NIOSH

TECHNICAL REPORT

Extent-of-Exposure Survey of Methylene Chloride

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health

EXTENT-OF-EXPOSURE SURVEY OF METHYLENE CHLORIDE

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Public Health Service
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PREFACE

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. 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 22(e) 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 SRI International to perform an extent of exposure study of methylene chloride. The funding for this work was provided by the Division of Cancer Cause and Prevention, National Cancer Institute, through the Interagency Agreement on Research on Occupational Carcinogens (Y-01-CP-60605).

ABSTRACT

Following preliminary, walk-through, industrial hygiene surveys of seven U.S. plants in which methylene chloride is used, three facilities were selected for further surveying of human exposures to the chemical. Ninety-four full-shift personal samples for methylene chloride covering workers in 19 job classifications, and area samples of 19 different sites at these three facilities were collected and analyzed. The findings were reported separately for the three plants. This report consolidates the findings for the individual plant surveys.

The report includes--in addition to background information on production and uses, toxicity and human exposure standards, and production processes--descriptions of operations and jobs, exposure control efforts, health and safety programs, air sampling data collected, summary tables of worker exposure levels to methylene chloride and associated substances (acetone, methanol, coffee dust, and ammonia), sampling and analytical procedures and methods, evaluation of findings, and recommendations.

Results of the survey showed time-weighted-average personal exposures for normal operations ranging from 0.3 to 561 ppm--four samples, at one plant, above 500 ppm and one sample, at another plant, above 200 ppm. Exposures to the other substances surveyed were all below current permissible levels.

This report was submitted in partial fulfillment of Contract No. 210-76-0158 by SRI International under the sponsorship of the National Institute for Occupational Safety and Health.

CONTENTS

FIGURES

TABLES

INTRODUCTION

Under the terms of the authority and responsibility given to the National Institute for Occupational Safety and Health (NIOSH) to develop needed information regarding potentially toxic substances in industry (see Preface), NIOSH contracted with SRI International to conduct an industrial hygiene study to assess exposure to four chlorinated hydrocarbons. Chlorinated hydrocarbons were selected as an area for study because vinyl chloride has been shown to be a human carcinogen and because a growing number of the compounds have been shown by research to be known animal carcinogens and suspected human carcinogens. The four compounds selected for study--benzyl chloride, monochlorobenzene, methylene chloride, and methyl chloride--were chosen on the bases of: the industry in which the compound is produced or used; history of production and use; processes and related new materials involved; and number of workers potentially exposed. The report that follows concerns industry exposures to methylene chloride.

OBJECTIVES AND SCOPE OF THIS STUDY

The objectives of this industrial hygiene study were to:

- Review and summarize the toxic effects of methylene chloride.
- Document and describe selected workplaces, including information on the production and use of methylene chloride.
- Identify job types and describe specific jobs.
- Describe current industrial hygiene and safety practices, including engineering controls, work practices, administrative controls, and biological and environmental sampling and control procedures.
- Document (1) job-function exposures to methylene chloride and (2) relevant process or production changes occurring during the survey that could affect the evaluation of job-function exposures.
- Describe analytical procedures for collection and analysis of methylene chloride.

Detailed industrial hygiene surveys reflecting these objectives were made at three U.S. facilities where methylene chloride is used. These detailed surveys, which had been preceded by preliminary surveys of seven facilities, were conducted during the period November 1978 - May 1979.

LIMITATIONS OF STUDY

The industrial hygiene surveys represent singular evaluations of worker exposures to methylene chloride 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. The possibility of encountering a highly unusual exposure situation during a sampling period of several shifts was remote; therefore, the resulting exposure measurements can be considered to represent only those exposures that are associated with the usual and normal operating conditions.

BACKGROUND

Methylene chloride, also known as methylene dichloride, methylene bichloride, and dichloromethane, is a colorless, heavy, mobile, and volatile liquid with a pleasant odor. The chemical formula and chemical and physical properties of the compound are given in Table 1.

PRODUCTION AND USES

The substance is widely used for a variety of purposes, including paint stripping, manufacturing of photographic film, propelling aerosols, manufacturing of triacetate fibers, metal degreasing, extraction in the food products industry, fumigation, and fire extinguishing. Paint removing accounts for the chemical's greatest use (30% of total consumption in 1977).[1,2] It has been estimated that 217,000 metric tons of methylene chloride were produced in the United States in 1977.[3]

TOXICITY AND HUMAN EXPOSURE STANDARDS

The current Occupational Safety and Health Administration (OSHA) standard for methylene chloride is 500 ppm for an eight-hour time-weighted average (TWA) exposure.[4] A Threshold Limit Value (TLV) of 200 ppm, adopted by the American Conference of Governmental Industrial Hygienists (ACGIH) is currently in effect, but there is a proposal to lower the TLV to 100 ppm.[5] In March of 1976, a National Institute for Occupational Safety and Health (NIOSH) criteria document on methylene chloride was released in which a still lower TWA of 75 ppm is recommended.[1]

The current OSHA standard of 500 ppm is based on work published in 1944 by Heppel and others, who demonstrated through animal experimentation that methylene chloride is a narcotic and irritant at high airborne concentrations (5,500-10,000 ppm).[6] Several reports and studies indicate that methylene chloride can produce stupor, headache, irritability, giddiness, and other central nervous system effects among exposed workers. At levels well above those normally found in the occupational environment, the compound can cause damage to lungs, liver and kidneys.[1]

Studies in the 1970s demonstrated that methylene chloride is metabolized in the body to carbon monoxide, ultimately causing an elevation in carboxyhemoglobin,[1,7,8,9] and it is on the basis of these studies that NIOSH has recommended a TWA of 75 ppm. As part of this recommendation, as well as to account for the concomitant effects of methylene chloride and carbon monoxide, NIOSH recommends that the exposure to methylene chloride be limited so that the combined exposure of methylene chloride and carbon monoxide (when levels of carbon monoxide exceed 9 ppm) follow this equation:[1]

$$\frac{C(CO)}{L(CO)} + \frac{C(CH_2Cl_2)}{L(CH_2Cl_2)} \leq 1$$

Table 1. Chemical and physical data for methylene chloride.

Chemical formula: CH_2Cl_2	
Some chemical and physical properties:	
Freezing point	-97°C
Boiling point (760 mm HG)	40.4°C
Specific gravity (20°C)	1.320
Density (20°C)	1315.7 kg/m^3
Molecular weight	84.93
Vapor density (Air = 1.02)	2.93
Diffusivity in air: 25°C, 1 atm	9×10^{-5} m^2/sec
Refractive index (20°C)	1.4244
Auto-ignition temp.	640°C
Flash point	none
Explosive limits: (25°C, vol. in air)	14-25%
Solubility (H_2O, 20°C)	13.2 g/kg
Vapor pressure (0°C)	147 mm Hg
at 20°C	349
at 30°C	511

Source: Compiled from Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Ed., Vol. 5. New York, Wiley-Interscience, 1979, p. 687.

where:

$C(CO)$	=	TWA carbon monoxide, ppm
$L(CO)$	=	recommended TWA carbon monoxide, ppm
$C(CH_2Cl_2)$	=	TWA methylene chloride, ppm
$L(CH_2Cl_2)$	=	recommended TWA methylene chloride, ppm

Several other effects have been attributed to methylene chloride exposure. A study published in the Soviet Union reported that methylene chloride was found to cross the placenta in pregnant workers;[10] some teratogenic effects, including cleft palate and rotated kidneys, were observed in experimental animals;[1] and the chemical has also been found to be mutagenic in salmonella typhimurium and E. coli that were exposed for 6-8 hours in a desiccator to concentrations as low as 11 ppm.[11]

The Eastman Kodak Company recently reported on the results of an epidemiologic study of a large working population exposed continuously to relatively low levels of methylene chloride for up to 30 years.[12] The purpose of the study was to determine whether employees exposed to methylene chloride exhibited an increased risk for specific causes of mortality, specifically ischemic heart disease, that could be attributed to the work environment. Air sampling results based on each sample obtained in the work area revealed a methylene chloride concentration range of 0-350 ppm with a mean value of less than 100 ppm. Continuous personal monitoring showed a time-weighted average concentration of 33 ppm.

While the results were not reported in complete detail, those that were published indicate no excess mortality for ischemic heart disease in the production workers exposed to methylene chloride. It would be helpful, however, to have a detailed presentation of standardized mortality ratios for ischemic heart disease, to know more about the selection procedure for hiring production workers; to see if the results change when the 7% of employees who have terminated are also included; and to learn whether the results are supported by another mortality study being performed by Dow Chemical and Celanese Corporation.

PROCESSES FOR PRODUCING METHYLENE CHLORIDE

Methylene chloride is commercially produced by two major processes: one beginning with the chlorination of methane, the other with the hydrochlorination of methanol. (See Figures 1 and 2.)

In the production of methylene chloride as a second step in the chlorination of methane, pre-heated gaseous methane and chlorine are forced into a reactor, where ultraviolet light from mercury-arc lamps promote the reaction. The temperature within the reactor is maintained at about 360°C (although some plants use temperatures at 450°-500°C to obtain particularly high yields of methylene chloride). It has been found that a ratio of 1.7 moles methane to 1 mole chlorine yields about 30% methylene chloride in the resultant chloromethane product mixture. If, however, the feed gas contains two volumes methane to one volume each of chlorine and (probably recycled) methyl chloride, the yield of methylene chloride may be as much as 80% of the total product mixture.

The basic chlorination reactions involved are as follows:

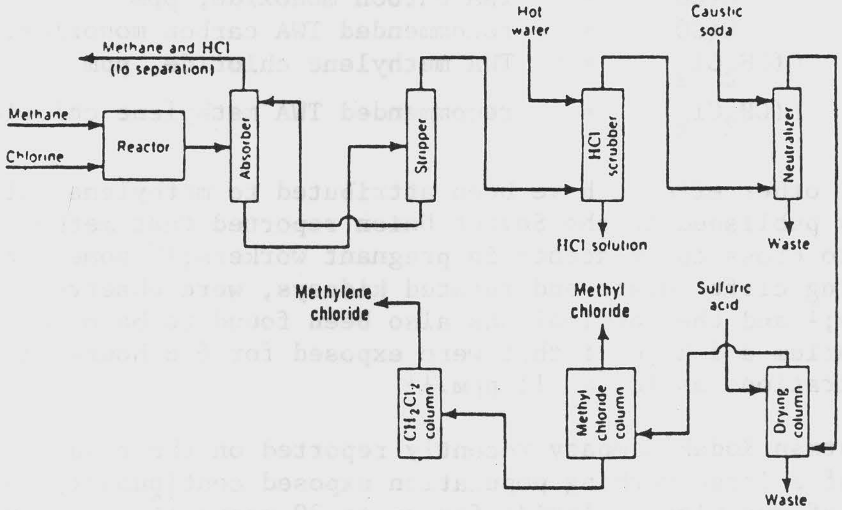

Figure 1. A schematic diagram of producing methylene chloride by chlorination of methane.[13]

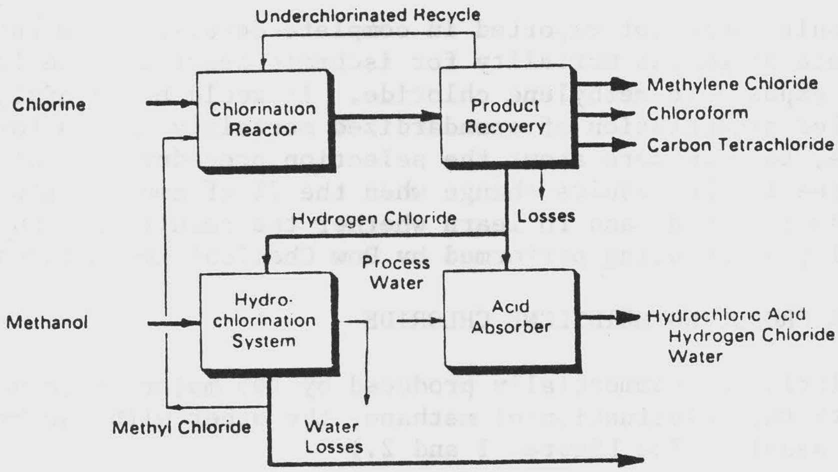

Figure 2. A schematic diagram of producing methylene chloride by hydrochlorination of methanol.[14]

$$\text{uv light}$$
$$Cl_2 \rightleftarrows 2Cl\cdot$$

methane	$CH_4 + 2Cl\cdot \rightarrow CH_3Cl + HCl$
methyl chloride	$CH_3Cl + 2Cl\cdot \rightarrow CH_2Cl_2 + HCl$
methylene chloride	$CH_2Cl_2 + 2Cl\cdot \rightarrow CHCl_3 + HCl$
chloroform	$CHCl_3 + 2Cl\cdot \rightarrow CCl_4 + HCl$
	carbon tetrachloride

Methylene chloride can also be produced by chlorinating methyl chloride that results from the hydrochlorination of methanol, with the advantage that waste hydrogen chloride is returned to the reactor for further methyl chloride production.[14,15] The reaction is as follows:

$$CH_3OH + HCl \rightarrow CH_3 + H_2O$$
$$CH_3Cl + 2Cl\cdot \rightarrow CH_2Cl_2 + HCl$$

A refinement in the process for producing methylene chloride involves using finely divided sand, suspended in a fluidized bed, as a reaction medium and maintaining the reaction temperature at 250-390°C. Hydrogen chloride liberated during reaction is recycled to produce fresh methyl chloride from methanol.

FACILITIES AND PERSONNEL SURVEYED

Three facilities at which methylene chloride is used were surveyed for this report: a plant that manufactures acetate and triacetate fibers; a coffee processing plant; and a U.S. Air Force base at which one of the principal missions is maintenance of aircraft and other equipment. In an attempt to provide as much of an exposure cross-section as possible, the plants were selected on the basis of such criteria as number of persons potentially exposed; level of substance concentrations as determined by preliminary area sampling; continuous operations and therefore relatively constant exposure levels; exposure situations limited primarily to the target chemical; unique use of the substance; and process representative of a major use of the substance.

The facilities are designated as Plants A, B, and C in this report. They are briefly described below, followed by descriptions of their process and control operations, personnel and jobs in which potential exposure to methylene chloride occurs, and health and safety programs that have been established.

DESCRIPTION OF FACILITIES

Following are brief overviews of the three facilities surveyed for this report.

Plant A--Overview

At this facility, located in the Southeast, methylene chloride is used in the conversion of cellulose acetate and triacetate flake into fibers. Production of fibers, which began in 1948, is carried out in four major buildings, designated as: (1) Cellulose Acetate, (2) Block I Extrusion, (3) Block II Extrusion, and (4) Textile. The plant operates continuously--24 hours per day, 7 days per week.

Plant B--Overview

Principal operations at Plant B, located in the Southwest, have been concerned since 1947 with the processing and packaging of coffee. A decaffeinating facility, in which methylene chloride is used as a solvent, began operations in the early 1950s. The company reports that this decaffeinating facility is the largest of two that it operates in the United States. Prior to mid-1975, the solvent that had been used in decaffeination (for some 20 years) was trichloroethylene.

Plant C--Overview

Plant C, one of several installations of the U.S. Air Force Logistics Command, began operations in 1941. About one third of the installation's operations, as measured in terms of persons, is concerned with the maintenance of Air Force aircraft and other equipment. A part of this maintenance activity, in turn, is the stripping of paint from aircraft, and methylene chloride is the major constituent in the stripping compounds used.

PROCESS AND CONTROL OPERATIONS

Plant A--Process and Control

Methylene chloride is used at Plant A to dissolve triacetate polymer flake, thereby converting this solid material into a liquid medium that is suitable for extruding fibers. The liquid form of the polymer is referred to as "dope."

The triacetate flake and other dry ingredients are added, automatically, to a batch mixer through a weigh hopper. A solution of methylene chloride and methanol is then fed into the mixer via a closed piping system and slowly mixed with the solids until they are completely dissolved. Following the mixing, the dope is filtered to ensure that it is absolutely free of materials that could block the holes in the jets, or "spinnerettes", through which the liquid polymer will be subsequently extruded.

During the mixing and filtration processes, the solution is maintained in an enclosed system, and there are no exposures under normal operating conditions. However, the filter presses require periodic stripping and replacement of the filter elements. Approximately 10-12 filter presses are stripped each week, and the elements are replaced with fresh cloth filters. The removed filters are permitted to partially dry before being processed to recover the solvent and polymer. To remove and replace the filter elements in each press takes two men approximately 45 minutes. A local exhaust system has been installed in the filter press rooms of Block I and Block II to aid in the removal of solvent vapors when the filters are dismantled.

Following filtration, the triacetate dope is pumped to the extrusion area, where it is preheated, filtered through a candle filter, and forced through an extrusion head (spinnerette or jet). The extruded fibers travel down through a drying cabinet in which air removes the solvent and dries the fibers. The fibers are brought together at the base of the cabinet, and the resulting triacetate yarn is spun onto a carrier package known as a bobbin. A number of individual cabinets are grouped together in a long row (called a metier).

The principal control of the solvent vapors--in addition to general ventilation--is the individual cabinet, through which air is constantly pulled from its openings to the work area. This air passes through the cabinet, collecting vapors from the drying filament, and finally passes through a charcoal recovery system to reclaim the solvent. There is a slight negative pressure inside the cabinet to prevent the solvent-laden air from escaping back into the work area. However, the fiber filaments continue to release some methylene chloride vapor while being spun onto the bobbin and throughout other operations which the yarn undergoes. These other operations include: twisting, which is mechanically performed to strengthen the yarn; coning, which transfers the yarn from a supply bobbin to a cone for use in the textile industry; and beaming, which is the transfer of filament from several hundred bobbins onto a large spool known as a weaving or section beam. All of these operations are conducted in the Textile Department of the plant.

The operations involved in producing triacetate fiber are illustrated in Figure 3.

Plant B--Process and Control

Methylene chloride is used at Plant B in the extraction of caffeine from green coffee beans. The extraction process is carried out throughout eight levels of a 14-level, partially enclosed structure.

The method of removing caffeine from the coffee beans is called solvent extraction (the leaching of a soluble substance from a solid using a liquid solvent). In this continuous process, caffeine is first extracted from green coffee beans in an extractor column. The now caffeine-rich extract is then fed to a rotating disc contactor (RDC) column in which a countercurrent liquid/liquid process removes the caffeine, using methylene chloride as the single solvent. Following this step, the water is stripped of its residual solvent by fractionation and recycled to the process; also, the solvent from the RDC is purified by distillation and is recycled. The entire process is illustrated in Figure 4. There are negligible amounts of solvent residue in the decaffeinated beans and in the crude caffeine, according to data collected by the company (see Appendix A).

The process was reported to be operating at about two-thirds capacity during the time of this survey. Each month, the process uses approximately 5100 gallons of methylene chloride, most of which leaves the facility in the wastewater or through a carbon bed vent system.

Two sets of quality-control product samples are taken by two different operators once each shift. In one set, an operator collects decaffeinated beans, prior to the drying stage, with a cup attached to a long handle. This worker removes a cover, opens a port to where beans are flowing through a four-inch pipe, lowers the cup into the port opening, and draws out a sample, which he places in a plastic bag. The port is then closed. The operator's exposure to methylene chloride during the collection of these samples is negligible.

Another worker obtains samples of the solvent extract from the top of the rotating disc column, where the solvent is flowing through a series of water-chilled sampling loops. For this set of samples, the worker opens a series of valves and places a glass jar under a spout, which is then opened until the jar is filled. During this sampling the operator wears protective gloves. Although a small amount of the extract drips onto the floor, the sampler's exposure to methylene chloride is negligible.

The company reports that the in-plant air is routinely monitored for methylene chloride and that bag or syringe grab sampling and also sampling using charcoal tubes are performed. Syringe grab sampling using 1 cc plastic disposable syringes was observed by the survey team. Samples are taken to a laboratory on the plant site where they are analyzed by gas chromatography with a flame ionization detector. A 5 ppm standard is injected into the gas chromatograph before and after each set of samples is analyzed.

Plant C--Process and Control

Methylene chloride is used at Plant C as the major constituent in stripping compounds for removing paint from the outer skin of aircraft. The bulk of the paint stripping operations are conducted in a newly-constructed depainting

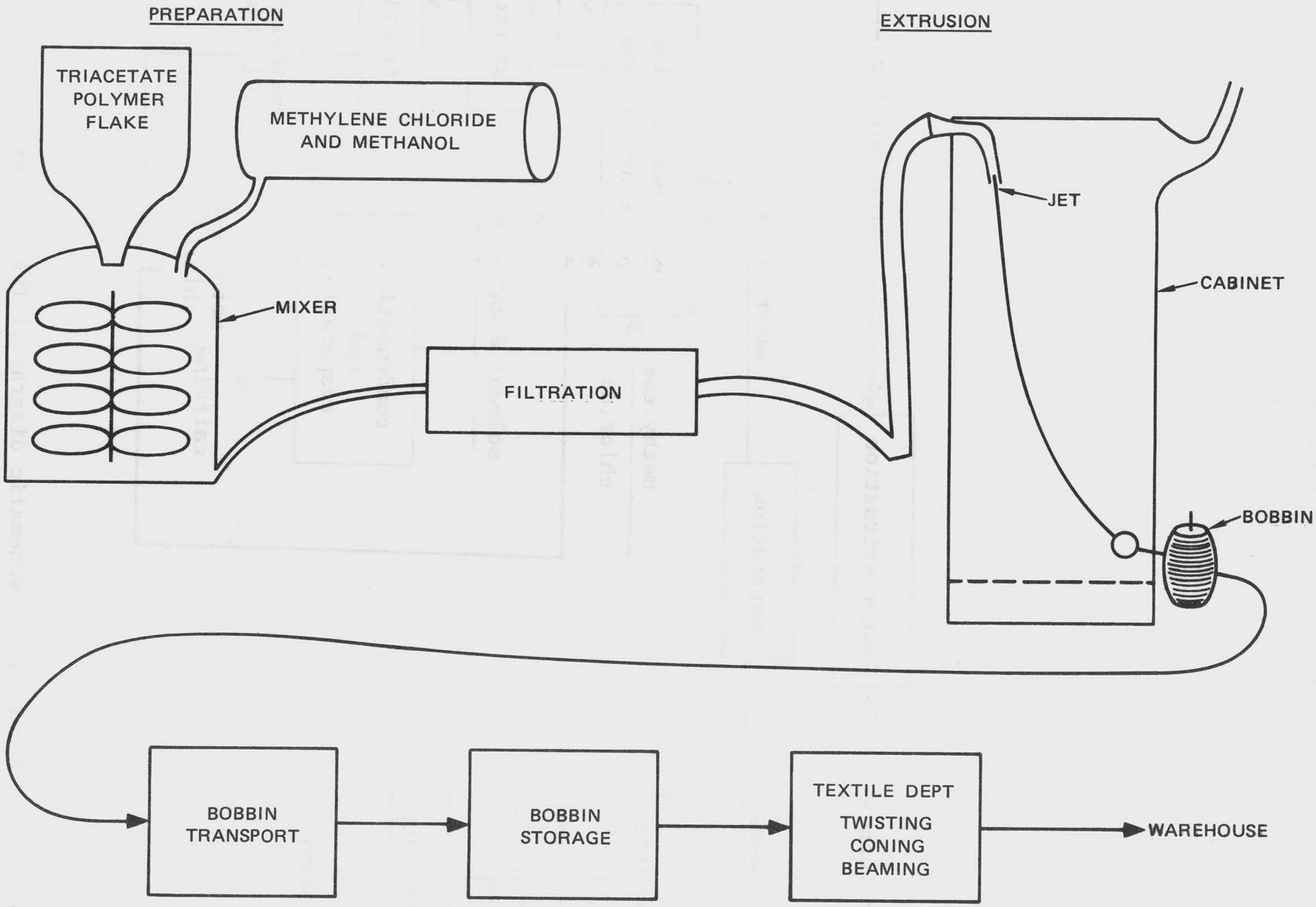

FIGURE 3 A SCHEMATIC DIAGRAM OF THE PROCESS FOR MAKING TRIACETATE FIBERS

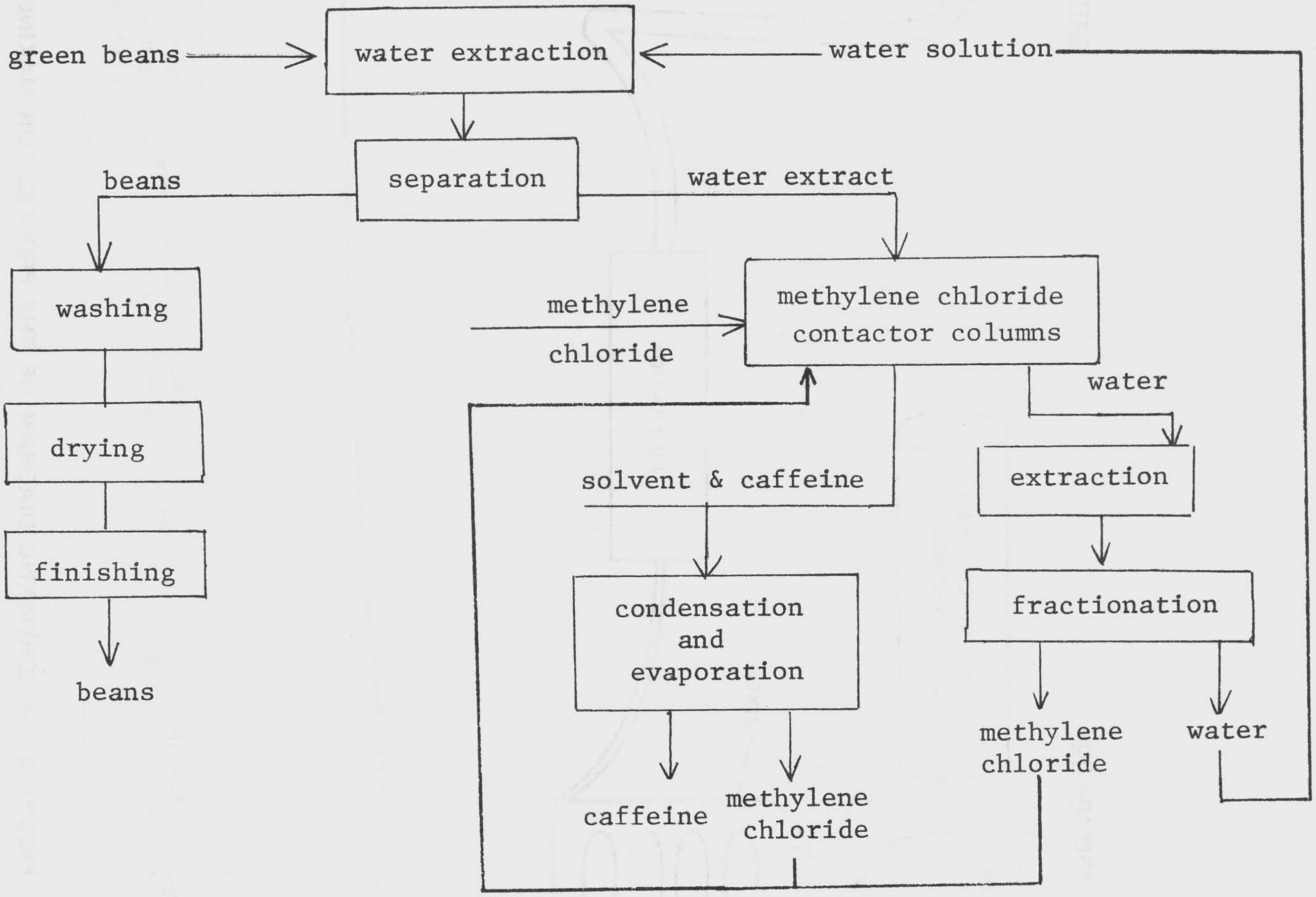

Figure 4. A schematic diagram of the process for producting decaffeinated coffee.

facility. The layout of this facility is shown in Figure 5.

Preparatory to stripping, the parts and equipment that are not to be stripped and that could be affected by the stripping compound are masked with aluminum sheeting and aluminum tape.

Once the aircraft is masked, the building doors are closed and the exhaust ventilation fans are turned on. Air enters the building from louver openings in the door and in the side walls. Personnel then apply the paint stripping compound to the various sections of the plane. The tail section, approximately 50' high, is sprayed from large, elevated, hydraulically-operated lifts. The top and sides of the fuselage are sprayed by personnel working from two cages suspended from overhead cranes. In addition to the personnel on the lifts and in the overhead cages, there are persons applying stripper from the ground, from elevated platforms, and from hydraulically operated stairs.

The stripping compound initially used is Intex 857 "mild" stripper, which contains approximately 50% methylene chloride, 25% aliphatic and aromatic hydrocarbons, 10% non-volatile hydrocarbons, and 15% water and ammonia. This compound is supplied in large, 300-gallon containers which are positioned at appropriate locations near the aircraft--two containers placed on either side of the tail section, two others positioned on either side of the fuselage in front of the wings.

Pneumatically-operated pumps in the containers force the stripping compound through hoses to the spray handle. The stripper is sprayed onto the painted surfaces in the form of a fine mist, in most cases from above with the spray directed downward. For certain areas, such as the underside of the aircraft, the spray was directed upwards, but by proper positioning of the lift and cages, this upward spraying was kept to a minimum. Several coats of the "mild" stripper are applied, with scraping and brushing of the surfaces between coats to assist in loosening and removing the paint. A phenolic-based, "hot" stripper is applied to stubborn areas. Table 2 lists several of the stripper solutions that could be used for the stripping operation.

Tools used for the stripping and removal of the paint include a polypropylene scrubbing brush, a rubber squeegee, aluminum wool on a mop handle, wire brush, and a scraping tool. For applying the stripping compound to small areas, such as around the windows of the cockpit, a bristle brush dipped in an open plastic pail of stripper is generally used.

Approximately 1000 gallons of the non-phenolic, "mild" stripper is used for an aircraft. Four to fifteen (an average of six) drums of "hot" phenolic stripper are used.

As noted in Figure 5, one wall of the depainting building consists of overlapping sliding doors. These doors, which are electrically operated, open to permit the aircraft to enter the bay and, during the stripping process, are closed, and exhaust ventilation fans on the opposite wall are activated to create an air flow across the building of between 25 and 50 linear feet per minute. At the entrance to the exhaust plenum, directly in front of the filters, the measured air velocity ranged from 100 fpm to as high as 625 fpm. These velocities were attained with three of the four fans in an operating mode.

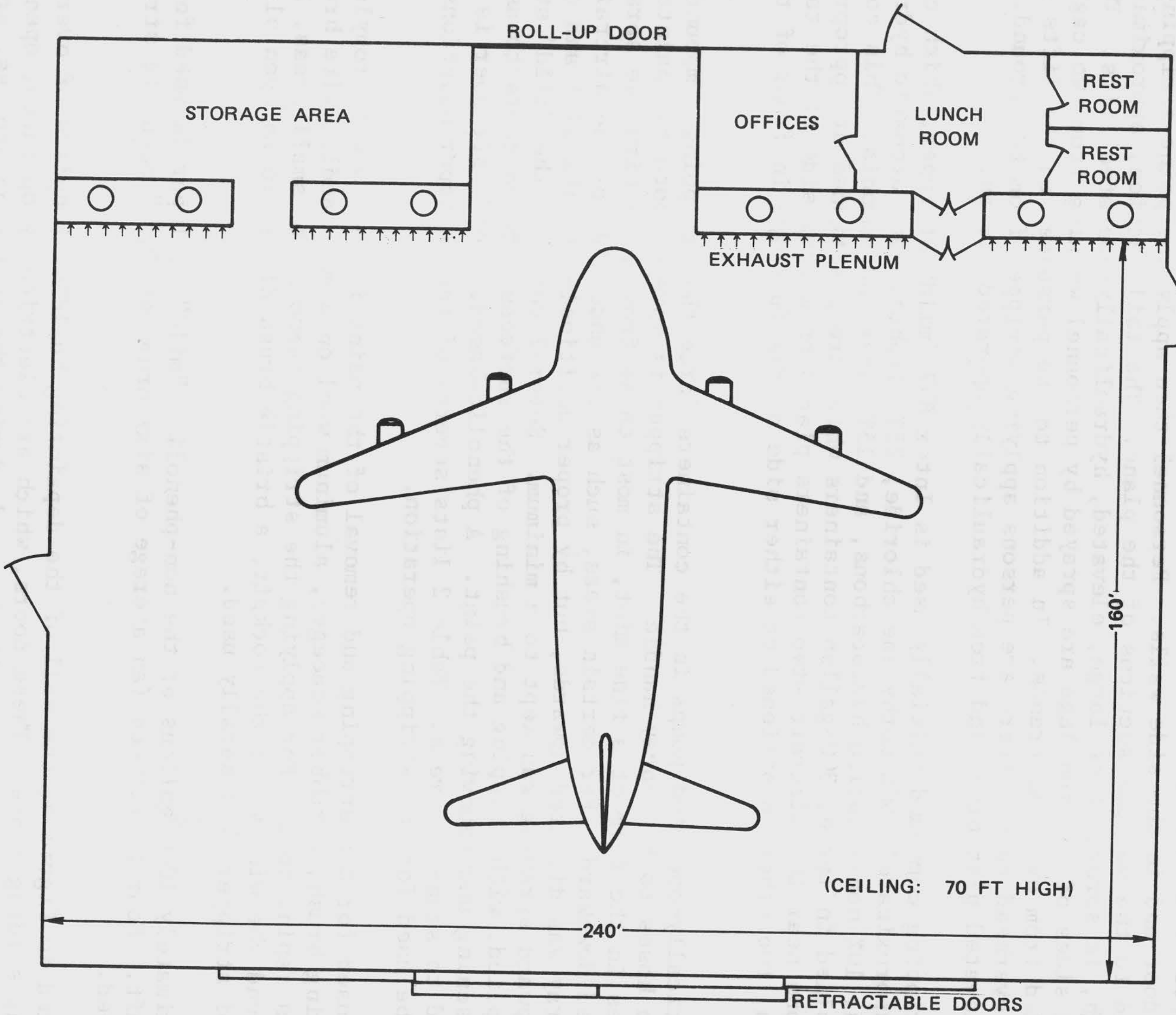

FIGURE 5 LAYOUT OF THE AIRCRAFT PAINT STRIPPING FACILITY AT PLANT C

Table 2. Principal ingredients of compounds used in paint stripping operations at Plant C.

Product	Ingredient	
	Substance	Percent*
Turco 5351 Thin	Phenols	24
	Methylene chloride	48
	Caustic soda	1
	Water, soaps, and corrosion inhibitors	
Turco 5873	Methylene chloride	58
	Water	18
	Ammonia	2
	Xylene	3
	Pine oil	6
	Chromate as total Cr.	(2000 ppm)
Pennwalt 739-A (hot strip)	Methylene chloride	55
	Sodium chromate	1
	Phenols	15
Eldorado PR-3400	Methylene chloride	72
	Tetrahydrofuran	2
	Ethanol	4
	Ammonium hydroxide	6
	Potassium hydroxide	3.5
Inland Chem. Co. AP-599	Methylene chloride	75
	Perchloroethylene	2
	Petronate HL	6.7
	Ammonium hydroxide	3.7
	Methanol	8.8
	Sodium chromate	0.5
Intex 857	Methylene chloride	50
	Aliphatic and aromatic hydrocarbons	25
	Nonvolatile aliphatic and aromatics	11
	Water and ammonia	13
	Chromates	0.16
Pennwlat 768-A+		
Alodine	Chromate salts	1/2-3 oz/gal
	Nitric acid (Ph--1.5-2.0)	8-12 mg/gal
	Inert ingredients	

*Except where noted.

+Data not readily available (phenolic-type paint remover).

Additional air removal is accomplished by pulling vapors through gratings into a trough in the floor.

The aircraft being stripped during the survey was a C-130 Hercules cargo plane. Work on the plane was to continue for approximately nine full shifts before the entire stripping job was completed.

PERSONNEL AND THEIR ACTIVITY

Plant A--Personnel

Of the approximately 1950 employees at Plant A, some 920 are potentially exposed to methylene chloride. However, all of these personnel may not be working with the triacetate fibers continuously throughout the entire work shift. The 920 employees potentially exposed are, roughly, equally divided over four rotating shifts, although there are fewer personnel in the work areas during the afternoon and night shifts.

There are 20 employees in the preparation area, where the "dope" (liquid polymer) for the fiber is mixed and filtered. In the extrusion areas, there are approximately 260 operators in Block I, where acetate fibers are primarily produced (some triacetate yarn is also produced) and some 80 employees in Block II, where most of the triacetate yarn is manufactured. There are approximately 100 employees in the Bobbin Stores area; and in the Textile Department, twisting employs approximately 130; coning has 140; and beaming has approximately 190 persons. As mentioned previously, not all of these personnel are continuously exposed to methylene chloride. (Extent of potential exposure depends primarily on whether acetate or triacetate fibers are being run.)

Job titles and description of the personnel in the fibers production areas are:

Preparation Area

Control Operators--charge and monitor the mixing of the triacetate flake and methylene chloride and methanol in the mixers. These persons are located in a remote control room and were not included in the detailed monitoring.

Pressmen--prepare the filter presses for filtration of the dope. They remove and replace filter elements and also operate the recovery system for reclamation of dope from the elements.

Extrusion Area

Jet Wiper--operates and maintains the extrusion equipment to ensure an even and continuous flow of the dope.

Doffer--removes and replaces bobbins on the metiers. Loads bobbins onto the transport, observes the operation of the individual cabinets.

Patroler--assists the Doffers. Removes "shorts," bobbins that do not have a full amount of yarn. Also observes the operation of the individual cabinets.

Bobbin Stores

Bobbin Stores Operator--loads and unloads transports, readies bobbins to be taken to the Textile Department. Also empties "shorts," which are recycled back to the mixers.

Textile Department

Twisting Operators-

- Creeler--doffs full packages (bobbins) after yarn had gone through mechanical twisting to increase its strength.
- Lace-up Operator--laces or threads ends of full bobbins through the twisting machine onto empty spools.

Coning Operators--doffs full cones, replaces empty bobbins, and laces up ends of full bobbins for transfer to cones.

Service Operator--provides transport with full bobbins for the twisting and coning operators; takes back empty bobbins. Not included in monitoring.

Conveyor Operator--operates conveyor "train" throughout all yarn-handling departments. Collects full transports and returns empty transports to Bobbin Stores. Not included in monitoring.

Beaming Operator--removes and replaces bobbins that transfer yarn onto weaving section beams. Ties end together to maintain continuous feeding and transfer of yarn.

In addition to the job categories mentioned above, there are plant maintenance, quality control, and supervising personnel who may receive intermittent exposures to methylene chloride.

The duration of exposure for these workers and the concentration of methylene chloride exposure may vary with the job. However, the potential for exposure is up to eight hours per day.

Plant B--Personnel

As many as 53-58 employees (salaried and hourly) work in the decaffeination area at Plant B. Included in this group are general laborers (two per shift), maintenance workers, and supervisors. The number of operators and their job titles are listed below:

Job classification	Workers per shift
Supervisor	1
Process Operator	2
Extractor Operator	3
Evaporator Operator	1
Coffee Handler	1
General Laborers	6-7 (two per shift)

(continued)

(continued)

Job classification	Workers per shift
Maintenance (for all areas)	5
Maintenance Supervisor	1

Job descriptions of each of the operators, as furnished by the company, are as follows:

Evaporator Operator: This operator is responsible for the methylene chloride evaporation system, the clean-solvent storage system, and caffeine recovery system. He maintains records on all of those systems and is continuously monitoring and adjusting the equipment to maintain proper levels in all of the tankage. This worker spends the majority of time on the second and third levels of the decaffeination facility.

Coffee Handler: This operator is responsible for the decaffeinated coffee from the time it enters the bean drying system, through the storage silos, to the user area. He controls bean moisture; maintains the identity of beans, by batch and silo location, and is also responsible for taking inventories of beans. This worker spends most of his time on the second and third levels of the process facility.

Extractor Operators: These operators are responsible for the extractors and their storage tankage. They maintain records of the operation and adjust, control, and maintain proper levels in their vessels. These operators spend the majority of their time on the second level.

Process Operators: These operators are responsible for the rotating disc columns, the extract solvent stripper, the wastewater stripper, and the carbon adsorption system. They maintain records on their systems and adjust, control, and maintain proper operating conditions and levels. These operators spend the majority of their time throughout the facility or in the control room.

Although not included in this list of workers, the caffeine dryer operator was included in the study since he spends most of his time on the first level of the extraction process and could be exposed to methylene chloride vapor.

The exposure duration for these workers is quite variable; however, the potential exposure to methylene chloride in the decaffeinating facility is up to eight hours per day.

Plant C--Personnel

There are 106 persons who work in the aircraft stripping operation at Plant C. They are all designated as Paint Strippers (with a job grade of WG-5). They work on a three-shift, five-day-per-week schedule. At the time of the survey made for this study, 22 Paint Strippers were working an aircraft, each stripper responsible for an assigned area of the plane. General area assignments are:

Location	Number of Workers
Nose	4
Fuselage, front	2
Fuselage, center	2
Fuselage, top	2
Wing, engine	2
Wing	3
Wheel Well	3
Tail Section	4

Each worker masks off, applies stripper to, and washes down his or her assigned area. In addition to the personnel identified above, there are supervisory personnel, drivers, maintenance personnel, and other "depainter" personnel who may be exposed intermittently to methylene chloride. The exposure duration for these workers is quite variable; however, for most of the paint stripping crew, the exposure to methylene chloride may be up to eight hours per day.

HEALTH AND SAFETY PROGRAMS

Each of the facilities surveyed has a formal health and safety program, which are described below.

Plant A--Health and Safety

The health and safety program of Plant A is under the direction of an Environmental Superintendent, whose responsibilities include directing the efforts of the plant safety committee, comprised of both management and hourly employees. This committee conducts department inspections and assists in resolving problems relating to safety and health. The Environmental Superintendent has direct responsibility for the plant safety and environmental program and has a staff of eight persons.

There is an environmental technician at the plant who performs periodic measurements and monitoring of work operations for assessing employee exposure to various chemicals, including methylene chloride (using charcoal tubes and a direct-reading portable gas chromatograph). Also available for technical assistance are industrial hygienists from the corporate staff located in New York City.

The medical needs of Plant A are handled by a nurse on each shift and by a physician employed part-time. They conduct pre-employment physical examinations and periodic examinations, as well as handling injury and illness cases. Some 85 persons throughout the plant have been trained in first aid and are able to provide immediate care in the event of an accident.

Medical monitoring is being provided to employees exposed to certain hazardous or toxic chemicals, including asbestos (insulation), chromic acid, and benzene. Also, periodic audiometric examinations are given to employees working in areas designated as high-noise exposure areas. Exempt salaried personnel are given biannual or annual physical examinations depending on age.

Personal protective equipment in general is not required in most areas of the plant. However, for persons working in areas of the Textile and Extrusion departments that have been designated as high-noise areas, hearing protection is required. Other operations sometimes may require protective clothing, safety glasses or chemical goggles, safety shoes, respirators, aprons, or gloves, and these are provided to the employee.

Plant B--Health and Safety

At Plant B, the health and safety program is under the direction of a Safety Coordinator. The coordinator's responsibilities include conducting safety meetings with department supervisors, providing safety information, performing safety audits, and conducting formal meetings between representatives of management and labor. A corporate industrial hygienist/toxicologist (located at corporate headquarters, in another state) is available to provide technical support for the Safety Coordinator. It was reported that personal sampling for methylene chloride, four times per year per operator, and routine area monitoring are performed using charcoal tubes and bags or syringes.

The medical department is staffed by one consulting physician and three full-time nurses. Medical assistance is augmented by the department supervisors, who are all trained in first aid. In addition, nine employees have been trained as Emergency Medical Technicians. A nearby hospital has facilities for emergency care.

Pre-employment physical examinations are required by Plant B for all of its employees. Periodic physical examinations are performed on a one- to three-year cycle (depending on the employee's job and age). Methylene chloride workers are required to have annual physicals. These physicals include a blood profile, EKG (if over the age of 40), urinalysis, hearing test, and pulmonary function test. Methylene chloride workers also receive a (SMA20) series of laboratory blood-evaluations.

The plant requires that every employee working in the production areas wear company-supplied work clothing. Bump hats, safety glasses, and safety shoes are optional but are made available to every production worker. During specialized operations, additional safety equipment is available (and/or required), including several different types of respirators such as nuisance-dust masks, cannister respirators, and self-contained breathing apparatus (Scott Air Pacs®). Gloves and safety shields are also provided, and emergency safety showers, eyewash facilities, change rooms, lockers, and showers are available.

Plant C--Health and Safety

The safety, medical, and industrial hygiene programs at the Base in which Plant C is located are the responsibility of the Safety Officer, Occupational Medical Services, and Bioenvironmental Engineering Services, respectively. The safety function at the Base, staffed by 19 persons, is responsible for flying, ground, explosive ordnance, and missile safety programs, as well as for safety in the paint stripping and other ground maintenance activities.

Occupational Medical Services comprises three physicians, four nurses, several technicians, and ancillary staff. This group operates a dispensary, which is open from 7:30 a.m. to 4:00 p.m. A hospital on the Base supplements the services of the dispensary.

The Bioenvironmental Engineering Services Division consists of four military officers, one civilian industrial hygienist, two civilian industrial hygiene technicians, and five military industrial hygiene technicians. An annual, routine sampling survey, in which charcoal tubes are utilized, is made for methylene chloride, ammonia, and phenols. This survey is augmented by sampling that is conducted when a problem arises, when special projects are undertaken, or when new materials are tested.

Pre-employment physical examinations are required of all Air Force personnel (except those in clerical positions). These physicals include medical history, audiograms, chest X-ray, EKG (if over the age of 40), vision tests, serology, and urinalysis. Annual examinations are required for certain jobs (paint stripping is a required job group) and are tailored to the exposure. Annual physicals are similar to the pre-employment examination. Those workers who perform paint stripping receive annually, in addition to the tests already mentioned, SGOT, audiometric examination, total blood count, and urinalysis. Exit physicals are required in certain jobs, such as those that expose workers to high levels of noise.

Personnel working in the depainting areas are required to wear protective clothing, which includes coveralls, monogoggles, rubber gloves, and safety shoes or rubberized boots. Organic-vapor-cartridge, half-mask respirators had been required for the stripping operation when it was carried out in a building used prior to the construction of the facility referred to previously; however, with the exhaust ventilation system in the new facility, respirators are no longer required. Workers are able to change from their work clothing in the locker room of the new facility, and the clothing may be left to be laundered by a private contractor.

SURVEY PROCEDURES AND METHODS

The procedures and sampling and analytical methods employed in this survey of exposure to methylene chloride are described in this chapter of the report. At all three plants, sampling for other potentially toxic substances that might be expected to be found in conjunction with methylene chloride exposure also were made--for acetone and methanol at Plant A, coffee dust and carbon monoxide at Plant B, and ammonia at Plant C--and this sampling is also discussed, separately in those instances where it differed from the sampling for methylene chloride. The detailed surveys at each of the three plants had all been preceded by preliminary walk-through surveys, the purpose of which was to identify suitable facilities for in-depth study.

GENERAL SURVEY PROCEDURES

At Plant A, personal (breathing zone) samples were collected on representative workers in each of the following work areas:

- Production
- Extrusion
- Bobbin stores
- Textiles

The breathing zone samples were for detection of methylene chloride and acetone using charcoal tube/sampling pump assemblies. (Area samples for detection of methanol in the filter press room were also made, using silica gel tube/sampling pump assemblies--see subsequent section in this chapter.) All personal samples were collected for at least two hours--most of them for more than six hours. The samples were collected during four successive work shifts, beginning with the afternoon shift of one day and ending with the afternoon shift of the following day.

At Plant B, the survey team sampled every operator working in the decaffeinating facility except for mantenance personnel. Breathing zone samples were taken with charcoal tube/sampling pump assemblies for approximately eight hours on all shifts, with additional samples taken for short durations during selected operations. In addition, area monitoring was performed, using a Century Systems Total Organic Vapor Analyzer (OVA) as well as charcoal tubes/sampling pumps. The Century OVA was used in a portable fashion to measure the presence of total hydrocarbons at several locations throughout the facility where there would seem to be a chance for exposure to methylene chloride--locations such as valves, flanges, pumps and quality-control sampling ports. The analyzer proved to be especially helpful in pinpointing areas of potential exposure. (Area sampling for coffee dust and carbon monoxide, which was also conducted, is discussed separately in this chapter.)

At Plant C, the survey team sampled for methylene chloride on 12 of the 22 members of the aircraft paint stripping crew as they were conducting a stripping operation. These breathing zone samples were collected with charcoal tube/sampling pump assemblies. Sampling time for the personal samples ranged from 6.5 to 7 hours. Personal sampling was limited to a single shift because of difficulties in scheduling aircraft for the operation. (Area sampling for the presence of ammonia from the stripping compounds, also carried out, is discussed separately in this chapter.)

PERSONAL SAMPLING AND ANALYSES

Personal sampling employed MDA Accuhaler® pumps, at Plant A and Plant C, or Bendix BDX-44 pumps, at Plant B, attached to belts or clothing worn by the workers. Each pump was connected by Tygon® tubing to the sampling medium, which was composed of two SKC charcoal tubes in series--a large one, 600 mg of charcoal, in front (upstream) and a Standard one, 150 mg of charcoal, in back (downstream). All tubes were from SKC Lot 106, with the exception of the Standard (backup) tubes in the assemblies at Plant B, which were from Lot 28. The tubes in the assemblies were connected by Tygon® tubing, which was kept at a minimum. Two tubes were used to keep completed methylene chloride samples from migrating due to the compound's high vapor pressure; also, use of two tubes would detect overloading, or pulling through, of methylene chloride during the sampling operation. The entire charcoal content (600 mg) of the front, or upstream, tube was combined (the charcoal in the tubes is divided into two-thirds and one-third sections) to yeild the primary sample, while the smaller (150 mg) tube located behind constituted backup (and was analyzed separately).

The sampling pumps were used to draw air through the charcoal tubes at a nominal rate of 20 milliliters per minute at Plant A and Plant C, 50 ml/min at Plant B. The pumps were calibrated (and rechecked after use) using a bubblemeter (inverted buret).

Personal sampling of workers on full-shift jobs was conducted over the total working shift at Plant B. At Plants A and C, while sampling was performed for less than eight hours, the nature of the operations are such that the exposure for the individuals would not be expected to vary. Hence, a time-weighted average (TWA) was calculated for every person on an eight-hour basis. The calculation was:

$$\text{TWA (ppm)} = \frac{24{,}450 \times \text{mg per liter}}{\text{MW}}$$

ppm = parts of methylene chloride vapor per million parts of air

MW = molecular weight (methylene chloride = 84.93)

mg per liter = milligrams of methylene chloride in one liter of air sample collected.

At Plant B, because of the nature of the operation, each job type was sampled separately. When a task was to be performed that would expose a worker to a potentially higher than normal concentration (e.g., quality control sampling), an additional sample was taken during the full length of time of the task to determine ceiling concentrations.

The methylene chloride samples were analyzed at an SRI International laboratory (accredited by the American Industrial Hygiene Association) using the NIOSH-approved analytical method S329, with minor adjustments in technique: the NIOSH method calls for desorption of the charcoal sample using 1 ml of carbon disulfide; however, since 600 mg of charcoal were used in the primary adsorbing tube, 2 ml of carbon disulfide were used to desorb. A desorption time of at least 30 minutes was used. Following desorption, a portion of the sample was injected into a gas-liquid chromatograph equpped with a flame ionization detector. The area under the sample peak was measured and integrated, and the results were read directly from a standard curve that was prepared earlier from injections of known quantities of methylene chloride.

In the case of Plant B, the decaffeination facility, the samples were also analyzed using a method developed by the company that operates that facility. This method calls for desorption of the charcoal using 2 ml of toluene. Like the method described above (NIOSH S329), the Plant B method requires desorption for at least 30 minutes, but electron capture, rather than flame ionization detection, is used. Desorption efficiency (DE) tests that were made for the NIOSH-approved analytical method indicated good precision. The average DE was 0.97 ± 0.02 (from 18 samples), and recovery was also very good, with an average recovery of 0.95 ± 0.03 for 17 samples (approximately three in each of six test levels--one-half, one, and two times the OSHA TWA and ceiling permissible contentrations). Desorption efficiency tests of the Plant B method also indicated good precision: the average DE was found to be 0.85 ± 0.02 (from four samples). The company reports an average DE of 0.96 from its tests of desorption efficiency. Both DEs were performed within the range of methylene chloride found in the company's plants.

SAMPLING FOR OTHER SUBSTANCES

As noted previously in this chapter, sampling was carried out for several potentially toxic substances, other than methylene chloride, that might be expected to be found in conjuction with methylene chloride. This sampling is discussed below.

Plant A--Other Substances

Sampling for methanol at Plant A was performed using silica gel tubes and Bendix BDX-44 pumps. The samplers were positioned close to the filter presses when they were being dismantled and were allowed to operate for approximately four and one-half hours at the rate of 50 ml per minutes. (Flow rates were calibrated with a bubblemeter). Following collection of the sample, the tubes were capped, refrigerated, and sumitted to the analytical laboratory for analysis using NIOSH-approved method S59.

Plant B--Other Substances

Area sampling for coffee dust and for carbon monoxide (which is a metabolic product of methylene chloride) was carried out at Plant B.

Both total and respirable <u>coffee dust</u> samples were collected on preweighed, 37-mm-diameter, 0.8-μm-pore-size polyvinyl chloride filters in a three-piece cassette filter holder. Respirable dust samples were also taken on the same filter media preceded by a Bendix BDX-99 10 mm cyclone assembly. Samples were taken for 8 hours at a nominal flow of 2 liters per minute for the total coffee dust sample and 1.7 liters per minute for the respirable dust samples.

Carbon monoxide samples were taken with Draeger short-term and long-term indicator tubes. The short-term tube samples were taken with a Draeger hand-held bellows pump; the long-term tube samples were taken with an MDA Accuhaler® pump. (In the presence of carbon monoxide, an indicating layer in the tubes discolors from white to brownish-green, and the length of the discoloration corresponds to the carbon monoxide concentration in parts per million.)

Plant C--Other Substances

Several area samples of air at Plant C were collected to detect the presence of ammonia from the stripping compounds used. In this sampling, both stationary and hand-held apparatus were used. The stationary samplers consisted of Draeger indicator tubes, a dilute (10 ml) solution of sulfuric acid, midget impinger, and a Bendix BDX-44 pump that drew air through the absorbing solution at the rate of 1 liter per minute. Flow rate was determined by calibration with a bubblemeter and was checked periodically during the sampling period. These samplers were attached to the railing of the elevated platform in the stripping facility, and samples were collected for periods of one hour at several intervals during the day.

Following collection of the samples, the absorbing solution was transferred into glass vials and capped. Analysis was performed using NIOSH Method No. P&CAM 205, in which Nessler reagent is added to the collected sample to produce a yellow-brown complex. (The absorbance of the yellow-brown solution at 440 nonameter is read on a spectrophotometer and compared with a standard curve to determine the ammonia concentration.)

Ammonia concentrations were also measured with a Draeger indicator tube and a Draeger hand-held bellows pump, a procedure in which air is drawn through the indicating packing in the glass tube. In the presence of ammonia, the packing turns from a yellow color to black, the length of stain or discoloration corresponding to the concentration of ammonia present. In several locations, the detector tube indicated the short-term concentration to be approximately 1 ppm; and in one instance, the level detected was approximately 5 ppm.

RESULTS AND RECOMMENDATIONS

Results of the in-depth exposure surveys carried out at Plants A, B, and C, together with summaries and recommendations, are presented in this chapter.

RESULTS OF SURVEY--PLANT A

Concentrations of methylene chloride (as well as of acetone) during yarn production and processing operations at Plant A were calculated following analysis of the collected personal and area samples, and the results for methylene chloride are shown in Table 3. (See Appendix B for acetone results.) The results of area sampling for the presence of methanol in the filter press area of the Preparation Department at Plant A are presented in Appendix B. (The time-weighted average (TWA) exposures for acetone were determined to be below the current OSHA standard of 1000 parts per million, and concentrations of methanol were well below the OSHA standard of 200 ppm.)

Personal TWA exposures for methylene chloride were determined to range from 31 ppm for a Coning Operator to 561 ppm for a Doffer in Block II. Area samples taken in the vicinity of the extrusion cabinets in Block II showed concentrations in the range of 409-950 ppm on the operating level and from 488 to 975 ppm on the catwalk area of Block II. During the survey period, ten metiers in Block II were producing triacetate yarn, and the remaining two were producing acetate staple.

The full-shift personal sampling data are shown in Table 4 in the form of concentrations for each job classification, by shift, together with geometric means, the geometric standard deviation, and the concentration range for each shift. The geometric standard deviation (GSD) is used as an indicator of variability. Variability can be caused by such factors as:

1) Small changes in ambient solvent concentration and operational differences; for example, start-ups and shut-downs of metiers generally take place on the day shift, and such activities can have a slight effect on concentrations in the immediate area of the metier.

2) Different operators do the same task in different ways--some get closer to the equipment, some take longer or shorter times to complete a task, etc.

As used here, a GSD $\leq$ 1.0 indicates little variability in the results, while a GSD $\geq$ 2.0 indicates relatively high variability.

It can be seen in Table 4 that two job classifications have GSDs greater than 2.0: Patroler, Block I, and Coning Operator. For Block I Patrolers, there was a great variability between samples, and three of the sample results were excluded from the computation (see Table 3). The 69 ppm concentration for the Patroler

Table 3. **Individual personal and area TWA concentrations of methylene chloride at Plant A, May 16-17, 1979.**

Job title/location and sample number		TWA concentration (ppm)
Personal samples		
Patroler, Block I	C-1	31.7*
	C-26	1911.8*
	C-45	68.8
	C-59	314.8
Patroler, Block II	C-4	266.8
	C-21	486.7
	C-37	268.4
	C-53	445.5
Doffer, Block I	C-2	490.0
	C-24	135.3
	C-44	343.8
	C-61	392.0
Doffer, Block II	C-5	168.4
	C-23	561.4
	C-36	522.9
	C-55	509.3
Jetwiper, Block I	C-3	387.3
	C-25	504.0
	C-46	286.0
	C-60	227.0
Jetwiper, Block II	C-6	117.7
	C-22	464.5
	C-38	196.6
	C-54	236.4
Bobbin Stores Operator	C-7	209.9
	C-20	75.8
	C-35	123.6
	C-52	208.9

(continued)

Table 3. (continued)

Job title/location and sample number		TWA concentration (ppm)
Personal samples		
Creeler	C-8	55.5
	C-18	57.3
	C-32	162.0
	C-49	128.9
Lacer	C-9	66.6
	C-19	208.9
	C-31	198.0
	C-48	140.4
Coning Operator	C-10	30.5
	C-16	572.1*
	C-33	62.9
	C-50	48.8
Beaming Operator	C-11	236.5
	C-17	68.0
	C-34	237.4
	C-51	277.5
Pressman Block II	C-42	374.6
	C-43	264.1
Area Samples		
Operating level, Block II between metiers 58 and 59	C-12	659.4
	C-28	409.6
	C-39	547.9
	C-56	587.4
Operating level, Block II between metiers 62 and 63	C-13	828.1
	C-29	679.0
	C-40	950.5
	C-57	730.8

(continued)

Table 3. (continued)

Job title/location and sample number		TWA concentration (ppm)
Area Samples		
Catwalk, Block II between metiers 58 and 59	C-14	786.9
	C-27	645.1
	C-41	975.1
	C-58	482.5
(Blank)	C-15	--
	C-30	--
	C-47	--
	C-62	--

*These values are questionable; sample possibly adulterated or error in analysis.

Table 4. Job and work-shift TWA concentrations of methylene chloride at Plant A, May 16-17, 1979.

Job title	TWA concentration by shift (ppm)			TWA Concentrations, all shifts		
	Day	Swing*	Night	Geometric mean† (ppm)	Geometric standard† deviation	Range (ppm)
Patroler, Block I	69	315	--	147	2.93	69-315
Patroler, Block II	268	357	487	353	1.38	267-487
Doffer, Block I	344	441	135	307	1.76	135-490
Doffer, Block II	523	339	561	397	1.78	168-561
Jetwiper, Block I	286	307	504	335	1.42	227-504
Jetwiper, Block II	197	177	465	225	1.76	118-465
Bobbin Stores Op.	124	210	76	142	1.62	76-210
Creeler	162	93	57	90	1.73	56-162
Lacer	198	104	209	140	1.69	67-209
Coning Operator	63	40	--	46	3.66	31-63
Beaming Operator	237	258	68	181	1.92	68-278
Pressmen	319††					264-375

*Except for the case of questionable value (see Table 3), this is a mean of two samples, (shift sampled on two days)

†Geometric mean = $\overline{X}g$ = antilog $\left[\frac{1}{n} \sum_{i=1}^{n} \log x_i)\right]$

$$\text{Geometric stnd. dev.} = s_g = \text{antilog} \left[\frac{n \sum_{i=1}^{n} \log^2 x_i - (\sum_{i=1}^{n} \log x_i)^2}{n\,(n-1)}\right]^{1/2}$$

††Mean of two samples, two pressmen monitored.

on the day shift is also somewhat suspect but was not excluded. There was also a high variability in data for Coning Operators, and one sample, collected during the night shift and showing a concentration of 572 ppm, was excluded from the computation. (Ambient concentrations of methylene chloride in this area have been determined by Plant A monitoring personnel to be less than 200 ppm.)

For all the job classifications, some variability in the exposure levels occurs from shift to shift, even though the operations are continuous and constant. Week-to-week variations may also occur, due to changes in the size of yarn being produced--i.e., smaller-denier giving off less vapor than the larger-denier filaments--and changes in the production rate.

In several cases, the survey results indicate that the OSHA standard of 500 ppm for an 8-hour TWA exposure was exceeded. However, only one duplicate sample made by Plant A monitoring personnel exceeded 500 ppm; also, long-term sampling and analyses by the Plant, and confirmed by a recent State OSHA industrial hygiene survey, show that the facility has been, and continues to be, in compliance with the current Federal OSHA standard.

Almost all of the samples from the Patrolers, Doffers, Jetwipers, and Pressmen exceeded the Threshold Limit Value (TLV) of 200 currently recommended by the American Conference of Governmental Industrial Hygienists (ACGIH), and some of the samples collected for Bobbin Stores Operator, Lacer, and Beaming Operator were also above the 200 ppm level. Samples for Creeler and Coning Operator did not exceed the 200 ppm TLV.

RESULTS OF SURVEY--PLANT B

Time-weighted average personal and area concentrations of methylene chloride during decaffeination operations at Plant B are shown in Table 5. The personal sampling data are shown in Table 6 in the form of concentrations for each job classification, together with geometric means, the geometric standard deviation, and the concentration range for each shift. (See "Plant A," above, for more information on use of the geometric means and deviations.)

All of the concentrations are well below the OSHA permissible exposure limit of 500 ppm, and the ACGIH recommended TLV of 200 ppm. The range of 8-hour exposure concentrations varied from 0.3 to 33.2 ppm, with an average concentration of 2.9 ppm.

As noted in Table 5, higher personal sample concentrations recorded during the evening shift are most likely from a system upset that occurred; moreover, residual quantities of methylene chloride from that upset most likely caused an elevation in samples of area concentrations, which were taken during the shift following the system upset. Full-shift area samples obtained by the survey team during the second day varied from 0.05 to 2.08 ppm (see Table 5).

The highest exposure concentration of methylene chloride was recorded in the Process Operator job category, which had a mean exposure of 5.1 ppm. The company reports an average exposure of 5.7 ppm from the sampling it performed over the past year for this job category. The range of values recorded for Process Operator varied from 0.9 to 30.6 ppm, with the highest levels recorded during the evening shift. (See above and footnote in Table 5 for this shift.)

Table 5. Individual personal and area TWA concentrations of methylene chloride at Plant B, week of November 6, 1978.

Job title/location and sample number		TWA concentration (ppm)
Personal samples		
Process Operator	6C	5.9
	9C	9.6
	11C*	30.6
	15C*	27.3
	21C	2.0
	26C	0.9
	38C	2.8
	41C	2.0
Extractor Operator	1C	2.8
	3C	1.5
	5C	4.5
	14C*	12.6
	17C*	33.2
	18C*	25.1
	19C	1.0
	24C	1.3
	29C	1.7
	40C	0.4
	42C	0.4
	46C	0.6
Evaporator Operator	7C	5.0
	20C	1.7
	39C	1.1
Coffee Handler	8C	1.9
	12C*	18.3
	27C	1.0
	36C	0.3
General Laborer	2C	2.7
	13C*	24.9
	16C*	9.1
	22C	3.5
	23C	1.6
	37C	0.6

(continued)

Table 5. (continued)

Job title/location and sample number		TWA concentration (ppm)
Caffeine Dryer Cperator	4C	12.6
	25C	1.2
	43C	0.5
Short-term sampling--during quality control		
Coffee Handler	33C	0.3
Extractor Operator	34C	0.9
Process Operator	35C	5.1
Area samples		
5th floor		
Above S_2 burp tank	44C	0.50
Between #3 & #4 sludge tanks	45C	0.42
RDC† draw off	28C	1.27
Between Swing & #1 fractionator	47C	2.08
2nd floor		
S6 #1 column, RDC† area	30C	0.52
S6 control room	32C	0.05
1st floor--caffeine dryer operator desk	31C	1.46
(Blanks)		BD††

*During the evening shift (first day of sampling), a relief valve began to lift and pressurize in the wastewater recovery system, causing amounts of wastewater containing solvent to back up into the drain system for an undetermined length of time. Under this upset condition, concentrations of methylene chloride determined on these workers may be higher than normal.

†Rotating disc contactor (column).

††Below detectable limits.

Table 6. Job and work-shift TWA concentrations of methylene chloride at Plant B, week of November 6, 1978.

Job title	TWA concentration by shift (ppm)			TWA concentration, all shifts		
	Day	Night	Evening*	Geometric Mean† (ppm)	Geometric Standard Deviation†	Range (ppm)
Process Operator	1.34	4.22	28.84	5.1	3.6	0.92-30.47
Extractor Operator	1.30	1.09	21.88	2.4	4.6	0.37-33.22
Evaporator Operator	1.69	2.28	--	2.1	2.2	1.05-4.95
Coffee Handler	0.95	0.78	18.28	1.8	5.5	0.32-18.28
General Laborer	2.37	1.27	15.03	2.8	4.4	0.61-24.94
Caffeine Dryer Operator	1.22	2.46	--	2.0	5.39	0.48-12.64
All jobs:						
Mean concentration (ppm)	1.5	1.7	20.9		2.9	
Standard deviation	1.5	3.2	1.6		2.9	
Number	10	18	8		4.0	
Range	(1)	(2)	(3)		(4)	

*See footnote (*), Table 5.

†See footnote (†) and "Note," Table 4.

(1) 0.92-3.5; (2) 0.32-12.64; (3) 9.06-33.22; (4) 0.32-33.22.

Personal samples taken from the General Laborers varied from 0.6 to 24.9 ppm, with a mean concentration of 2.8 ppm. Extractor Operators had an 8-hour TWA concentration that varied from 0.4 to 33.2 ppm, with a mean of 2.4 ppm. Evaporator Operators had an average concentration of (nominally) 2 ppm, as did Caffeine Dryer Operators. The lowest average concentration, 1.8 ppm, was recorded for Coffee Handlers.

In terms of work shifts, the lowest 8-hour TWA mean concentration, 1.5 ppm, was recorded during the day shift; the night shift was slightly higher at 1.7 ppm. The system upset during the evening shift has already been noted. (There was a mean concentration of 20.9 ppm during this shift.)

Short-term exposure sampling for methylene chloride was performed while personnel were obtaining product samples for purposes of quality control. The Process Operator was found to have the highest exposure level among the samples taken--5 ppm, still well below the current TLVs.

Work-area samples for carbon monoxide and for total and respirable coffee dust showed only trace amounts of carbon monoxide and negligible amounts--well below 1 mg per cubic meter--of dust.

RESULTS OF SURVEY--PLANT C

Results of sampling for methylene chloride during paint stripping operations at Plant C, which were limited to those from a single shift due to aircraft scheduling difficulties, are presented in Table 7. (The results of area sampling for the presence of ammonia from the paint stripping compounds are given in Appendix C.) Time-weighted-average exposures for personnel working in the depainting facility were well below the OSHA permissible exposure limit of 500 ppm, and with one exception (Sample R-10), were below the American Conference of Governmental Industrial Hygienists recommended Threshold Limit Value of 200 ppm. The range of methylene chloride exposure concentrations was 15.7 to 268 ppm, with an average concentration of 64 ppm.

The highest exposure concentration of methylene chloride, 268 ppm, was to the paint stripper personnel who worked on the wheel well of the aircraft. This is an area where airflow is probably disrupted, creating pockets of stagnant air in which the vapor content is higher. Concentrations of methylene chloride at other locations around the aircraft were less than 100 ppm, indicating that the exhaust system in this new facility was functioning well.

During the preliminary, walk-through survey conducted in the previous year, the stripping operation was carried out in a facility that had no exhaust ventilation system, but that relied instead upon natural ventilation through open doors to dilute and disperse the vapors. The movement of wind was, however, apparently sufficient to maintain low levels of methylene chloride, since the results of sampling done at that time are similar to those of the recent survey. However, operations in the new facility do not have to be exposed to inclement weather.

Table 7. Personal TWA concentrations of methylene chloride at various locations during an aircraft paint stripping operation at Plant C, May 15, 1979.

Location* and number		TWA concentration (ppm)
Tail section, right side	R-1	28.7
Fuselage, right side	R-2	21.4
Fuselage, right front side	R-3	40.1
Wing	R-4	33.1
Fuselage and top	R-5	15.7
Wing	R-6	91.7
Wing, engine	R-7	29.7
Fuselage, Center	R-8	88.6
Tail section, left side	R-9	33.6
Wheel well	R-10	268.0
Wheel well, tail	R-11	84.2
Tail section, right side	R-12	28.0
Blank	R-13	ND†

*Area of aircraft worked primarily.

†None detected. Detection limit: 10 micrograms.

SUMMARY AND RECOMMENDATIONS

From the data collected during this exposure-level survey, the following summaries and recommendations are made:

- TWA personal exposures of workers at Plant A to methylene chloride were found in some instances to exceed the current Federal OSHA standard of 500 ppm, although long-term Plant A data and State OSHA data show the facility to be in compliance with the Federal OSHA standard. Continued and careful monitoring and evaluation of the work-exposure situations should be performed in an effort to minimize exposure of personnel to methylene chloride.

- The Dow Chemical-Celanese epidemiologic study referred to under "Toxicity and Human Exposure Standards" in the "Background" chapter of this report should be reviewed by NIOSH to determine whether it meets the NIOSH requirements of this type of study.

- The 8-hour TWA exposures of workers to methylene chloride during normal operations at Plant B, averaging 2.9 ppm, were found to be well below the current OSHA standard and the American Conference of Governmental Industrial Hygienists (ACGIH) recommended Threshold Limit Value (TLV) of 200 ppm. This is due principally to the fact that the decaffeination process is in a closed system that is rarely opened. Levels of methylene chloride in the atmosphere at the Plant are highest during quality-control sampling of the product or during a system failure. (During the failure that occurred in the course of this survey, concentrations of methylene chloride were higher than usual, but even then they were still below the OSHA standard and the TLV of the ACGIH.

- The analytical method used by the Plant B company for determining the presence of methylene chloride from long-term sampling with charcoal tubes proved to be highly reliable and effective, especially at concentrations below the OSHA standard. NIOSH method S329 may not have the sensitivity necessary for precise determinations at such lower concentrations.

- Time-weighted-average personal exposures to methylene chloride in the work-area atmosphere at Plant C, ranging from 15.7 to 268 ppm and averaging 64 ppm, were below the current OSHA standard of 500 ppm and, with one exception, were below the ACGIH recommended TLV of 200 ppm. The single sample in which 200 ppm was exceeded (268 ppm) was for a worker in the wheel well of the aircraft, indicating less ventilation at this location than at other locations around the aircraft. The installation of an auxiliary fan at the wheel well location should be considered to dissipate the build-up of paint stripping vapors.

- The new facility for depainting of aircraft appears to be well designed and equipped to maintain potential worker exposure within the current OSHA standard.

- A reassessment by NIOSH of methylene chloride toxicity has resulted in a recommendation that the OSHA standard for the substance be lowered to 75 ppm, and it can be seen in the survey results in this report that a number of personal exposure levels exceed such a figure, particularly ones at Plant A (two at Plant C). It would appear that compliance with a 75 ppm standard could present a significant problem in connection with production operations of the type carried out at Plant A (see "Facilities and Personnel Surveyed" in this report). At Plant C, it would appear that utilization of the full capacity of the facility's exhaust system, augmented if necessary, with an auxiliary fan at the aircraft wheel well location as noted above, could provide the necessary ventilation.

- With regard to sampling that was conducted for substances other than methylene chloride: airborne concentrations of acetone (Plant A) were well below the OSHA standard of 1000 ppm; concentrations of methanol (Plant A) were well below the OSHA standard of 200 ppm; and sampling for carbon monoxide and coffee dust (Plant B) revealed only trace and neglible amounts.

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Appendix A. Residual methylene chloride found in decaffeinated coffee beans and crude caffeine, as reported by Plant B, November 1978

Decaffeinated beans		
Sample date (month/year)	Average methylene chloride (ppm)	Number of samples
5-78	0.35	295
6-78	0.35	115
7-78	0.42	208
8-78	0.36	230
9-78	0.32	174

Crude caffeine	
Sample date (1978)	Methylene chloride (ppm)
10-17	0.14
10-26	0.10
11-1	0.24
11-3	0.13

Appendix B. Results of sampling for acetone and methanol at Plant A

Results of sampling for acetone at Plant A are shown in Table B-1. Since the purpose of this study was to determine the exposure of personnel to methylene chloride, the personnel monitored in Block I were those involved with production of triacetate yarn, and not with the acetate. Disregarding the one questionable sample, the range of exposure values were from 4 ppm for a Pressman working in the Preparation Area of Block II to 574 ppm for a patroler in the Extrusion Area of Block I. (Two results from company-collected samples indicated concentrations of 768 ppm and 747 ppm for the Patroler and the Jetwiper, respectively, in Block I.)

At the recent meeting of the Threshold Limit Value (TLV) Committee of the American Conference of Governmental Industrial Hygienists (ACGIH) (in May 1979), an intended change was proposed for acetone, lowering the TLV from the current 1000 ppm to 750 ppm. This intended change will remain as a notice for at least two years, after which it may become adopted as a recommended TLV by the ACGIH.

Results of area sampling for the presence of methanol in the filter press area of the Preparation Department at Plant A are shown in Table B-2.

Table B-1. Results of personal sampling for acetone at Plant A, May 16-17, 1979.

Sample number and location	TWA concentration (ppm)
C-1 Patroler, Block I	91.1
C-2 Doffer, Block I	340.2
C-3 Jetwiper, Block I	54.9
C-4 Patroler-Doffer, Block II	26.4
C-5 Doffer, Block II	44.4
C-6 Jetwiper, Block II	21.6
C-7 Bobbin Stores Operator	86.5
C-8 Creeler, Textiles	113.9
C-9 Lacer, Textiles	271.9
C-10 Coning Operator	71.1
C-11 Beamer, Line 3	123.8
C-12 Operating level, Block II between Metiers 58 and 59	96.5
C-13 Operating level, Block II between Metiers 62 and 63	56.9
C-14 Catwalk, Block II between Metiers 58 and 59	137.7
C-15 Blank	--
C-16 Coning Operator	585.6*
C-17 Beaming, Gauging Operator	63.2
C-18 Creeler	137.0

(continued)

Table B-1 (continued)

Sample number and location	TWA concentration (ppm)
C-19 Lace-up Operator	479.5
C-20 Bobbin Stores Operator	69.6
C-21 Patroler, Block II	117.6
C-22 Jetwiper, Block II	63.5
C-23 Doffer, Block II	24.0
C-24 Doffer, Block I	61.5
C-25 Jetwiper, Block I	401.1
C-26 Patroler, Block I	573.7
C-27 Catwalk, Block II between Metiers 58 and 59	124.7
C-28 Operating level, Block II between Metiers 58 and 59	21.9
C-29 Operating level, Block II between Metiers 62 and 63	37.7
C-30 Blank	--
C-31 Lacer	29.6
C-32 Creeler	202.6
C-33 Coning Operator	101.3
C-34 Beaming Operator	191.7
C-35 Bobbin Stores Operator	193.6
C-36 Doffer, Block II	164.6
C-37 Patroler, Block II	15.5

(continued)

Table B-1 (continued)

Sample number and location	TWA concentration (ppm)
C-38 Jetwiper, Block II	10.6
C-39 Operating level, Block II between Metiers 58 and 59	35.3
C-40 Operating level, Block II between Metiers 62 and 63	40.6
C-41 Catwalk, Block II between Metiers 58 and 59	109.7
C-42 Pressman, Block II	63.3
C-43 Pressman, Block II	4.2
C-44 Doffer, Block I	146.6
C-45 Patroler, Block I	8.1
C-46 Jetwiper, Block I	302.9
C-47 Blank	--
C-48 Creeler-Lacer	185.2
C-49 Creeler	144.0
C-50 Coning Operator	96.4
C-51 Beaming Operator	139.3
C-52 Bobbin Stores Operator	168.6
C-53 Patroler, Block II	21.4
C-54 Jetwiper, Block II	27.9
C-55 Doffer, Block II	18.1
C-56 Operating level, Block II between Metiers 58 and 59	28.0

(continued)

Table B-1 (Continued)

Sample number and location		TWA concentration (ppm)
C-57	Operating level, Block II between Metiers 62 and 63	28.0
C-58	Catwalk, Block II between Metiers 58 and 59	86.6
C-59	Patroler, Block I	168.6
C-60	Jetwiper, Block I	128.4
C-61	Doffer, Block I	112.3
C-62	Blank	--

*This value is questionable; sample possibly adulterated or error in analysis.

Table B-2 Results of area sampling for methanol in the filter press area at Plant A, May 17, 1979.

Sample number and location		Concentration (ppm)
CM-1	Between presses 104-A and 105A maintenance on press 105-A	38.3
CM-2	Between presses 108-A and 109-A maintenance on press 109-A	43.3
CM-3		--

Appendix C. Results of sampling for ammonia from the paint stripping compounds used at Plant C

Concentrations of ammonia during an aircraft paint stripping operation at Plant C are shown in the tabulation below. Concentrations were determined by area samples using an impinger with absorbing reagent. They ranged from less than 1 ppm to 5.6 ppm. Average concentration for the workday was 2.6 ppm. The current permissible exposure level (OSHA) for ammonia is 50 ppm, and the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) is currently at 25 ppm. The levels present in the depaining facility were well below these standards and should not be considered an exposure problem.

Sample number and location (all front fuselage)	Ammonia concentration (ppm)
1 Left side	0.9
2 Right side	1.9
3 Right side	1.8
4 Left side	5.1
5 Left side	1.3
6 Right side	1.4
7 Left side	5.6
8 Blank	--

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