pipefitter 2	1	5 Hours	N.D.	N.D.	
Pipefitter 3	1	5 Hours	N.D.	N.D.	
Packing Op. 1 - Drums	1	4 Hours, 20 Minutes	0.08		
Packing Op. 2 - Drums	1	4 Hours, 20 Minutes	0.06		
Packing Op. 1 - Tank Car	1	3 Hours, 10 Minutes	0.28		

* Non-detectable based on sampling method and analytical limit of 0.05 ppm.

Table C2
TWA Exposure Levels for Jobs and Air Concentrations for Selected Work Areas
Plant B Epichlorohydrin Manufacturing

Job/Area	Description	Shift	Sample Type	Epichlorohydrin (ppm)	Allyl Chloride (ppm)
Operator	AC leak; Shut-down AC and IPC unit-repair	Graveyard	TWA	N.D.*	8.9
Operator	Routine	Graveyard	TWA	N.D.	N.D.
Operator	Routine	Graveyard	TWA	N.D.	N.D.
Foreman	Routine	Graveyard	TWA	N.D.	N.D.
(Glycerine Control Room)	Routine	Graveyard	GA	N.D.	N.D.
Operator	Downwind from hot well	Graveyard	PS (2 hours)	0.19	0.5
(Center Glycerine Area)		Graveyard	GA	N.D.	0.1
Operator	Routine Rounds	Graveyard	PS (5 hours)	N.D.	0.1
(C Plant Control Room)	Control room downwind from hot well	Graveyard	GA	0.37	

* Non-detectable based on sampling method and analytical limit of 0.05 ppm epichlorohydrin and 0.1 ppm allyl chloride

Table C3

TWA Exposure Levels for Jobs and Air Concentrations for Selected Areas⁺

Plant B Epichlorohydrin Manufacturing

<u>Job/Area</u>	<u>Shift</u>	<u>Epichlorohydrin</u> (ppm)	<u>Allyl Chloride</u> (ppm)
Tank Loading	Day	0.27	N.D*
Maintenance Foreman	Day	0.08	0.17
Operator G100	Day	N.D*	N.D.
	Evening	0.26	N.D.
	Graveyard	N.D.	8.9
Operator G300	Day	2.12	N.D.
	Evening	N.D.	0.42
	Graveyard	N.D.	N.D.
Operator HTH	Day	1.92	0.65
	Evening	0.54	N.D.
	Graveyard	N.D.	N.D.
Foreman G300	Day	N.D.	0.20
	Evening	0.31	0.17
	Graveyard	N.D.	N.D.
(Control Room G300)	Day	0.50	N.D.
	Evening	N.D.	N.D.
	Graveyard	N.D.	N.D.
(Area G300)	Graveyard	N.D.	0.10
Operator C Plant	Day	0.16	N.D.
	Evening	0.34	N.D.
	Graveyard	0.12	0.2
(Control Room C)	Graveyard	0.37	

* Non-detectable based on sampling method and analytical limit of 0.05 ppm epichlorohydrin and 0.1 ppm allyl chloride.

⁺ Day and evening shift samples collected and analyzed by NIOSH; graveyard shift samples collected by Tracor Jitco.

Table C4
Air Concentrations for Selected Areas
Plant C

Sample Location/Description	Operation	Duration	Epichlorohydrin ppm
Resin Kettle Area - 3rd level. Side of Kettle (weigh scale)	Charge EPI - Draw off	92 minutes	0.35 +
Resin Kettle Area - 3rd level. Top of Kettle (Catwalk)	Charge EPI - Draw off	92 minutes	0.59 +
Wet Tank Room	Normal	4 hours	1.5 +
Control Room - 3rd level	Normal	3 hours 52 minutes	N.D.*
Resin Kettle and Weigh Scale Area - 3rd level	Charge Bisphenol A	25 minutes	0.05
Resin Kettle and Weigh Scale Area - 3rd level	Charge Epichlorohydrin	69 minutes	0.07+
Blank	----	----	nil
Resin Kettle and Weigh Scale Area - 3rd level	Pressure on Kettle-Draw off	30 minutes	0.13+
Resin Kettle and Weigh Scale Area - 3rd level	Charge Solvent and Draw down	100 minutes	0.05+

* Non-detectable based on sampling method and analytical limit of 0.05 ppm.

+ All contained a peak for MIBK which would be well below 10 ppm.

Table C5

Air Concentrations and Operator's Time In Selected Work Areas

Plant C

Work Area	Approximate Time Operator in Area Per Shift (Hours)	Operation	Epichlorohydrin Air Concentration (ppm)	
			(2/24/76)	(2/25/76)
Control Room	4.0	Normal Conditions and Duties		N.D.*
3rd Level - Resin Kettle Area	0.5	Charge Bisphenol A		0.05
3rd Level - Resin Kettle Area	1.1	Charge Epichlorohydrin	0.35, 0.59 (av. 0.47)	0.07 (av. 0.10)
3rd Level - Resin Kettle Area	0.5	Pressure on Kettle Draw Off		0.13
3rd Level - Resin Kettle Area	1.7	Charge Solvent and Draw Down		0.05
Wet Tank and Pump Room	0.1	Normal Operating Conditions		1.5

Chemical Operator TWA Exposure =

$$\frac{(4)(0) + (0.5)(0.05) + (1.6)(0.28) + (1.7)(0.05) + (0.1)(1.5)}{8} = 0.09 \text{ ppm}$$

* Non-detectable based on sampling method and analytical limit of 0.05 ppm.

Table C6.

TWA Exposure Levels for Jobs and Air Concentrations for Selected Areas

Plant D

Job/Sample Description	Sample Location	Shift	Sample Type	Epichlorohydrin Air Concentration
Kettle Area	Resin Building 2nd level	1	GA	0.36 ppm
Resin Operator	Resin Building	1	TWA	0.15
Adj. to Polymer Kettle Pump	Resin Building 1st level	1	GA	N.D.*
Resin Kettle	Resin Building 1st level	1	GA	N.D.
(Total EPI reaction period) Add EPI to reaction kill	Resin Building 2nd level	1	OP BZ	N.D.
Resin Operator	Resin Building 2nd level	2	TWA	0.05
Kettle Area	Resin Building 2nd level	2	GA	0.42
(Blank)				nil

* Non-detectable based on sampling method and analytical limit of 0.05 ppm.

Table C7

TWA Exposure Levels for Jobs and Air Concentrations for Selected Areas

Plant E

Job/Area	Shift	Type	Epichlorohydrin (ppm)	Toluene (ppm)	Xylene (ppm)	Acetone (ppm)	MEK (ppm)	Methyl Cellosolve (ppm)
Chemical Operator 3rd Floor	Evening	TWA	N.D*	2.1				N.D
Chemical Operator 2nd Level	Evening	TWA	N.D	0.58				
Chemical Operator 2nd Level	Evening	TWA	N.D	0.88	0.10	N.D		
C-7 Chemical Operator 2nd Level	Evening	TWA	N.D	1.7			N.D	N.D
Foreman (operating) (2nd Floor Office)	Evening	TWA	N.D	1.7			N.D	N.D
Chemical Operator 1st Level	Evening	TWA	N.D	0.59		0.23		N.D
Chemical Operator 3rd Level	Day	TWA	N.D	1.4				N.D
Chemical Operator 2nd Level	Day	TWA	N.D	3.8				
Chemical Operator 2nd Level	Day	TWA	N.D	3.2				N.D

Table C7 TWA Exposure Levels for Jobs and Air Concentrations for Selected Areas (continued)

Job/Area	Shift	Type	Epichlorohydrin (ppm)	Toluene (ppm)	Xylene (ppm)	Acetone (ppm)	MEK (ppm)	Methyl Cellosolve (ppm)
Chemical Operator 2nd Level	Day	TWA	N.D	2.5		N.D		
Flaker Operator 1st Level	Day	TWA	N.D	4.4		N.D	N.D	
Chemical Operator 2nd Level/East Side	Day	TWA	N.D	4.2		0.16		
Chemical Operator 3rd Level	Night	TWA	N.D	11.7				
Chemical Operator 3rd Level	Night	TWA	N.D	3.5				N.D
Chemical Operator 2nd Level, NW	Night	TWA	N.D	3.5				
Chemical Operator 2nd Level, NW	Night	TWA	N.D	3.0				
Flaker Operator 1st Level	Night	TWA	N.D	3.2				N.D
Chemical Operator 2nd Level/East Side	Night	TWA	N.D	0.84				

Table C7 TWA Exposure Levels for Jobs and Air Concentrations for Selected Areas (continued)

Job/Area	Shift	Type	Epichlorohydrin (ppm)	Toluene (ppm)	Xylene (ppm)	Acetone (ppm)	MEK (ppm)	Methyl Cellosolve (ppm)
3rd Floor Center Control Panel	Day	GA	N.D	0.49				N.D
3rd Floor North End	Day	GA	N.D				N.D	
2nd Floor Center Kettle Area	Day	GA	N.D				N.D	
2nd Level - West Side, Kettle Area	Day	GA	N.D	3.9	0.81			
2nd Level - East Side, Kettle Area	Day	GA	N.D	1.7				N.D
1st Floor Sparkler Filter Area	Day	GA	N.D	0.25				N.D

* Non-detectable based on sampling method and analytical limit of 0.1 ppm.

Table C8

TWA Exposure Levels for Jobs

Plant A Epoxy Production

Job	Shift	Type or Duration of Sample	Epichlorohydrin (ppm)	MEK (ppm)	Methylene Chloride (ppm)	Toluene (ppm)
Epoxy B Operator	1	TWA	N.D*	N.D	1.0	6.8
Epoxy B Operator	2	TWA	N.D	N.D	4.7	1.7
Epoxy B Operator	3	TWA	N.D	N.D	7.4	0.6
Epoxy C Operator	1	TWA	N.D	N.D	3.8	0.6
Epoxy C Operator	2	TWA	N.D	N.D	4.0	1.0
Epoxy C Operator	3	TWA	0.43	N.D	10.6	6.5

* Non-detectable based on sampling method and analytical limit of 0.05 ppm for epichlorohydrin and 0.1 ppm for MEK.

Table C9

TWA Exposure Levels for Jobs and Air Concentrations for Selected Areas
Plant B Epoxy Manufacturing

Job/Area	Description	Shift	Sample Type	Epichloro- hydrin ppm	Acetone ppm	MEK ppm	MIBK ppm
Shift Foreman	Routine	Evening	TWA	N.D.*		0.2	
Shift Foreman	Routine	Evening	TWA	N.D.	N.D.	0.2	0.7
Kettle Operator	Routine	Evening	TWA	N.D.			3.6
Kettle Operator	Routine	Evening	TWA	N.D.	3.8		16.3
	Blank			N.D.	N.D.	N.D.	N.D.
Resin Train Operator	Routine	Evening	TWA	0.07	0.8		
Feed & Re- covery Operator	Routine	Evening		0.10	N.D.		
Utility Operator	Routine	Evening	TWA	N.D.			
3rd level Kettle Area		Evening	GA	N.D.			

Table C9 (cont'd)

Kettle Operator	Routine	Day	TWA	N.D.	4.5	0.9	20.2
Kettle Operator	Routine	Day	TWA	N.D.			
Shift Foreman Epoxy Mfg.	Routine	Day	TWA	N.D.			
Maintenance Foreman	Routine	Day	TWA	N.D.	0.2	N.D.	0.8
Feed & Recovery Operator	Solvent Sampling	Day	TWA	0.42	0.1	N.D.	N.D.
Finishing Operator	Routine	Day	TWA	N.D.	2.8	2.1	5.8
Resin Train Operator	Routine	Day	TWA	0.12	0.1	N.D.	N.D.

* Non-detectable based on sampling method and analytical limit of 0.05 ppm for epichlorohydrin and 0.1 ppm for acetone, MEK, and MIBK.

Table C10

TWA Exposure Levels for Jobs and Air Concentration for Selected Areas⁺

<u>Job/Area</u>	<u>Shift</u>	<u>Epichlorohydrin (ppm)</u>
Shift Foreman A	Evening	N.D.*
Shift Foreman B	Day	N.D.
	Graveyard	0.36
Shift Foreman, Resin	Graveyard	0.60
Shift Foreman C	Evening	N.D.
Kettle Operator 2A	Day	N.D.
	Evening	N.D.
	Graveyard	N.D.
Kettle Operator 3A	Day	N.D.
	Evening	N.D.
Kettle Operator 3A	Graveyard	0.56
Resin Train Operator	Day	0.12
	Evening	0.07
	Graveyard	0.34
Resin Train Operator	Graveyard	0.83
Feed & Recovery Operator	Day	0.42
	Evening	0.10
	Graveyard	0.52
Utility Operator	Evening	N.D.
	Graveyard	N.D.
Kettle Area	Evening	N.D.
Maintenance Foreman	Day	N.D.
Finishing Operator	Day	N.D.

* Non-detectable based on sampling method and analytical limit of 0.05 ppm.

⁺ All graveyard shift samples collected and analyzed by NIOSH; all day and evening shift samples collected by Tracor Jitco.



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16. Abstract (Limit: 200 words) An industrial hygiene study to determine worker exposure to epichlorohydrin is presented to document existing engineering controls, work practices, administrative controls, and biological and environmental sampling requirements and control procedures being used by the companies. Individual walk-through and complete industrial hygiene survey reports were prepared for each plant and submitted individually. Five plants were surveyed. Two plants were both manufacturers and users of epichlorohydrin and three plants were users only. Detailed industrial hygiene surveys were made to conduct personal and area sampling in these plants over periods of three shifts. Air sampling data are included, as are summary tables of worker exposure levels to epichlorohydrin and associated solvents or process materials, evaluation of exposure level measurements, exposure control efforts, and recommendations. Chemical operators represent the job type that has the greatest exposure to epichlorohydrin in the manufacturing and resin manufacturing processes. Exposures ranging from nondetectable to 2.1 ppm for epichlorohydrin and from nondetectable to 8.9ppm allyl chloride for samples in two plants were reported. The five resin processing plants representing 39 samples showed exposure to chemical operators ranging from nondetectable to 0.83 ppm for epichlorohydrin.		13. Type of Report & Period Covered	
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