AN INDUSTRIAL HYGIENE STUDY OF POLYURETHANE FOAM INSULATION MANUFACTURING AT CPR, UPJOHN COMPANY

PLANT LOCATION:
TORRANCE, CALIFORNIA

SURVEY DATES:
24-25 OCTOBER 1979

SURVEY CONDUCTED BY:
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ABSTRACT

This industrial hygiene study is part of an industrywide industrial hygiene characterization of thermal insulation manufacturing and application activities. This survey was conducted at a polyurethane products manufacturing facility where liquid, two-component, polyurethane foam systems are produced. Personal sampling was conducted to determine worker exposure to MDI, fluorotrichloromethane, *alpha*-methyl styrene, methylene chloride, dimethylethanolamine, and dimethylcyclohexylamine (all components of polyurethane products). MDI was detected in one of five samples; the measured concentration was 0.002 ppm. Fluorotrichloromethane work shift TWA concentrations ranged from 0.95 to 96.0 ppm. *alpha*-Methyl styrene was not detected during the survey. The methylene chloride work shift TWA concentration was 11.0 ppm. Dimethylethanolamine was detected in two of ten samples (0.11 and 0.17 ppm). Dimethylcyclohexylamine was detected in eight of ten samples; the concentrations ranged from 0.054 to 0.81 ppm. The exposures to workers in all job classifications were found to be within the limits established by NIOSH and ACGIH and the OSHA standards for the compounds mentioned above. (Dimethylethanolamine and dimethylcyclohexylamine have no workplace standards for exposure.)

Atmospheric sampling was also conducted for TDI. The measured concentrations ranged from 0.022 ppm to 0.31 ppm. The measured concentrations exceed the ACGIH- and NIOSH-recommended limits and the OSHA standard. TDI is not a component of polyurethane thermal insulation products; however, exposure to this compound was evaluated because normal work activities involve the handling of TDI as well as materials used in thermal insulation products.

CONTENTS

TABLES

I. INTRODUCTION

AUTHORITY

The Williams-Steiger "Occupational Safety and Health Act of 1970" was passed into law "to assure safe and healthful working conditions for working men and women...." This Act established the National Institute for Occupational Safety and Health (NIOSH) in the Department of Health, Education, and Welfare and the Occupational Safety and Health Administration (OSHA) in the Department of Labor. The Act provided for research, informational programs, education, and training in the field of occupational safety and health and authorizes the enforcement of standards.

NIOSH has been given the authority and responsibility under the Act to conduct field research studies in industry, evaluate findings, and report on those findings. Section 20(a)(1) of the Act mandates NIOSH to "conduct (directly or by grants or contracts) research, experiments, and demonstrations relating to occupational safety and health...." 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 has established a contractual agreement with Enviro Control, Inc. (Enviro) to sutdy worker exposures at the Torrance, California facility of the CPR Division of the Upjohn Company as part of an industrywide study.

PURPOSE AND NEED FOR STUDY

Members of the insulation trade have long been noted to experience excess mortality due to malignant and nonmalignant respiratory diseases (Fleisher 1046, Marr 1964, Selikoff et al 1964, Keane et al 1966). Much of this observed disease has been attributed to exposures to asbestos fiber. However, the hazards associated with many of the other thermal insulation materials used remain unknown. With the great increase in the use of thermal insulation and the proliferation of insulation materials, there is need for a study to identify hazards associated with these materials.

The purpose of this study is to determine the types and quantities of thermal insulation materials commonly used in the United States, the end use categories for these materials, and information regarding past worker exposure data. Current occupational exposure levels of workers to two commonly used thermal insulation materials have been determined by industrial hygiene surveys.

MATERIAL SELECTION

To select the thermal insulation materials most appropriate for study within the resources available for this contract, the following selection criteria were applied to the more than two dozen materials currently being commonly used:

- Number of potentially exposed workers
- Present extent of use
- Projections of future extent of use
- Toxicity
- Purity of material in use
- Length of time material has been used
- Availability of worker exposure data

Since worker exposures to asbestos, glass fiber and mineral wool have been extensively studied, materials on which less information was available and which contained substantial toxic components were further considered for study. Applying the selection criteria with this emphasis led to the selection of plastic foam systems. Those materials foamed in place were considered to present a greater potential for worker exposure than preformed foam products. Therefore, considering past growth and potential future growth as well as the toxic components contained in urea formaldehyde and polyurethane foam systems for thermal insulation, these two foam systems were selected by NIOSH for detailed study.

The diisocyanate addition polymerization used for the preparation of polyurethane was discovered in 1937. Since then the area of polyurethane chemistry and applications has continuously grown. In 1968, approximately 500 million pounds of finished polymer were produced in the United States (1); in 1974, 1520 million pounds were produced (2). Considering the increasing use of polyurethane foams and the severe respiratory reaction associated with worker exposure to diisocyanates the selection of polyurethane foam thermal insulation systems for study is appropriate and timely.

SITE SELECTION

Two manufacturers and two applicators of polyurethane foam insulation systems were selected for study. An attempt was made to select two sets, each consisting of a manufacturer and an applicator of that manufacturer's material. This concept as well as the following factors were considered in selecting for study manufacturers and applicators of polyurethane foam insulation:

- Representativeness of the facility to the industry
- Number of potentially exposed workers
- Turnover rate
- Use of engineering controls
- History of production
- Whether potential exposure is mixed with other exposures
- Availability of data regarding past exposure levels and work practices

Based on these considerations, two of the largest manufacturers of polyurethane foam thermal insulation systems, CPR, Upjohn Company and Witco Chemical Company were selected for study. As appropriate applicators of each of these manufacturer's materials the Thermal Acoustic Foam Insulation Company and the John L. Renshaw Company, respectively, were selected for study of worker exposures.

II. PLANT SURVEY

DESCRIPTION OF PLANT

The CPR Division of the Upjohn Company (CPR Upjohn) has been engaged in the manufacture of polyurethane products for 20 years at its Torrance, California, facility. Products manufactured at this facility include rigid polyurethane foam systems (used in the thermal insulation industry), flexible foams and foam systems, and elastomers.

Of the some 235,000 square feet of plant area, only a portion is devoted to the production of polyurethane foam systems. The remainder of the facility is given over to the manufacture of the other products, as well as quality control and research and development laboratories, sales and administrative offices, and warehouses.

DESCRIPTION OF PROCESS

Rigid polyurethane foam systems for thermal insulation consist of an "A" and a "B" component. Most "A" components are not manufactured at this facility, but are repackaged into drums from tank car storage. Production of the "B" component at this facility is either a compounding or a blending operation.

"A" Component

The "A" component is principally diphenylmethane diisocyanate (MDI). Specifically, it is a mixture of polymeric (50%) and monomeric (50%) MDI that is made by the Upjohn Co. at another facility and marketed under the trade name of PAPI®.

The MDI repackaging processing is conducted several times per week, as needed, and usually involves only one employee. Twenty to fifty thousand pounds (40-100 drums) may be drummed per day. This operation takes place inside a 100' x 290' building which also serves as a warehouse. The bulk MDI tank car is located adjacent to this building; there is a permanent pipe connection to the MDI loading area.

"B" Component

The "B" component, or resin, is a mixture of ingredients that are prepared by either a compounding or a blending process. Neither process involves a chemical reaction. The formulation of a resin may vary depending upon the end use of that product. Resins intended for a variety of uses including thermal insulation are produced at this CPR Upjohn facility.

The resins used for thermal insulation contain one or more polyols (polyhydroxy compounds), a silicone oil copolymer, one or more tertiary amine catalysts, an organotin catalyst, fluorotrichloromethane (used as a blowing agent), and *alpha*-methyl styrene (used as a stabilizer). A phosphate ester-based, flame-retarding agent may also be added.

In the compounding process, any one of several various sized vessels may be used. All of the vessels are located inside the 40' x 50' compounding room. Raw materials are poured from drums into the top opening of the vessel using an electric drum lifter. The Compounder measures ingredients by weighing each drum before and after pouring. Ingredients are mechanically stirred until homogeneous and then sampled for quality control.

After compounding, the resin is pumped into 55-gallon drums. Drum loading takes place in an open area adjacent to the compounding vessels using a 3-inch feeder hose connecting the vessel with the drum.

Compounders routinely wear chemical splash goggles and rubber gloves when performing compounding and drum-loading activities. There are five production days per week in the compounding room. Each Compounder generally compounds several products per day.

Various resins are also produced in blending operations. The various ingredients are thoroughly mixed and the finished resin is transferred to 55-gallon drums. Essentially no spillage of resin occurs during this process. Two employees, a Blender and a Drum Handler, normally conduct the blending process. These employees routinely wear chemical splash goggles and rubber gloves. Eighty to a hundred drums may be filled on an average blending day.

Until mid-1979, another polyurethane insulation product, bun (board) stock, was produced at this plant. This process has been moved to a different Upjohn plant.

MEDICAL, INDUSTRIAL HYGIENE AND SAFETY PROGRAMS

The medical program at CPR Upjohn's Torrance facility includes preemployment physical examinations for all employees, including administrative employees. The program is administered by a consulting physician at the plant's clinic. Parameters included in the examination are: height, weight, blood pressure, temperature, and respiratory function. In addition, comprehensive medical and work histories are taken with emphasis on preexisting respiratory conditions. Yearly physical examinations are required for each employee with emphasis on the condition and performance of the respiratory tract. A medical examination is required following an overt exposure to a hazardous chemical. The clinic, located inside the plant, is staffed by a part-time nurse. Records have been maintained since the medical program was initiated approximately 20 years ago.

An important aspect of the medical program is the surveillance for employees who may have become sensitized to isocyanate compounds. As part of this surveillance, employees are required to report all colds and cold-like symptoms to the nurse or doctor. If conditions warrant it, the employee may be relocated.

The safety program was initiated in 1960; an industrial hygiene program was added in 1976. Both programs are under the supervision of the plant's

Administrator of Safety and Occupational Health, with some direction being provided by the Corporate Occupational Health and Safety Unit.

As part of the safety program, all personnel entering the production area are required to wear safety shoes and safety glasses. With regard to the compounding or blending of polyurethane products, safety procedures have been developed for the handling of the materials during specific tasks. These tasks, including the sampling, handling, and drum loading of both the "A" and "B" components, require the use of rubber gloves and chemical splash goggles.

Area and personal monitoring surveys have been conducted at the plant; however, only one survey has been conducted in thermal insulation product manufacturing areas. Many of the surveys were conducted to determine exposure to toluene diisocyanate (TDI). TDI, which is not used in the blending of thermal insulation products, has a much higher vapor pressure than MDI; consequently, its potential for exposure is considered to be greater than that for MDI. Recently, personal and area samples for *alpha*-methyl styrene were taken at the blending operation. *alpha*-Methyl styrene was not detected in any of the five samples taken.

RECORDKEEPING

The CPR Upjohn plant in Torrance began production of polyurethane products in 1960. The plant currently employs 80 people. Personnel records are available and contain general information such as date of birth, social security number, dates of employment, department and operations, and home address.

JOB DESCRIPTIONS

The Torrance plant operates with one shift (7:00 a.m.-3:30 p.m.) per day, five days per week. Employees performing compounding or blending operations include Compounders, Blenders, Drum Handlers, and Quality Control Technicians. Repackaging of the "A" component involves Drum Loaders. All production employees at the plant are involved in the manufacture of a variety of polyurethane products in addition to those used for thermal insulation.

Other persons who routinely enter the compounding or blending area for brief periods include the supervisor, the lead man, and several warehouse personnel. Access to locations where polyurethane products are manufactured or handled is not controlled. Anyone from the plant might enter these areas.

Compounder

The Compounder is responsible for the compounding of polyurethane products including the compounding of drum-sized batches of TDI prepolymers. Work activities are similar for the production of both the thermal and the nonthermal polyurethane products. Specifically, the Compounder adds raw materials to the compounding vessels by following a product formulation sheet. The Compounder weighs each drum of raw material and pours the contents into the top opening of the vessel using an electric drum lifter. He then reweighs each drum. (Due to the high viscosity of many of the raw materials, residues may be left in the drum after pouring.) Certain raw materials, such as the catalysts which are used in small quantities, are first poured into smaller containers for more precise weighing, and then poured by hand into the compounding vessels. After the materials have been compounded, the Compounder collects a sample for quality control by dipping a paper container into the top opening of the vessel; he then takes the sample to the laboratory for a quality control check. Adjustments to the resin may be conducted depending upon the laboratory results. If the sample is acceptable, the Compounder transfers the finished resin into drums. This is performed by lining up the drums on the compounding area floor, making a hose connection to the vessel, and filling the drums one at a time. Exposures may occur when ingredients are poured into the vessels, during drum loading, and when a sample is collected. The Compounders spend more than 90 percent of their time in the compounding room.

Blender

The Blender maintains the levels of raw materials in the supply tanks, monitors the flow of finished resin during drum filling, takes periodic samples for laboratory tests, and performs required maintenance and cleaning on the equipment. The Blender spends 100 percent of his time at the blending fill station when the equipment is in operation. When the operation is finished, the Blender may be involved in maintenance and repair, cleanup, filling the tanks, or ordering materials. His assigned tasks generally do not require him to enter other areas of production except for the "A" component drumming area which is located next to the blending operation in the same room. The blending process affords little opportunity for exposure.

Drum Handler/Drum Loader

During the survey, the Drum Handler for the blending operation also served as a Drum Loader for "A" component drum loading. During the blending operation, he assists the Blender by supplying empty drums at the fill station and by removing and sealing the full drums. During the operation he spends all of his time in close proximity to the fill station. When the blending process is not in operation he may be loading "A" component (MDI) into 55-gallon drums. Drum loading involves lining up the drums in an open area adjacent to the blending operation, making a hose connection to the MDI pipe, filling drums one at a time, and then sealing each drum. Employee exposure may occur during the filling of either resin or MDI drums.

Quality Control Technician

The Quality Control Technician is responsible for conducting quality control testing of the resin at the blending operation. He picks up samples of the current run of resin from the Blender and performs a test foaming operation by mixing the resin with MDI and observing various foam characteristics. He then sections and weighs the foam to determine the foam (end product) density. He conducts all testing at an open table located about 25 feet from the fill station. The Technician takes about five minutes to complete each test. While the blending process is in operation, the Technician spends about 70 percent of his time at or near the table.

EXISTING CONTROLS

Safety glasses are required at all times in the plant and laboratory areas. Chemical goggles are required in the vicinity of the compounding vessels during compounding. Employees engaged in the transfer and compounding of TDI wear full-facepiece, chin-style gas masks (NIOSH Approval No. TC-14G-86). Gas masks are not worn during the production of thermal insulation systems.

Exposure control at the blending operation is accomplished through the use of a local exhaust ventilation system, maintenance of the integrity of the components, and use of beveled couplings which insert directly into the drums during filling and prevent spillage.

Area monitoring of TDI vapor is conducted using an MDA No. 7005 isocyanate continuous monitor (MDA Scientific, Inc., Park Ridge, Illinois).

The local exhaust ventilation system vents the displaced air from the drum during filling. The system has branch ducts which lead to the drum locations at the fill station. The ducts terminate in a three-inch circular, plain (nonflanged) hood opening located above the open pressure relief bungs. Another branch duct terminates in a flanged canopy hood located over an overflow drum. The distance from the drum opening to the hood opening is about four inches; the hood openings were not positioned directly above the drum openings. Air flow measurements indicate an average face velocity of 660 fpm in the first duct and 840 fpm in a second duct (located upstream from the first duct). However, the calculated air velocities at each of the drum openings (based on measured air flows) are only 29 fpm and 37 fpm, respectively.

Other controls include a walk-in booth (15' x 18') located in the compounding area which is used for the transfer of TDI and for the mixing of polyurethane products containing TDI. Located within the booth are flexible hose air ducts which can be placed at the top of a drum during mixing. This booth has been in operation for three years. A walk-in oven, also located in the compounding area, was equipped with slot hood in 1977.

This oven is used to heat drums of raw materials including TDI. Two of the larger compounding vessels are equipped with local exhaust ventilation ducts which vent vapors generated while filling and mixing.

SURVEY LIMITATIONS

This industrial hygiene study represents an evaluation of conditions present on October 24-25, 1979. All apparent potential chemical and physical hazards were evaluated. Sampling was limited to those agents considered to be capable of causing significant exposures under existing conditions. Personal monitoring was conducted on five persons: two Compounders, one Blender, one Quality Control Technician, and one Drum Handler/Drum Loader. Area monitoring was used to supplement the personal monitoring. Generally, conditions monitored during the survey were considered to be representative of typical plant conditions, with the exception of the "A" component drum loading which was limited due to a short supply of bulk MDI.

SURVEY PROCEDURES

The survey procedures involved a discussion with the plant Manager of Technical Services and the Administrator of Safety and Occupational Health to obtain detailed information on the manufacture of polyurethane insulation products and the job classifications associated with their production. A personal monitoring schedule was developed to obtain data for an evaluation of worker exposure to selected raw materials associated with the production of polyurethane insulation products. Area monitoring sites were identified to supplement the personal monitoring and to define potential exposure areas. In addition, short-term personal monitoring samples for MDI and TDI were taken during performance of certain specific activities which were considered to present a significant potential exposure.

SAMPLING AND ANALYTICAL METHODS

Personal samples were collected in the breathing zone of individual employees. These were obtained by attaching the sampling device (sampling tube or impinger) to the shirt collar or lapel of the employee. Plastic tubing was used to connect the sampling device to the personal sampling pump located on the employee's belt. The flow rates through these sampling trains were determined both before and after sampling by use of a buret (soapbubble meter).

The following chemical air contaminants, identified as being potential air contaminants associated with the production of polyurethane insulation products, were monitored at the CPR Upjohn plant: TDI, MDI, dimethylethanolamine (DMEA), dimethylcyclohexylamine (DMCHA), fluorotrichloromethane (F-11), *alpha*-methyl styrene, and methylene chloride.

TDI and MDI

NIOSH Method No. P&CAM 141 (3) and Method No. P&CAM 142 (4) were selected for sampling and analysis of TDI and MDI, respectively. The two methods have identical sampling procedures. Sampling was conducted by drawing a known volume of air through a Bendix midget impinger containing 15 mℓ of absorbing solution (hydrochloric acid and glacial acetic acid in distilled water). The sampling rate was 1 liter per minute. MSA Model G or S sampling pumps were used. After each sampling period, the impinger contents were transferred to glass vials with Teflon-lined caps. Two impingers, each containing 15 mℓ of absorbing solution, were handled in the same manner as the samples, except that no air was drawn through them. The contents of these were analyzed by the laboratory as blanks.

Analysis of TDI and MDI involves the formation of a colored complex which is subsequently quantified utilizing a spectrophotometer. The analytical method cannot be used to differentiate between polymeric and monomeric forms; consequently, the sample results may reflect concentrations of both forms. The limit of detection for this analytical method was 0.5 microgram (μg) per sample for TDI and 0.2 μg per sample for MDI.

DMEA and DMCHA

Currently, NIOSH and OSHA do not have sampling and analytical methods specific for either of the amine compounds, DMEA and DMCHA. NIOSH Method No. P&CAM 270 (5) was selected for this survey based on chemical similarity between DMEA and other aminoethanol compounds which are covered in this method. This method was followed for both compounds with a slight variation in the sampling phase. The method recommends stabilization of the amine by adding hydrochloric acid (with a microliter syringe) to the collection tube immediately after sampling is completed. However, shelf-life stability studies conducted by the analytical laboratory indicated that both compounds were stable for up to two weeks; consequently, the stabilization procedure was not performed.

Sampling was conducted by drawing a known volume of air through a silica gel tube to trap the amine compounds. MSA Model C-200 and SKC Model 222-3 personal sampling pumps, set at or near 100 mℓ per minute, were used. The silica gel tubes consist of glass tubes, 7 cm long, packed with 150 mg of silica gel in two section. The absorbing section contains 100 mg of silica gel and the backup section contains 50 mg. Two of the tubes containing silica gel were handled in the same manner as the samples, except that no air was drawn through them. These tubes were submitted for analysis as blanks.

At the laboratory, the samples were desorbed with methanol:water (4:1). An aliquot was taken and made basic (pH > 8) with 0.5 mℓ of a 0.2 N NaOH-methanol:water (4:1) solution, and then analyzed by gas chromatography. Desorption efficiency tests were also conducted by the laboratory by spiking silica gel tubes with known amounts of dimethylethanolamine and dimethylcyclohexylamine, and then analyzing in the same manner as that used for the samples. The desorption efficiencies for the two compounds are 92 percent and 88 percent, respectively. The silica gel tube-loading range for the desorption efficiency tests was several orders of magnitude greater than the field samples. Consequently the reported desorption efficiencies may not be an accurate reflection of the sample desorption efficiencies.

Fluorotrichloromethane (F-11)

Sampling and analysis for F-11 was conducted in accordance with NIOSH Method No. S102 (6). A known volume of air was drawn through a charcoal tube to trap the F-11 vapor present. MSA Model C-200 and SKC Model 222-3 personal sampling pumps, set at 30 mℓ per minute, were used. The charcoal tubes consist of glass tubes, 10 cm long, packed with two sections of 20/40 mesh activated coconut charcoal. The front section contains 400 mg of charcoal, and the backup section contains 200 mg. Analysis involves desorbing the F-11 with carbon disulfide and subsequent analysis by gas chromatography. A tube from the same batch as the samples was handled in the same manner as the samples, except that no air was drawn through it. This tube was also submitted for analysis as a blank.

alpha-Methyl Styrene and Methylene Chloride

NIOSH Method Nos. S26 (7) and S329 (8), respectively, were selected for sampling of *alpha*-methyl styrene and methylene chloride. Sampling methods for both compounds are similar, and both are compatible with the sampling method for F-11. Consequently, one collection tube was generally used for sampling and analysis for all three compounds. The analytical methods for *alpha*-methyl styrene and methylene chloride involve desorption with carbon disulfide and injection of an aliquot into a gas chromatograph. A tube from the same batch as the samples was handled in the same manner as the samples, except that no air was drawn through it. This tube was also submitted for analysis as a blank.

At the end of the survey, all samples were shipped by air to Clayton Environmental Consultants, Inc., in Southfield, Michigan. All analyses were performed by Clayton which is accredited under the Laboratory Accreditation Program of the American Industrial Hygiene Association.

EVALUATION CRITERIA

TDI and MDI

The American Conference of Governmental Industrial Hygienists (ACGIH) in 1959 adopted a Threshold Limit Value (TLV) for TDI of 0.1 ppm as an 8-hour TWA concentration limit. In 1962, the ACGIH reduced the TLV to 0.02 ppm based upon a study which demonstrated respiratory irritation and asthma-like symptoms in workers in several plants where TDI concentrations were considerably below 0.1 ppm. In 1963, the TLV for TDI which remained at 0.02 ppm was changed to a ceiling value (9). The current ACGIH TLV (10) is 0.02 ppm. In 1979, a notice of intended change for TDI was proposed by the ACGIH (11). The change, if adopted, would reduce the current TLV of 0.02 ppm to 0.005 ppm as an 8-hour TWA with a short-term exposure limit (STEL) of 0.02 ppm.

The ACGIH adopted a TLV for MDI of 0.02 ppm as a ceiling value in 1965. Although the vapor pressure of MDI is relatively low, significant vapor concentrations were reported in the workplace. Available data indicated that MDI was similar to TDI in its irritant and sensitizing properties, suggesting that a similar ceiling value of 0.02 ppm was warranted (9).

In 1973, NIOSH published criteria for a recommended standard for occupational exposure to TDI, recommending a TWA limit of 0.005 ppm and a ceiling limit of 0.02 ppm. In 1978, this recommended standard was extended to include all diisocyanates including MDI. Exposure to diisocyanates should be controlled so that no employee is exposed at concentrations in excess of 5 ppb as a TWA for a 10-hour workshift, 40-hour workweek, and a ceiling limit of 20 ppb for a 10-minute sampling period (9).

The current OSHA standards (29 CFR 1910.1000) for occupational exposure to TDI and MDI are ceiling limits of 0.02 ppm for each compound.

Fluorotrichloromethane (F-11)

The current ACGIH TLV for F-11 is 1000 ppm (10). F-11 is a central nervous system depressant in animals; however, there are no reported effects in humans. The current OSHA standard for F-11 is 1000 ppm. There is no NIOSH recommendation for occupational exposure to this compound.

alpha-Methyl Styrene

The current ACGIH TLV for *alpha*-methyl styrene is 100 ppm (10) expressed as a ceiling concentration. This TLV was set to prevent eye irritation (12). The present OSHA standard for *alpha*-methyl styrene is 100 ppm, expressed as a ceiling concentration. There is no NIOSH recommendation for occupational exposure to this compound.

Methylene Chloride

The ACGIH TLV for methylene chloride is 200 ppm (10) with a STEL of 250 ppm. A notice of intended change has been published which, if adopted, will reduce the TLV to 100 ppm with a STEL of 500 ppm. The current TLV was established to prevent interference with delivery of oxygen to tissues and to prevent depression of the central nervous system (10).

The NIOSH recommendation for a standard for occupational exposure to methylene chloride is 75 ppm averaged over a work shift up to 10 hours per day, 40 hours per week, with a ceiling exposure limit of 500 ppm averaged over 15 minutes. The basis for this recommendation is prevention of significant interference with delivery of oxygen to tissues and abnormalities in central nervous system function. Methylene chloride has been shown to be metabolized to carbon monoxide in the body (11).

The current OSHA standard for methylene chloride is 500 ppm averaged over an 8-hour work shift, with an acceptable ceiling level of 1000 ppm and a maximum peak concentration of 2000 ppm for five minutes in any 2-hour period.

DMEA and DMCHA

There are currently no standards or recommended values for occupational exposure to dimethylethanolamine (DMEA) or dimethylcyclohexylamine (DMCHA).

III. RESULTS AND DISCUSSION

Results of personal monitoring for ceiling and TWA concentration determinations obtained during the 24-25 October 1979 survey of the CPR Upjohn plant are presented in Tables 1 through 8. The sampling periods do not include lunch breaks, equipment setup times, or end-of-shift cleanup periods. Unscheduled breaks are included. The results of blank sample analyses were less than the detectable limit for all compounds sampled.

MDI

Results and activities performed during the sampling period are presented in Table 1. The series of short-term sampling periods used encompasses all of the MDI loading for the entire week. As noted previously, supplies of MDI were low during the week of the survey. Under normal conditions, MDI loading might require several days per week.

An MSA Model G pump was used in the MDI-collection sampling train. The coefficient of variation based on multiple calibration at a fixed rotameter setting was 0.02. The laboratory reported an analytical coefficient of variation of 0.05 or less. The total coefficient of variation (C_T) is equal to the square root of the sum of the squares of the pump and analytical coefficients of variation. Assuming an analytical coefficient of variation of 0.05, the C_T is 0.05.

The Drum Loader spends nearly 100 percent of his time beside the drums. This is essentially a clean operation, although there is some spillage (a few drops) when the pump stem is removed from one drum and placed into the next drum.

TABLE 1

MDI Exposure for Drum Loader

Sample #	Date	Sampling Period (min)	Activities	Concentration (ppm)
1	10/24	21	Filling drums with MDI	<0.001
2	10/24	11	Filling drums with MDI	<0.002
3	10/25	16	Filling drums with MDI	<0.001
4	10/25	25	Filling drums with MDI	<0.0008
5	10/25	20	Filling drums with MDI	0.002

Personal monitoring results indicate that the NIOSH and ACGIH limits and the OSHA ceiling standard of 0.02 ppm were not exceeded during the MDI loading operation. All concentrations were less than the detectable limit, with the exception of Sample #5 which was 0.002 ppm. The NIOSH recommended limit for a TWA concentration for a normal workday is 0.005 ppm. One area sample was taken during the loading operation (see Table 2); MDI was not detected in this sample. Neither MDI or TDI was detected in either of the two blanks.

TABLE 2

Results of Area Sampling for MDI and TDI

Sample #	Date	Sampling Period (min)	Compound	Location	Concentration (ppm)
1	10/24	27	MDI	In drum-loading area	<0.0005
2	10/24	33	TDI	Inside walk-in booth	0.19
3	10/25	16	TDI	Inside walk-in booth	0.014

TDI

Table 3 shows the results of personal monitoring samples for Compounder B. The series of short-term samples represents only a portion of the total exposure time of Compounder B during the compounding of a TDI 80/20 prepolymer. Although this product is not a component of polyurethane thermal insulation products, exposure to TDI was evaluated because the normal work activities of Compounders at this plant include the compounding of TDI prepolymers several times a month. An employee 8-hour TWA was not constructed because this operation represents only a peripheral exposure in the manufacture of thermal insulation products.

The compounding of the TDI prepolymer takes place inside a walk-in booth. The Compounder, however, spends less than 25 percent of his time inside the booth during the 5-hour blending process over a 2-day period. Samples #2 and #3 reflect exposures to the TDI prepolymer when it was hot (50°C). All three samples indicate that the NIOSH-recommended limit and the OSHA ceiling standard were exceeded during the compounding of TDI 80/20 prepolymer. However, in Sample #1 the lower confidence limit (LCL) at the 95 percent confidence level is below the standard; consequently, noncompliance cannot be concluded in this instance. The relatively higher concentrations reported in Samples #2 and #3 occurred on the second day of the survey when the TDI blend was hot (50°C). Sample #1 was taken when TDI was at room temperature. This difference in operating conditions may account for the wide variation in sample results between the two sampling days.

TABLE 3

TDI Exposure for Compounder B
During the Compounding of a TDI Prepolymer

Sample #	Date	Sampling Period (min)	Activities	Concentration (ppm)
1	10/24	37	Adds raw materials to TDI	0.022
2	10/25	12	Adds raw materials to TDI (TDI at 50°C)	0.31
3	10/25	10	Adds raw materials to TDI (TDI at 50°C)	0.14

Area samples taken inside the booth (see Table 2) show concentrations of 0.19 and 0.014 ppm on two different days. Personal protective equipment (described previously in this report) was worn while the Compounder was inside the booth.

FLUOROTRICHLOROMETHANE (F-11) AND *alpha*-METHYL STYRENE

Employees' TWA exposures to F-11 and *alpha*-methyl styrene are presented in Table 4. Samples #1 and #2 were collected over essentially the whole shift and represent 8-hour TWA concentrations. Samples #4, #5, and #6, although less than 8 hours, encompass all probable exposure periods for that day; consequently, the estimated 8-hour TWA may be somewhat less than the reported concentrations. Sample #3 represents the exposure of Compounder B only during the compounding of product 480-B, a commonly produced thermal insulation product. The brief sampling period of Sample #7 encompasses only a portion of this employee's work activities at the blending operation. Based on observations, the unsampled time periods are estimated to be equal to or less than the sampled periods in exposure potential.

TABLE 4

Employees' Time-weighted-Average Exposure to Fluorotrichloromethane (F-11) and *alpha*-Methyl Styrene

Sample #	Employee	Date	Sampling Period (min)	Activity	Concentration (ppm)	
					F-11	*alpha*-Methyl Styrene
1	Compounder A	10/24	438	Compounds 489-C, withdraws sample, does paperwork at desk	96.0	<0.084
2	Compounder A	10/25	428	Compounds 347-B, drums 2158-90 (contains no F-11 or *alpha*-methyl styrene)	35.0	<0.085
3	Compounder B	10/25	96	Compounds 480-B	94.0	<0.52
4	Blender	10/24	357	Operates blending equipment (product 480-2.5-B)	3.6	<0.78
5	Blender	10/25	344	Maintenance of equipment, general cleanup, paperwork	0.95	<0.13
6	Quality Control Tech'ian.	10/24	312	Conducts quality control tests at blending operation	6.4	<0.15
7	Drum Handler	10/24	92	Supplies drums to blending operation fill station, seals and weighs drums	6.8	<0.37

Fluorotrichloromethane (F-11)

Personal monitoring results indicate that the 8-hour TWA OSHA standard for F-11 of 1000 ppm was not exceeded during the survey. The relatively higher concentrations obtained from personal samples of Compounders A and B are attributed to an observed increased employee contact with F-11. The Compounders pour F-11 from drums into open compounding vessels, whereas the Blender, Quality Control Technician, and Drum Handler, who work at the blending operation, have less contact with F-11. Visible amounts of F-11 vapors are released during the pouring of F-11 in the compounding room.

Results of area samples (Table 5) support the personal monitoring sample results in showing the differences in F-11 concentrations between compounding and blending operations. Area Sample #4 and personal Sample #3 (Table 4) encompass the same operation. The elevated concentration in the area sample is attributed to the proximity of the sampling device to the compounding vessel. F-11 was not detected in the blank.

TABLE 5

Results of Area Samples for
Fluorotrichloromethane (F-11) and *alpha*-Methyl Styrene

Sample #	Date	Sampling Period (min)	Location	Concentration (ppm)	
				F-11	*alpha*-Methyl Styrene
1	10/24	286	In compounding room on loading platform adjacent to compounding vessel, sampling period includes compounding 469-C	113.0	<0.16
2	10/24	415	Near drum fill station at blending operation during production of 480-2.5-3	3.9	<0.67
3	10/25	89	In compounding room near compounding vessel during production of 347-8	110.0	<0.52
4	10/25	94	In compounding room near compounding vessel during production of 430-8	321.0	<0.37

alpha-Methyl Styrene

The personal monitoring results show that *alpha*-methyl styrene was not detected during the survey. This could be attributed to the relatively small amount of the compound used in the production of resins (usually 0.4 percent of the amount of F-11 used). Neither *alpha*-methyl sytrene nor methylene chloride was detected in the blank.

AMINE COMPOUNDS

Employees' time-weighted average exposures to dimethylethanolamine (DMEA) and dimethylcyclohexylamine (DMCHA) are presented in Table 6. Neither DMEA nor DMCHA was detected in either of the two blanks. Samples #1 and #2 represent employee exposures in the compounding room. The relatively higher concentration of DMCHA obtained from the personal samples on Compounder B, compared with that of Compounder A, is attributed to the use of DMCHA in the compounding of product 480-B (a thermal insulation product). Amine compounds were not used in the compounding of any other products in the compounding room during the survey; consequently, exposure of Compounders to amines during unsampled time periods is estimated to be zero.

TABLE 6

Employees' Time-Weighted Average Exposure to Dimethylethanolamine (DMEA) and Dimethylcyclohexylamine (DMCHA)

Sample #	Employee	Date	Sampling Period (min)	Activity	Concentration (ppm)	
					DMEA	DMCHA
1	Compounder A	10/24	289	Compounds 489-C (does not contain amines), withdraws sample, does paperwork at desk	<0.02	<0.007
2	Compounder B	10/25	96	Compounds 480-B	<0.14	0.62
3	Blender	10/24	262	Operates blending equipment (product 480-2.5-B)	0.17	0.45
4	Blender	10/24	93	Operates blending equipment (product 480-2.5-B)	0.11	0.81
5	Quality Control Tech'ian.	10/24	215	Conducts quality control tests at the blending operation	<0.064	0.061
6	Quality Control Tech'ian.	10/24	99	Conducts quality control tests at the blending operation	<0.13	0.11
7	Drum Handler	10/24	195	Supplies drums to the blending operation fill station, seals and weighs drums	<0.073	0.054
8	Drum Handler	10/24	99	Supplies drums to the blending operation fill station, seals and weighs drums	<0.15	0.20
9	Blender	10/25	259	Maintenance of equipment, general cleanup	<0.095	0.056
10	Blender	10/25	95	General cleanup in blending equipment area, paperwork	<0.22	<0.077

Although amine (and other) catalysts are added to the resins in small amounts (resins generally contain less than 1% by weight), their addition in the compounding process presents a greater potential exposure than other ingredients because it involves an additional step. In the compounding of product 480-B, the amine catalysts were first poured from the drum into a smaller container in order to obtain a precise weight; the catalysts were then poured into the opening of the compounding vessel.

Based on the observed increased worker contact with raw material in the compounding room compared with the blending operation, differences in exposure levels are expected between the two areas. However, a comparison of Compounder B and the Blender, who were producing products containing equivalent levels of DMEA and DMCHA, shows that both workers had detectable exposures to DMCHA but only the Blender showed any exposure to DMEA. The higher concentration of DMCHA obtained in the Blender's samples may have been caused by DMCHA leaking in the blending area; the detectable concentrations of DMEA obtained in the Blender's samples cannot be explained on the basis of worker activities.

Samples #4 through #8 represent employee exposure during the manufacture of product 480-B in the blending operation. The relatively higher concentrations of DMCHA obtained in each employee's second sample (i.e., Samples #4, #6, and #8) could be attributed to a small DMCHA leak (mentioned previously) which developed a few hours into the shift and remained until the blending operation was shut down. (The duration of the leak encompassed the last part of the first sample period and all of the second sample period.) A strong amine-like odor was detected in the blending area coincidental with this leak. The relatively higher concentrations of DMCHA obtained in the Blender's sample compared with the Quality Control Technician and the Drum Handler may be due to this worker's closer proximity to the leaking DMCHA or the drum fill station, or both.

Samples #9 and #10 show the Blender's exposure in the blending area on the following, nonproduction day. Sample #9, in which a relatively higher concentration of DMCHA was obtained, includes repair work on the DMCHA supply pipe and filling the supply tanks. Sample #10 does not include any activities involving direct exposure to amine catalysts.

Results of area samples are presented in Table 7. Area samples #1 through #4 correspond with the worker activities represented in the personal monitoring Samples #1 through #4. The area sample results support the personal monitoring sample results in that detectable concentrations were obtained for the same worker activities in both sets of samples.

TABLE 7

Results of Area Samples for DMEA and DMCHA

Sample #	Date	Sampling Period (min)	Location	Concentration (ppm)	
				DMEA	DMCHA
1	10/24	286	In compounding room near compounding vessel, includes compounding of 489-C	<0.075	<0.026
2	10/24	94	In compounding room near compounding vessel during production of 480-B	<0.085	0.20
3	10/24	250	Near drum fill station at blending operation during production of 480-B	0.31	0.57
4	10/24	111	Near drum fill station at blending operation during production of 480-B	0.25	0.11

METHYLENE CHLORIDE

The Blender's time-weighted average exposure to methylene chloride is presented in Table 8. This sample includes the weekly cleanup in the blending area. The cleanup involves mopping the floor with methylene chloride. Cleanup generally takes less than one hour. Sample results show that the Blender is not exposed to methylene chloride in excess of the ACGIH- or NIOSH-recommended limits or the OSHA standard.

TABLE 8

Blender: Time-Weighted-Average Exposure to Methylene Chloride

Sample #	Date	Sampling Period (min)	Activity	Concentration (ppm)
1	10/25	344	Maintenance of equipment, general cleanup (including washing floor with solvent), paperwork	11.0

IV. CONCLUSIONS AND RECOMMENDATIONS

Existing precautions are adequate to maintain vapor concentrations of materials associated with the manufacturing of polyurethane thermal insulation systems within the limits established by NIOSH and ACGIH, and the present OSHA standards. The compounds dimethylethanolamine and dimethylcyclohexylamine, which were detected in the personal samples of several employees, have no standards or recommended limits for occupational exposure; consequently, the significance of the detected concentrations relative to worker health has not been assessed.

Additional controls are necessary to reduce TDI levels below the current workplace standard during TDI blending operations. On two occasions, the personal samples (Table 3) exceeded the acceptable ceiling concentration of 0.02 ppm, which is the OSHA standard and the ACGIH- and NIOSH-recommended limit. Local exhaust ventilation controls should be applied to the TDI mixing drum to capture TDI vapors at the source of contamination. In the interim, adequate respiratory protective devices should be used during TDI blending operations, and a respiratory protection program including respirator fit testing should be implemented. NIOSH recommends a type C supplied-air respirator with full-facepiece operated in positive-pressure mode for use with diisocyanates, rather than the full-facepiece, chin-style gas masks used.

The local exhaust ventilation system at the blending operation may not be capturing air contaminants released from the pressure relief drum opening. The velocity at the drum opening is only a fraction of the measured exhaust duct velocity. Repositioning, lowering, or flanging of the exhaust duct may be necessary to increase air velocity at the source of contamination. The ACGIH (14) guidelines for this type of operation are 100-200 fpm.

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