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A SURVEY OF HEALTH HAZARD CONTROL SYSTEMS FOR FORMALDEHYDE PRODUCTION FACILITIES

SUMMARY REPORT

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EXECUTIVE SUMMARY

The principal objective of this study was to survey the health hazardous control systems used in the formaldehyde production industry to control exposures of its personnel. Because formaldehyde is a very irritating chemical with low exposure limits (OSHA time-weighted average permissible exposure limit of 3 ppm), the formaldehyde production industry has had to work diligently to reduce the exposure to which its employees are subjected. This industry was selected for study, not with the thought that it was badly in need of further controls development or government regulation, but rather that it has successfully learned to control a hazardous chemical and that some of its methods for doing this might be very helpful if applied in other parts of the organic chemicals manufacturing industry.

Representatives of the Monsanto Research Corporation, Dayton Laboratory, project team visited 11 of the 52 formaldehyde production plants in the United States and, based upon these preliminary visits, selected four facilities for detailed studies. These plants were selected to represent both of the principal processes used to produce formaldehyde (the metal oxide and the silver catalyst processes), both large and small plants, and plants from different parts of the country (east, southeast, south, and west).

One-week on-site survey visits were made as a part of each of the four detailed plant surveys. These visits included personal and area sampling for formaldehyde and methanol concentrations. Analyses of these samples demonstrated that the plants visited were well within OSHA standards during the times visited.

Observations were made of work practices and control equipment used by this industry to control formaldehyde exposure. These are described in detail in this report, along with the conclusions reached by the project team concerning these control measures and their recommendations as to which worker practices and engineering controls should be used to minimize worker exposure at formaldehyde production plants.

1. INTRODUCTION

1.1 BACKGROUND

The National Institute for Occupational Safety and Health (NIOSH) and the U.S. Environmental Protection Agency (EPA) entered into an interagency agreement to perform a study to determine the levels of pollutants to which workers in the formaldehyde production industry are exposed and to evaluate the effectiveness of control technologies currently used to minimize exposures. EPA contracted with Monsanto Research Corporation (MRC) to perform the study on the formaldehyde production industry, under EPA Contract Number 68-03-3025, entitled "Technical and Engineering Services." MRC was assisted in the study by personnel from GEOMET Technologies, Inc. (GTI).

Formaldehyde is definitely an irritating compound. Its long-term, time-weighted average, permissible exposure limit (PEL) is only 3.0 ppm, as set by the Occupational Safety and Health Administration (OSHA). Its short-term permisible exposure limit has been set by OSHA as 5.0 ppm. It is well known for its irritation of the eyes and respiratory tract, as well as its causing nausea, headache, tiredness, and thirst [1]. Formaldehyde solutions cause eye damage and skin irritation upon contact. Some studies have indicated that formaldehyde can cause nasal cancer in laboratory animals. Most people note mild eye, nose, and throat irritation at a concentration of only 1 ppm [2-3].

Methanol, which is always found at formaldehyde production plants since it is the reactant from which the product is made, is much less irritating than formaldehyde. This is indicated by the fact that OSHA has set the long-term, time-weighted average, PEL for methanol at 200 ppm, a much less restrictive limit [4]. However, methanol must also be evaluated as a potential fire and explosion hazard.

This study of the formaldehyde industry was directed toward a cross-section of production facilities. Of principal importance was the assessment of worker exposure to potentially hazardous agents in the workplace and an evaluation of control technologies applied to those agents. The worker exposure (industrial hygiene) study focused on formaldehyde and methanol as the agents of principal concern. The workforce exposed to such agents was identified, concentrations evaluated, and the operations and process parameters of the work-site were characterized.

The focus of the workplace control technology study was the assessment of control technology currently in use for minimizing worker exposure to harmful chemical or physical agents. This study was done so as to emphasize the best worksites in the formaldehyde industry -- those with the most effective methods and practices. Since no one plant is likely to be best in all aspects of formaldehyde control, it was important to survey a representative sample of the best-controlled plants to increase the probability of finding a high percentage of the best practices. It is expected that studies such as this which concentrate on the effective ways of controlling chemial exposure will be helpful in providing guidance for a wide variety of situations in various industries.

This assessment included examination of processes and process equipment. Control effectiveness was determined through observation of work practices; examination of the equipment condition and engineering controls (e.g., ventilation), monitoring devices, and personal protective equipment; and air sampling and analysis.

1.2 SCOPE OF WORK OF THE INDUSTRIAL HYGIENE/CONTROL TECHNOLOGY ASSESSMENT (IH/CTA) STUDY

The objectives of this IH/CTA study were to:

a. evaluate the state-of-the-art control technology in the formaldehyde production industry,

b. identify potential hazards to workers,

c. evaluate these potential hazards for the effects on workers,

d. evaluate the effectiveness of industrial hygiene control programs to control these potential hazards,

e. assess current formaldehyde production technology with respect to control of potential exposures of workers,

f. assist the transfer of control technology inter- and intra-industry, and

g. identify processes for which engineering controls are not available or are ineffective, where further research and development are needed, and to indicate priorities for application of control technology.

The study was divided into two phases; preliminary surveys and detailed surveys. Preliminary industrial hygiene surveys (PIHS) were conducted at 11 plants, representing a cross-section of formaldehyde production facilities. Control equipment and worker practices were discussed and observed. Walk-through surveys (plant tours) were conducted at each plant. Potential exposures to hazardous agents and technologies used to control those agents were identified. Reports were prepared on the findings from nine of these surveys [5-13].

Four plants were selected from the eleven for detailed industrial hygiene surveys, based on the preliminary survey findings.

The plants chosen were selected because they used the best control technology and work practices seen during the preliminary surveys. Plants selected included large (>140 x 10^6 pounds per year), and small (less than 100 x 10^6 pounds per year) plants, plants which issued both types of catalyst, and plants located in widely separated parts of the country (east, southeast, south, and west). The detailed industrial hygiene surveys included the following activities:

- observation of operator work practices,
- quantitative determination of worker exposure through personal sampling,
- evaluation of engineering control techniques, monitoring devices, and personal protective equipment used by the industry to reduce exposures, and
- preparation of a detailed plant visit report for each of the four surveys, detailing worker practices and evaluating the engineering controls used by the plant [14-17].

2. FORMALDEHYDE PRODUCTION PROCESSES

Commercial capacity for producing formaldehyde in the United States during 1980 was over 8.5 billion pounds [18]. Fifty-two plants representing fifteen companies were involved in formaldehyde manufacture. These plants are widely dispersed as shown in Figure 1. Most of the formaldehyde produced is used on-site to produce resin for plywood, particle board, or plastics. Over 61 percent of the formaldehyde produced is used in resin production [19].

Formaldehyde produced in the United States is manufactured by two general processes. One process using a metal oxide catalyst is shown schematically in Figure 2 [20]. The other, which uses a silver catalyst, is depicted in Figure 3 [21]. These two processes are very similar except for the addition of a distillation column in the silver process to concentrate the aqueous formaldehyde to a usable concentration and to reduce its methanol content.

Methanol, normally received from offsite, is transferred from storage tanks and vaporized in a vaporizer. Vaporized methanol, mixed with preheated air, enters the converter and is oxidized (or dehydrogenated and oxidized if silver catalyst is used) to formaldehyde. Typically, the converter has a packed tower configuration, but catalyst beds are also used. Efficiency of conversion of methanol to formaldehyde range from 65 to 90 percent for the silver process and is approximately 99 percent for the metal oxide process [22].

After conversion, the hot formaldehyde gas (the reactor is generally operated at approximately 635°C [22]) is cooled in an aftercooler to a temperature of about 70°C and then absorbed in water. Aqueous formaldehyde solution is recirculated through the absorption tower until the desired concentration is achieved. If a silver catalyst is used in the converter, the product is concentrated in a distillation column, a step in which methanol is also recovered. Formaldehyde is generally stored as a 50 percent solution at 50°C (which helps prevent its spontaneous polymerization to form paraformaldehyde).

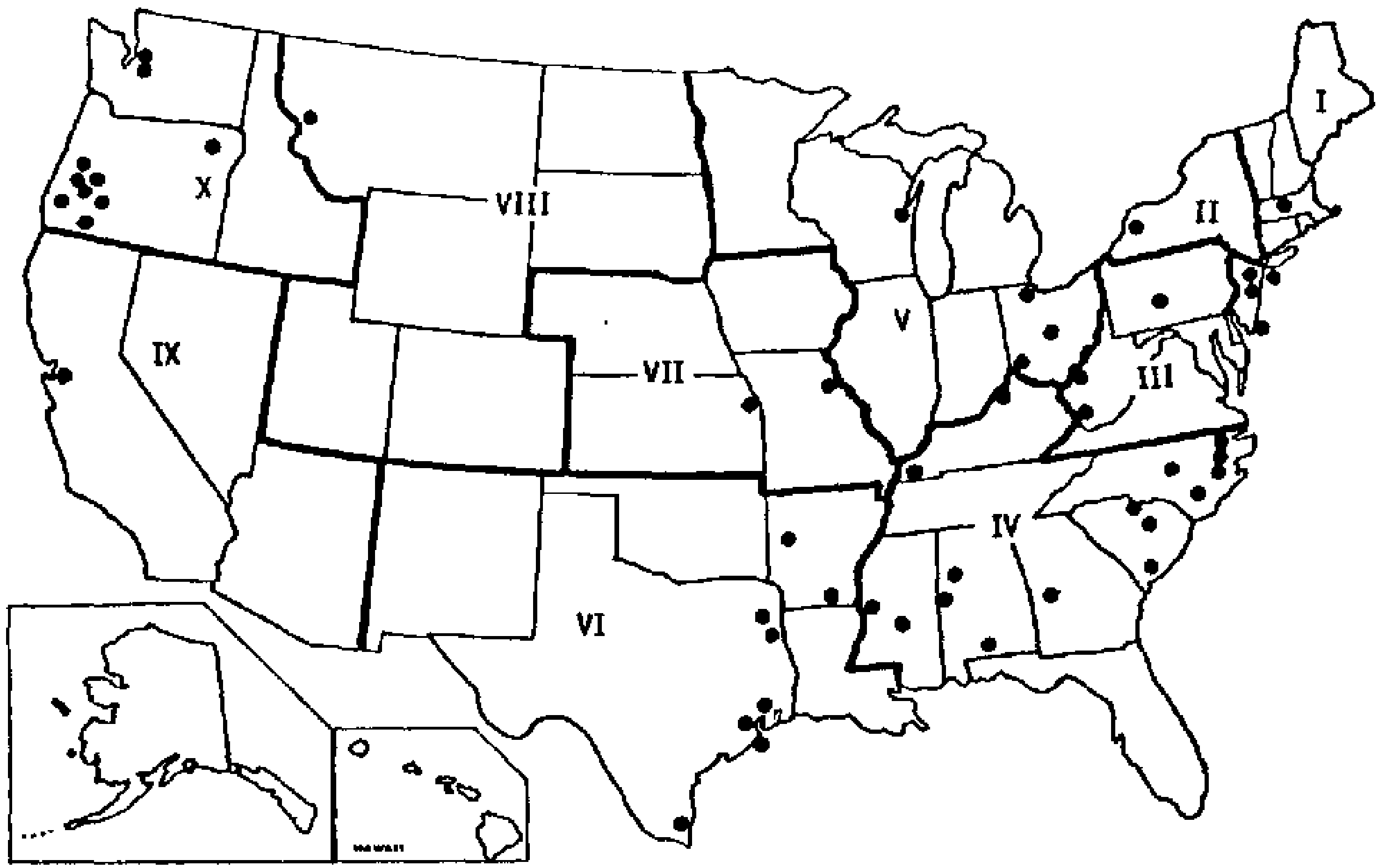

Figure 1. Formaldehyde plant locations [19].

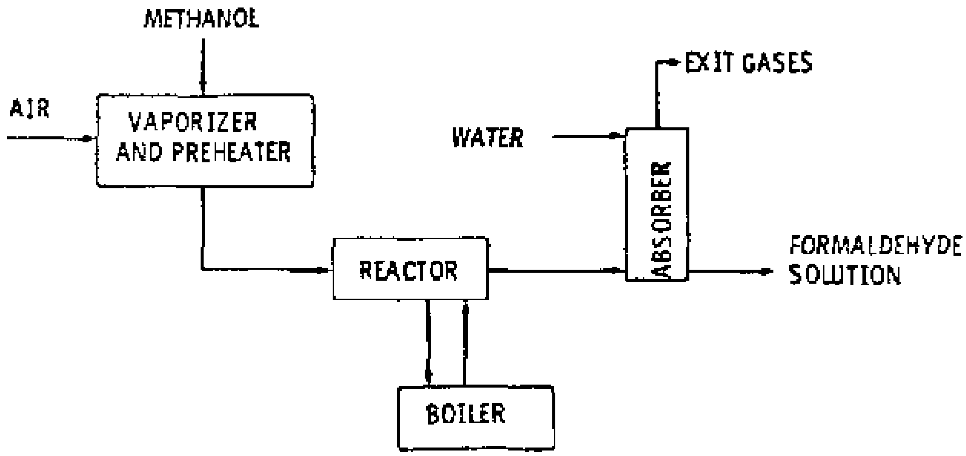

Figure 2. Formaldehyde production process using a metal oxide catalyst [20].

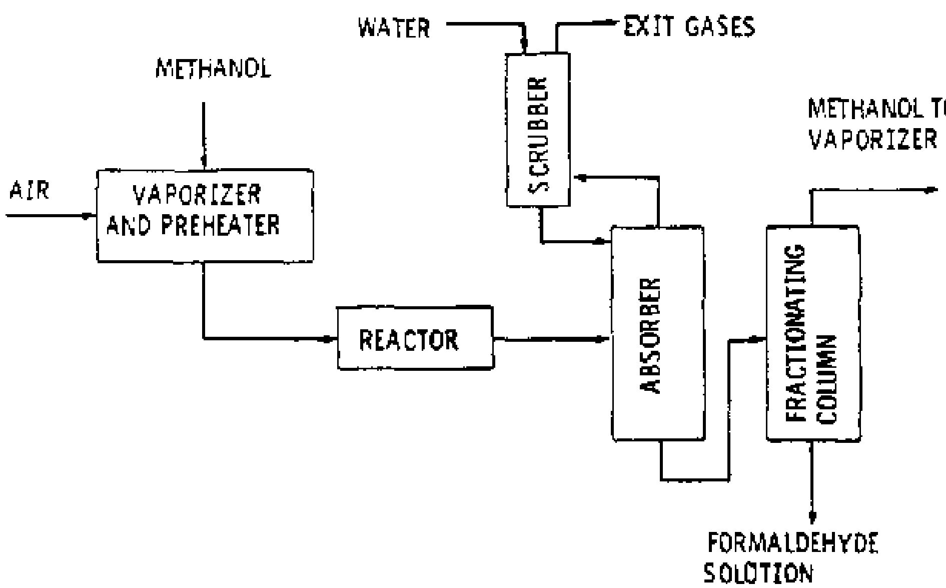

Figure 3. Formaldehyde production process using a silver catalyst [21].

3. SUMMARY OF INDUSTRIAL HYGIENE AND SAFETY PROGRAMS

3.1 INDUSTRIAL HYGIENE AND SAFETY PROGRAMS

All of the plants surveyed are provided a written safety and health program from their corporate headquarters. While most plants are required to strictly adhere to the corporate program, others can modify the program according to their own specific plant operations. Of those programs which are modified by the plant, some programs have become almost autonomous in cases where the corporate office feels the program has been successful and accident and illness experience has been acceptable.

All of the plants surveyed conducted safety meetings. Most meetings are attended by management safety committees. Important information is transferred to workers through their supervisors. Routine safety and health inspections are conducted at some plants.

Some plant corporate offices have developed safety manuals which are distributed to all employees. Others include occupational safety and health directives in sections of their plant employee manuals. One plant informs employees of recent formaldehyde health hazard findings by posting articles on the formaldehyde unit control room bulletin board.

3.2 MONITORING

Although most (8 out of 9 plants) have not routinely sampled for methanol since they feel it is not a major problem, they all have taken or were in the process of taking formaldehyde samples. All sampling is being performed by corporate industrial hygienists or by plant personnel (chemists, technicians, industrial hygienists, etc.) under corporate industrial hygiene supervision. Some 4 out of 9 plants have set their own internal standards lower than the OSHA PEL, and have implemented improved controls to reduce exposures to a level acceptable by the corporate office. One plant has characterized the formaldehyde exposure for each exposed employee within a specific exposure zone. Their the objective is to further reduce employee exposure, if necessary.

Many different sampling methods have been used, including the sodium bisulfite impinger method (use of one impinger or two in series), silica gel tube method, passive dosimeter badge method, continuous direct reading instrument method, colorimetric detector tube grab sample method, and Tenax sampling tube method. The methods used by the different plants surveyed are listed below:

Plant	Method(s) of Formaldehyde Analysis
A	Impingers, sodium bisulfite
B	Colorimetric detector tube Dosimeter badges Continuous reading wet chemical instrument
C	Silica gel tubes Two impingers in series, filled with sodium bisulfite
D	Impinger method, sodium sulfite
E	Impinger method, sodium bisulfite
F	Dosimeter badges Direct reading wet chemical instrument
G	Impinger method, sodium bisulfite
H	None in routine use
I	Colorimetric detector tubes Impinger method, sodium bisulfite Tenax tube method

3.3 CONTINGENCY PROCEDURES

Contingency procedures for fire, explosion, and chemical spills are well defined at most plants. Only one of the plants did not have a written emergency chemical spill program. Another plant's fire contingency procedure was so thorough that fire drills, which are conducted during all shifts approximately 10 times per year, include simulation of release of toxic air contaminants.

3.4 ACCIDENT AND ILLNESS EXPERIENCE

Since operations began, most of the plants surveyed have experienced very few compensable lost-time accidents or illnesses, although such events have occurred. On-site reviews of OSHA plant safety and health records were made at two of the plants at which in-depth surveys were done. Neither of these two plants had reported illnesses due to chronic inhalation of formaldehyde or methanol.

3.5 TRAINING

All plants provide on-the-job training as a part of their new employee safety and health program. Some plants provide detailed classroom job training. One plant used a process simulator and showed their own safety- and health-related training films. Several plants begin workers in a probationary status, in which the worker is supervised daily by an experienced worker or supervisor. Workers are then advanced as they become more responsible. Some plants have written operating procedures for each specific operation, such as loading, unloading, process sampling, etc., and train workers in proper operating procedures in the classroom and as a part of their probationary on-the-job training. One plant retrains employees in safety every two years. No other plants informed the survey team of any safety retraining program.

Most plant workers are trained in first aid, and some are also trained in cardiopulmonary resuscitation. One plant sent its workers to a hazardous chemical handling course put on by the state.

3.6 MEDICAL MONITORING PROGRAM

Almost all (8 out of 9) of the plants give pre-employment physical examinations to all employees. Two of the plants require their employees to take periodic specialty physical examinations for specific toxic exposures, whereas another plant requires a general periodic physical examination. One of the larger plants has a part-time on-site occupational physician and a full time on-site registered nurse. The larger plants seem to have either a full-time registered nurse on-site or a part-time on-site nurse

3.7 PERSONAL PROTECTIVE - EQUIPMENT (PPE) AND SAFETY EQUIPMENT

All plants are equipped with emergency eye washers and showers at key locations, such as formaldehyde loading areas and the production units. One plant was not equipped with an emergency eye wash and shower at the methanol unloading area. Most (8 out of 9) plants required workers to wear hard hats and safety glasses while on the company premises.

The following PPE is required for specific operations listed:

Formaldehyde Loading

Most (7 out of 9) plants required gloves to be worn. Only five plants required respiratory protection during loading. Respiratory protection required was either a half or full-face organic vapor cartridge respirator. Fit testing of respirators to individual operators was only being done at one of 9 plants during the visits, although another plant was initiating such a program.

Methanol Unloading

The majority of plants required gloves to be worn. Only one plant required a half-face organic vapor cartridge respirator to be worn.

Process Sampling and Analysis

Most plants required gloves to be worn during sampling collection. Only one plant required the wearing of a full-face acid gas cartridge respirator during sample collection. No personal protective equipment was required during sample analysis.

Formaldehyde Gas Sample Withdrawal

The plants that required the taking of a gas sample required gloves and either a half- or full-face organic vapor cartridge respirator to be worn during collection.

Formaldehyde Storage Tank Entry

Numerous plants required a full-protective suit, gloves, and boots to be worn when working inside formaldehyde storage tanks. Also, most plants required respiratory protection to be worn. Some plants required respiratory protection to be worn only if tests taken prior to entry for formaldehyde concentration, oxygen content, and lower explosive limit indicate a potentially hazardous environment. Four plants require air-supplied respirators as respiratory protection, one required a self-contained breathing apparatus, and another required a full-face cartridge respirator approved for acid gas and organic vapors.

Maintenance - Major Leak Repair

A few (2 out of 9) plants require maintenance personnel to wear gloves when repairing a major leak. Also, respiratory protection is usually (at 6 out of 9 plants) required. Most of the plants had written respiratory protection programs. Types of respiratory protection worn are a half-face organic vapor cartridge respirator, a self-contained breathing apparatus or supplied-air respirator, or a full-face gas mask approved for acid gas, organic vapors, toxic dusts, and mists.

4. SUMMARY OF WORKER JOB DESCRIPTIONS

Work practices are summarized below for the types of workers involved in formaldehyde production.

FORMALDEHYDE UNIT OPERATORS

In general the formaldehyde unit operators perform a wide variety of operations, including monitoring and control of the process, the taking and analysis of process samples, blending and loading the formaldehyde, and the unloading of methanol. At one of the plants visited, the chief operators were also responsible, along with the unit operators, for operation of the formaldehyde units. At this plant, the chief operators were located in a separate building and were directly responsible for the operation of the units, while the unit operators did the blending and loading of the formaldehyde, the process sampling and analysis, and the methanol truck sample analysis. At that plant methanol unloading was done by the truck driver who delivered it.

At another plant the unit operators were responsible for the operation of boiler house controls which were located within the control room from which they also operated the formaldehyde units. At that plant the unit operators did not unload methanol since it was manufactured on site. They also did not load formaldehyde since that was the responsibility of blender and loading operators, who were physically located at the loading stations rather than in the control room.

The unit operators spend a significant amount of their time (30% to 80%) in the unit control building, either monitoring the controls or analyzing the formaldehyde and methanol samples. The unit operators normally eat lunch at designated locations within the control buildings.

All unit operators are required to report major malfunctions and leaks to maintenance personnel for repair. They can perform minor maintenance themselves. At one of the plants the operators were required to patrol the unit every two hours to check for malfunctioning equipment and leaks. At the other plants the unit operators are out in the equipment area only during the process of collecting samples.

CHIEF OPERATORS

One of the plants employed chief operators. One chief operator is assigned per shift to operate the controls for the formaldehyde unit and for another chemical manufacturing unit. The controls for both units were located within the same building. This control building was located across the street from the formaldehyde unit in the blending/control laboratory building where the unit operator worked. The chief operators spent the majority of their time within the control building. It was also their responsibility to check and to blow down boilers once or more per shift as needed. This required them to enter the formaldehyde reactor area.

BLENDER OPERATORS

One of the plants visited employed blender operators who operate the controls from a blending control building. It was their job to transfer formaldehyde solutions between tanks within a central tank farm and to load rail cars or tank car trucks while using in-line blending to insure uniformity of product. Blender operators spend approximately 80% of their time within the blending control building, but they work only during the day shift. The blending operator does leave the building occassionally to read level gauges on hold tanks, to open valves to transfer solutions, or to collect holding tank samples to be analyzed by the plant's main laboratory personnel.

LOADING OPERATORS

One of the plants employed loading operators, whose job it was to load formaldehyde and other chemicals manufactured by that same plant. These operators were assigned at the central loading location for the plant and were assigned to either load the tank trucks or rail cars. These loading operations were done only during the day shift. The specific procedures they used are discussed in Sections 5.1.2 and 5.1.3.

PRODUCTION SUPERVISORS

At one of the plants, production supervisors supervised the formaldehyde operation during the day shift. Their office is across the street from the formaldehyde unit and is next to the unit control building where the chief operator works. The production supervisor works in the formaldehyde unit area when necessary to insure smooth operations and as a result has the potential of being exposed to formaldehyde gas.

MAINTENANCE PERSONNEL

Each plant provides maintenance personnel for upkeep of the formaldehyde unit. At most of the plants the maintenance personnel are responsible for maintenance of the entire plant in addition to the formaldehyde unit itself. At one of the plants the maintenance personnel were responsible for maintenance for the entire plant complex. All of the maintenance personnel provide maintenance only during the day shift of a Monday thru Friday work week. They are on call for repair of any major malfunctions or leaks.

One of the plants also had service operators who provide maintenance specifically for the formaldehyde unit and the other chemical manufacturing units run by the chief operator. These service operators work on all three shifts, but most of their time is spent in manfacturing areas other than the formaldehyde production facilities. These service operators provide miscellaneous maintenance service and clean up as needed.

All regular maintenance personnel provide detailed maintenance for the formaldehyde unit, which includes replacing the converter catalyst, entering and cleaning tanks, repair of formaldehyde and methanol leaks, and repair of any type of malfunctioning equipment. None of the plants visited operated a comprehensive periodic maintenance program, although one of the plants does try to maintain a yearly turn-around formaldehyde unit maintenance program.

5. SUMMARY OF WORK PRACTICES

5 1 SPECIFIC PROCEDURES - FORMALDEHYDE EXPOSURE

5.1.1 Process Sampling and Analysis

- Unit operators at all of the plants visited draw formaldehyde samples from the absorber for analysis. These same operators also draw samples from the distillation column at some of the plants.

- The unit operators collect formaldehyde samples in glass containers, either glass jars, Erlenmeyer flasks, or graduated cylinders.

- Each sample point is equipped with a ball valve to facilitate the collection of samples.

- All unit operators purged the sample line into the collection device in order to obtain a reliable sample.

- Purge from the sample points at most of the plants is dumped into a nearby catch basin, which recycles the purge back to the unit or is directed to a closed collection tank or to the plant sewer system. Purge from the sample point at one plant was dumped into a bucket below the sample point. This bucket is covered, and the accumulated purge solution in the bucket is dumped into the unit sump by the unit operator at the end of each shift.

- The collection device used at most of the plants is then filled and stoppered or covered with a screw top. The unit operator at one plant fills a graduated cylinder and leaves it open, allowing continuous vapor loss to the workplace.

- Indirect sample collection devices which do not require purging and sample enclosures such as those described by Lovelace [23], are not used by the formaldehyde industry.

- The collection devices are then manually transported to the control room for lab analysis.

- The unit operators then runs percent methanol, formic acid, and formaldehyde analyses within the control room as follows:

- At one plant all analyses are run within a ventilated (less than 100 feet per minute inward face velocity at the time of the survey) lab hood. Percent methanol is determined by a specific gravity test, formic acid is determined by titrating a sample aliquot with sodium hydroxide, and percent formaldehyde is determined by titrating a sample aliquot with sulfuric acid.

- At another plant, the percent formic acid is analyzed by titration with sodium hydroxide in a ventilated lab hood. Percent formaldehyde is determined by titration of a sample aliquot with hydrogen chloride outside the lab hood. For the percent methanol determination, acetonitrile is added to an aliquot of the sample within the lab hood and a 5 µL portion is injected into a GC located outside the lab hood.

- At a third plant, small vials are filled with sample aliquots within a ventilated lab hood. The vials are then weighed outside the hood. Three formaldehyde determinations are performed in the lab hood by titration of sample aliquots with sulfuric acid. A portion of the absorber sample is titrated in the hood with sodium hydroxide to determine percent formic acid. Approximately 4-5 mL of sample are taken from the stream from the top of the distillation column, and an aliquot is injected into a GC located outside the hood to determine the percent methanol.

- At the other plant, each unit operator performs analyses on each absorber sample within a ventilated laboratory hood. An aliquot of each absorber sample is poured by each unit operator into an Erlenmeyer flask, which is placed in a temperature-controlled cabinet within the lab hood. The collective solution is analyzed for percent formic acid and formaldehyde once every third shift by that shift's unit operator. A specific gravity analysis is also performed. The specific gravity test is performed inside the lab hood. A sample is automatically titrated with sodium hydroxide outside the hood to determine percent formic acid. Another portion of the sample is also titrated automatically outside the lab hood with sulfuric acid to determine percent formaldehyde.

- At one plant, formaldehyde gas sample is usually drawn by the unit operator or quality control supervisor once every third shift, or more often if process changes such as catalyst adjustment are involved. The sample is drawn into a syringe through a sample valve in the aftercooler inlet. The sample is then injected into the GC in the control room.

- At two of the plants, unit operators dump sample analyses waste down a sink within the lab hood, which either recirculates the waste back to the formaldehyde unit or to the plant's waste treatment facility. At another plant, the unit operator dumps analyses waste into an open 500-mL flask within the hood. When the flask is full, the unit operator will dump the collective waste into a dump located outside the blending control/laboratory building.

- Unit operators or the blender operator at one of the plants collected samples in glass jars from final storage or blend flasks prior to or during loading so as to verify required solution concentrations. As with collection of regular process samples, most purges are dumped into a nearby catch basin, which recycles the purge back to the unit, to a closed collection tank, or to the plant sewer system. A purge from the sample point at one plant is dumped into a bucket below the sample point. The bucket is covered and the accumulated purge solution is manually dumped into the unit sump by the unit operator when the bucket is filled.

- Once the sample is collected, the jar is covered. Those unit operators who collected the sample transport the sample back to a control room or blending control/lab room for analysis. At another plant, the blender operator who collects the sample gives the sample to another plant worker who transports it to the main lab for analysis by lab technicians. Analyses performed are either all or one of the following: percent formaldehyde, percent formic acid, or specific gravity. These analyses are performed as previously described for regular process samples. Analysis waste is also eliminated as previously described.

5.1.2 Tank Truck Loading

- Tank truck loading is performed at two of the plants by the unit operator, at another plant by an independent truck driver under unit operator supervision, and at the fourth plant by a loading operator who only performs formaldehyde or other chemical loading. Unit operators may perform formaldehyde resin or other chemical loading, depending on what products are manufactured at the plant.

- Loading is performed at some plants only during the day shift and at others during all shifts. The frequency of loading is dictated by the market available for each plant.

- Prior to loading, the truck hatch is opened. At one of the plants, a dip tube is inserted through the hatch opening. At two of the other plants, a dip tube is inserted through the hatch opening and a rigid local exhaust ventilation duct is positioned in or slightly above the hatch opening. At the fourth plant, an air displacement duct and the loading line are connected to the tank top next to the open hatch with quick connect fittings.

- All plants utilize automatic delivery and metering. Either the unit operator or the blender operator initiates loading by operation of loading controls. These are located either on an outside panel at the loading site or within a control building or shed adjacent to the loading site

- Some unit or loading operators remain at the loading site most of the time, while others are able to leave the area for the majority of the loading time.

- At one of the plants, a sample is collected when the truck tank is approximately half full. If the sample meets specifications, the truck is completely filled, the loading line is flushed with air, the line is removed, and the hatch is closed. At the remaining plants, the tank is completely filled and either the loading line is flushed with air, the line disconnected, and a sample collected, or a sample is collected and the loading line is flushed with air and disconnected.

- The sample is collected by lowering an open glass jar on the end of a chain or dip stick through the open hatch into the solution. The filled jar is removed from the tank solution, covered, and transported either to a control room lab or main plant lab for analysis.

- Most truck samples are usually analyzed for percent formaldehyde and formic acid. A specific gravity test is also run on truck samples at one of the plants. All analyses are performed as previously described for process samples.

- Once the delivery line is purged and this line and all exhaust and air displacement ducts are disconnected, the hatch is closed.

- Any formaldehyde spills on the trucks, ground, or contaminated equipment are hosed down with water. Drainage sumps, which are situated at some truck loading sites, conduct contaminated water to the plant wastewater treatment facility.

5.1.3 Railcar Loading

- Railcar loading is performed by the unit operator at three of the plants and the loading operator at the fourth plant at which detailed surveys were done. These workers may perform formaldehyde resin or other chemical loading, depending on what products are manufactured at the plant.

- Railcar loading is performed less frequently than tank truck loading at the plants visited.

- At three of the plants at which detailed surveys were made, the cars are top-loaded, while at the fourth, cars are bottom-loaded.

- The loading setup was different at each of the four plants surveyed. At one plant, the unit operator opens the hatch, inserts a dip tube, and initiates loading by operating controls in a blending shed located away from the loading site. At another plant, the unit operator opens the hatch, connects a reinforced flexible delivery line to the bottom of the car with the use of a quick-connect fitting, and then initiates loading at a control panel located at the loading site. At the third plant, the unit operator opens the hatch, positions an exhaust duct over the hatch, inserts a dip tube into the car and initiates loading through operation of automatic controls in the adjacent blending control/lab building. At the fourth plant, the loading operator connected the delivery line and an air displacement duct to a retrofitted rail car dome and the blender operator initiates loading by operation of computerized controls in the adjacent blending control building.

- Formaldehyde is automatically metered at all the plants.

- Some unit or loading operators remain at the loading site most of the time, while at other plants they are able to leave the area for the majority of the loading time.

- After loading is complete, the unit operator at two of the plants flushes the delivery line with air, removes the dip tube from the car, obtains a sample, and closes the hatch. At a third plant, a sample is collected when the car is approximately half full. If sample analytical results meet specifications, the car is filled, the dip tube is purged with air, the dip tube and exhaust duct removed from the car, and the hatch closed. The loading operator at the fourth plant must visually check the level of solution in the car by opening the second non-retrofitted dome near loading completion. This is a result of a malfunctioning computerized metering system. The solution level is verbally relayed to the blender operator in the blending control building until the car is properly filled. Once the car is filled, the loading operator obtains two samples, the delivery line is flushed with air, the delivery line and air displacement duct are removed from the retrofitted dome, and the second open dome is closed.

- Samples are obtained by lowering open glass jars on the end of a chain, or dip stick through an open hatch into the formaldehyde solution. Filled jars are raised out of the car, covered, and transported to the control building or main lab for analysis.

- Most samples are usually analyzed for percent formaldehyde and formic acid. A specific gravity test is also run on rail car samples at one of the plants. All analyses are performed as previously described for process samples.

- Any formaldehyde spills or contaminated equipment are hosed down with water. Drainage sumps are situated at some loading sites which direct contaminated water to wastewater treatment facilities.

5.2 SPECIFIC PROCEDURES - METHANOL EXPOSURE

5.2.1 Unloading

- At two of the plants, the unit operator unloads methanol from rail cars. At the third plant, an independent truck driver performs all truck unloading activities. Methanol is manufactured on site at the fourth plant and pumped in an enclosed system to the unit.

- Methanol is bottom-unloaded.

- Prior to unloading, the unit operator withdraws a sample from the rail car.

- The top hatch is left opened. A quick-connect adapter is connected to the car discharge outlet and a reinforced rubber flexible hose with quick-connection fittings is attached to the quick-connect adapter.

- Occasionally, a small quantity of methanol spills on the ground (when the cap is removed from the car discharge outlet prior to unloading).

- Prior to unloading, the unit operator at one plant bleeds the unloading line air, and a small amount of methanol is purged from the line into a bucket. This methanol is either back-fed into the line by suction, or if the quantity is very small, the unit operator manually dumps the methanol back in the rail car through the hatch.

- The unloading pump at another plant is kept continuously primed. An uncovered glass jug is kept beneath the tank car loading platform for priming by the unit operator if needed.

- Once the unit operator initiates unloading, he leaves the unloading site for the majority of unloading.

- Unloading at one plant takes 8-10 hours, whereas unloading at another plant can be completed within an 8-hour shift.

- Once unloading is complete, the unit operator bleeds the unloading line, disconnects the unloading line, and then closes and secures the top hatch.

5.2.2 Sampling and Analysis

- At the two plants where the unit operator unloads a methanol rail car, the unit operator withdraws a sample from the car prior to unloading. This is done by either manually dipping an open glass jar into the methanol or dipping an open glass jar on the end of a dip stick into the methanol. The jar is dipped into the methanol by inserting it through the open top hatch.

- Once the jar is filled, it is removed from the car capped, and transported to the control room for analysis.

- At the plant where an independent truck driver unloads methanol, the sample which the truck driver collects is hand-delivered by the truck driver to the unit operator in the blending control/lab building for analysis by the unit operator.

- Each unit operator performs a different set of analyses. They are the following:

  - boiling point determination within an adequate exhaust ventilated laboratory hood.

  - Injection of a portion of the sample into a GC or an occasional specific gravity test run in an adequate exhaust-ventilated laboratory hood.

  - A specific gravity test performed outside an existing lab hood without the benefit of local exhaust ventilation control.

6. CONTROL TECHNOLOGY

6.1 GENERAL PROCESS

6.1.1 Potential Problems

Several areas of formaldehyde production create a significant exposure potential for workers during a normal eight-hour shift. In an effort to protect the worker in these areas, plants have installed a variety of engineering controls that prevent or reduce emissions from process equipment or operations. The engineering controls found at the formaldehyde plants during the pre-survey and detailed survey visits are discussed below.

Formaldehyde production occurs by vaporizing methanol and converting it to formaldehyde over a metal oxide or silver catalyst, absorbing the formaldehyde to make an aqueous solution, which is then shipped to the point of use. These operations involve high temperatures, moderate pressures, high noise levels, and potential leakage of hazardous materials.

Parts of the system are operated at elevated temperatures. The methanol vaporizor must evaporate the methanol (normal boiling point is 65°C), which is potentially "touch hot", the temperature at which human reflexes are not fast enough to prevent burning ones fingers if the hot object is touched. The reactors which oxidize the methanol to formaldehyde operate at approximately 635°C. The absorption of the formaldehyde and water takes place at approximately 70°C, and the product is stored at 50°C. Workers are protected from the sources of heat by insulation on the system components and by the use of a continuous system which does not require the operators to be in physical contact with these pieces of equipment under normal circumstances.

Pressure is needed to force the air/methanol mixtures into the reactors. This produces a potential for vapor leakage. The blowers or compressors used to force the air/methanol mixtures into the reactors run at high speed and produce high noise levels.

There are numerous sites of potential leakage in a formaldehyde production system. A production unit might have from two to twenty reactors connected into a single system. Numerous valves are needed to isolate individual reactors. The reactors vary in diameter from a few inches up to eight feet in diameter, hence, the size of the valves needed varies considerably from plant to plant. This is independent of the type of catalyst used. Other valves are needed to control flow rates. There are also many flanged joints and pump seals which could leak.

6.1.2 Engineering Control Approach

The first line of defense for this process is the use of a closed process. Formaldehyde production systems are always continuous, from methanol storage up through the absorber. The piping network used is either welded or flanged and gasketed. The reactors are gasketed. The valves used are tightly packed gate and globe valves, with gaskets made of heat resistant fiber. Individual reactors are often valved so they can be isolated to repair leaks in one reactor while the others are still in operation.

The closed systems are provided with protection to minimize exposure to personnel in cases of malfunction. The formaldehyde production systems are continuously monitored and are shut down automatically if malfunctions are detected, normally by turning off the methanol feed pumps, and in some cases, also by turning off the air compressors. Malfunctions for which the systems are monitored include 1) too high a temperature at the reactor, indicating heat exchange inefficiency, 2) low temperature at the reator, indicating poor conversion, 3) too high an oxygen concentration, caused by poor system control, 4) too high a pressure at the reactor, caused by catalyst plugging or blinding or 5) low conversion in the reactor, indicating the channeling in the catalyst bed.

The closed systems are equipped with rupture discs, which prevent intensive equipment damage if the automatic procedures for shutdown fail or act too slowly. The rupture discs are normally equipped with explosion shields to protect workers. Rupture would result in a gas release which could expose workers, but is much preferred to allowing continued overpressurization with a possibility of catastrophic failure.

Heat exchangers are used to control the reactor temperature, and indirectly the reactor pressure. They are often used to heat or vaporize the inlet stream to the reactors and to cool the product gases.

Most of the formaldehyde production plants in the U.S. use open air structures rather than enclosed building to contain the equipment. This allows dilution by natural ventilation, which minimizes the build-up of formaldehyde or methanol concentrations in an area. It also prevents the build-up of heat and hence reduces the cooling needs for operator safety and comfort. The only negative factor to the open air structure is that it exposes the equipment to weathering and thus may increase maintenance.

The formaldehyde production facilities are designed to limit the amount of time the operators stay in the production area. Only infrequent equipment checks are needed. Maintenance problems are infrequent. Once a system is set in operation, it often runs continuously for six months or more without being shut down.

6.2 METHANOL HANDLING

6.2.1 Potential Hazards

Direct contact with liquid methanol does present certain hazards. However, methanol is not highly toxic. The OSHA time-weighted-average is only 200 parts per million. However, methanol is flammable, and it does have a sufficiently high vapor pressure (100 torr at 21.2°C) to cause the formation of flammable concentrations in air at room temperature.

The application of engineering controls to methanol handling is made more difficult by the intermitent operation and batch processing mode which typifies the unloading of tank trucks and rail cars. Direct operator activities require them to open hatches, to hook up flexible unloading lines, and to release these lines after the unloading is finished. The sampling done to check the purity of the delivered methanol also is done by the operator. It may expose his gloved hand or his arm as he uses a reach extendor such as a chain or rope attached to the bottle holder This operation is the one with the greatest opportunity for methanol contact. It is generally controlled only by the use of personal protective equipment.

6.2.2 Engineering Controls

Automation of methanol handling activities to reduce operator contact with methanol could be done, although engineering controls to isolate the worker from exposure are made difficult by the intermittant varied nature of this activity. However, several controls have been installed at the plants visited to reduce potential exposure of the worker.

The tank cars and rail cars in which the methanol is delivered are always chocked before unloading. These tanks are also grounded to prevent static electricity from igniting vapors. The operator then uses flexible, reinforced rubber hose with quick-connect fittings to connect the tanks in which the methanol is delivered to those used for storage at the plant. This reduces the amount of time to contact the unloading lines and, thus, reduces the exposure potential. Self-priming or continuously-primed pumps are found at the plants, which also minimize worker exposure. The quick-connect fittings are equipped with neoprene gaskets, which do an effective job of preventing leakage, and they are capped when not in use to prevent vaporization of residual methanol into the plant area.

The methanol is pumped to the storage tanks using centrifugal pumps, most of which are equipped with single mechanical seals to prevent leaks. The methanol is recycled in some cases and pumped to the seals to lubricate them. Double seal pumps could be used to minimize leakage and exposure, if these were found to be problems.

The open areas promote natural ventilation to prevent the buildup of methanol vapors. Underground piping used in some plants would prevents methanol leakage from evaporating quickly.

No engineering controls were found for several of the sub-activities that created some of the potential exposures, such as sampling the methanol from the tank and opening the covers of the tank. Both of these sub-activities can create direct liquid contact. To prevent exposure, plants generally require personal protective equipment, such as, gloves, organic vapor respirators, and splash goggles. Methods such as those described in Lovelace [20] could be used to minimize sampling exposure.

Methanol is stored in large storage tanks, typically with fixed roofs, although several floating roof tanks were also found. Fixed roof tanks were normally vented to the atmosphere, creating a potential for methanol emissions. One plant used a small condenser fitted with chilled plant water to condense and return any vaporized methanol to the tank. No estimate was available on the emission rate from the tanks. Each methanol storage tank was grounded. They were all diked to prevent accidental leaks or spills from contaminating large areas. Exterior level gauges also minimized worker exposure to methanol by preventing the necessity of opening the tank to determine how much was left in it. Some other plants in the chemical industry store methanol in fixed-roof tanks with internal floating-roof covers, but none of these were seen during the plant surveys done as a part of this project.

Methanol was pumped to the production area by centrifugal pumps with single mechanical seals. Automatic shut-off valves allowed automatic cut-off at the methanol source in case of system upset. The operators need to spend very little time in the area of the methanol storage tanks, thus, reducing the potential for exposure there.

6.3 ABSORBER AREA

6.3.1 Potential Problems

After the methanol storage area, the methanol flows through an enclosed system and is converted to formaldehyde. The enclosed process ends at the absorber, where the hot gas is contacted by cool water in absorber column. The absorber is the process control point in that process samples taken from the absorper are used to determined the reactor conversion efficiency. When the operator takes the sample, he is in direct contact with the formaldehyde solution and there is the potential for spills.

The solution being sampled is high in formaldehyde concentration (30 to 50 weight percent). The solution is also hot (30°C to 40°C). The vapor pressure from the hot concentrated formaldehyde solution is significant and thus poses the potential for exposure.

The operators collect samples from the absorber during every shift in order to obtain good process control information. These regular visits offer the potential for exposure. In addition to the potential exposure during the taking of samples, further possibilities for exposure occur during disposal of process sample purge material and transport of the samples taken to the laboratory for analysis.

The absorber is actually a closed system, except for the atmospheric vent at the top of the column. This vent can release vapor emissions that contain formaldehyde.

6.3.2 Engineering Controls

Two of the plants return gases from the top of the absorption column to the process. In one of them, the gas is fed back into the process with recycle air, and at the other plant it is fed to a waste heat boiler. The gas is recycled at one of the metal oxide catalyst plants to help control the oxygen concentration in the inlet air stream. Oxygen is used in the reaction sequence, and an excess could create a potentially explosive situation. Since oxygen is consumed in the reaction, the gas reaching the absorber is deficient and, hence, is an excellent source of gas to dilute the air fed to the reactors.

The silver catalyst process produces hydrogen gas, which can not be returned to the reactors. However, the heating value of the gas is sufficient to supplement boiler operation at the plant. Not only is the energy recovered, but formaldehyde remissions are reduced with the procedure. The hydrogen concentration can be as high as 20%, hence, it has a significant fuel value.

In addition to gas emissions from the absorber, liquid formaldehyde must be considered. Liquid process samples are normally taken two to four times per shift, depending upon the procedures specified at each plant. The purge of the sample lines was done each time to insure that the sample being taken was representative of the material being produced at the time.

Some plants provide purge catch basins to control emissions from the purge and prevent a secondary handling of this liquid. The purged catch is either returned to the absorber by a pressurized air system or else is sent to the wastewater treatment plant. The air-pressurized purge collectors also had a water flush system to prevent formaldehyde solution from remaining in the catch basin These automatic discard stations are a significant improvement over the normal bucket collection method in which excess solution is disposed of only when the purge bucket is full. Figure 4 shows the schematic diagram of a process sampling/purge collection system.

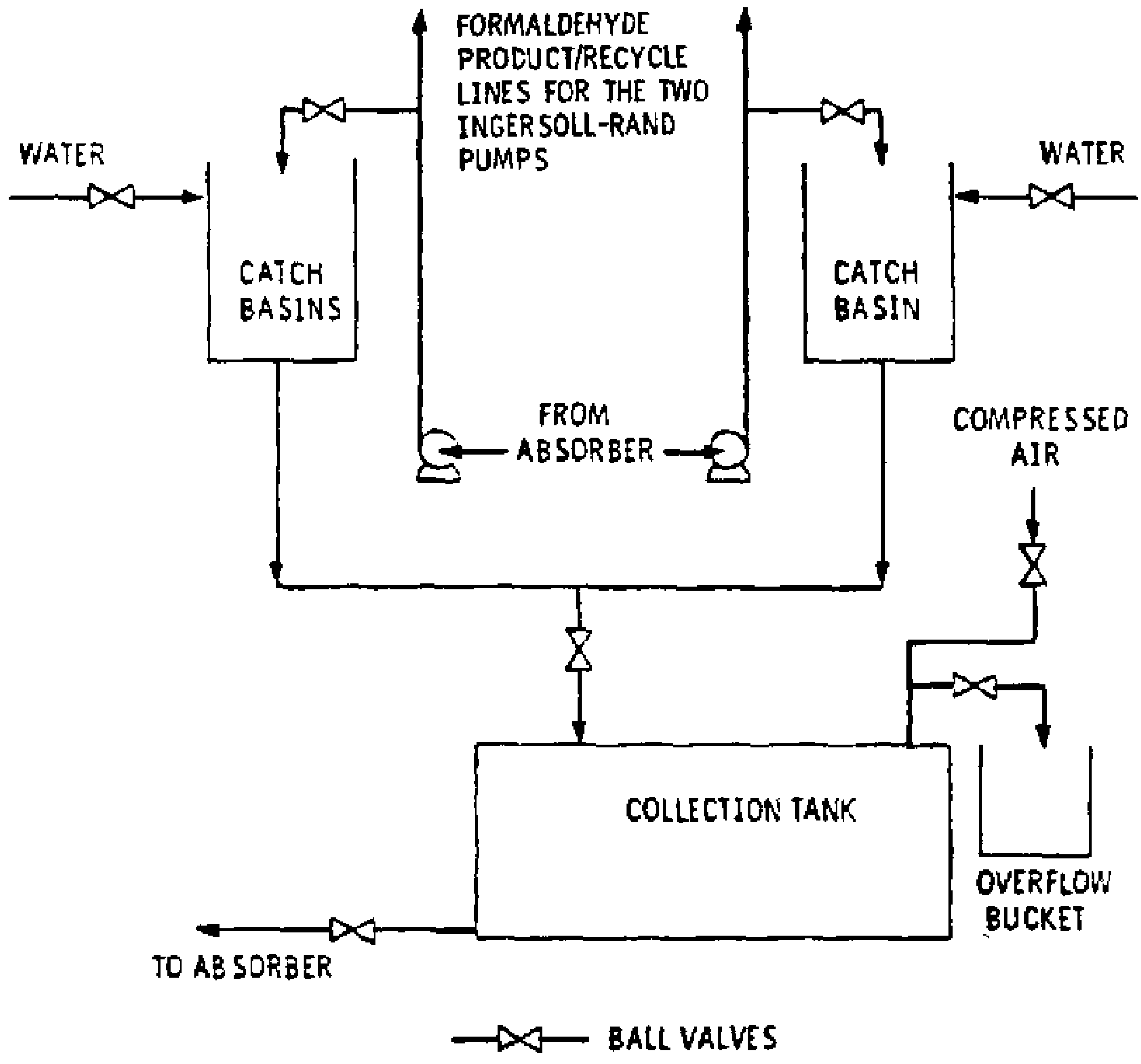

Figure 4. Schematic of process sampling/purge collection system.

The use of capped flasks and sample vial carriers keeps the formaldehyde exposure of operators down during the transport of samples to analysis laboratories. As a result of potential direct exposure to liquid formaldehyde, plants typically require the use of additional personal protective equipment, such as gloves and splash goggles. Respirators are also available, but are not used in most cases.

6.4 CENTRIFUGAL PUMPS

6.4.1 Potential Problems

There are normally three to five pumps connected with each absorber. Since these pumps are handling hot concentrated formaldehyde solution, the potential for leakage of hazardous material is present. There is also the possibility of formation of paraformaldehyde through the polymerization of formaldehyde. Paraformaldehyde can etch pump shafts because it is acidic or score them because it forms very hard deposits on the pump shafts. This can create additional maintenance problems, with their attendent increased formaldehyde exposure.

6.4.2 Engineering Controls

Most of the plants use centrifugal pumps with single mechanical seals. These are better than pumps with packed seals because they require relatively little lubrication, and they do not have paraformaldehyde formation, which so commonly occurs with packed seals. The constant flushing action with mechanical seals prevents the buildup of paraformaldehyde deposits on them. This in turn reduces leaks from the mechanical seal pumps. The recirculation of formaldehyde solution to the seals helps lubricate them as well as to seal the face of the pump. Steam jackets are also used in some cases since heat helps to prevent the formation of paraformaldehyde on the seals. Fiber insulation boxes are also used to keep the seals warm and prevent the formation of paraformaldehyde.

Pumps with double mechanical seals have been used on an experimental basis. If these were successful in reducing leaks and the amount of maintenance needed, they could contribute to reduced emissions. A brief study made during one of our surveys indicated that double mechanical seals could possibly reduce emissions by a factor of ten.

The number of centrifugal pumps in an average formaldehyde production and shipping plant numbers approximately 10. The use of mechanical seals as opposed to packed seals appears to give better control of pump maintenance and emissions, thus, reducing potential exposure. The double mechanical seal pumps use an inert material to lubricate, flush, and seal. They are reported in literature to be much better than single seal pumps at preventing leakage. They are, however, significantly more expensive. The leakage is reduced because the solution must pass through two seals instead of one before it escapes from the system.

6.5 FORMALDEHYDE STORAGE AND SHIPPING

6.5.1 Potential Problems

The operators have significant potential for exposure to formaldehyde during the loading of formaldehyde solution into tank cars and tank trucks. It is necessary for the operators to open the hatches on the receiving tanks and then to introduce the hot concentrated solution into them. During the filling of the tanks, the gas inside is displaced and can be expected to carry with it some formaldehyde fumes. Sampling of the tank trucks and storage tanks is necessary during these operations, during which time operator exposure is possible. Also, one must be concerned about the potential for spills and hose down of the tank cars and tank trucks after filling. Emissions from material on the ground could also expose operators. One can also get emissions from the storage tanks which breathe as they are filled and emptied.

6.5.2 Engineering Controls

Most formaldehyde production plants use formaldehyde on site in resin or chemical manufacturing. However, most plants also produce excess formaldehyde during their seven day per week, 24 hour per day operation and sell it to off-site customers. For the aqueous formaldehyde solutions stored on site in fixed-roof tanks prior to shipment, the continual filling and emptying of these tanks containing formaldehyde solution at 50°C can produce significant emissions. Some plants put simple scrubbers on the atmospheric vents to these tanks to recover the formaldehyde which exists from the tank as it is being filled. Using water sprays of less than one gallon per minute in scrubbers with the pressure drop of two to three inches of water, a weak formaldehyde solution containing 1/2 to 2% formaldehyde is formed, which is recycled to the process and hence becomes a part of the product instead of becoming an atmospheric emission.

The solution in the storage tanks needs to be maintained at approximately 50°C to minimize paraformaldehyde formation. Heat can be supplied to the solution by using external recycle pumps with a heat exchanger. Good mixing in the tank occurs and this prevents the need to enter the tank in case a repair is needed on the heat exchanger. Installed spare pumps allow flexibility in case of breakdown.

Another method to prevent having to enter the tank in the case of heat exchanger maintenance is to place the heat exchanger on a manhole cover which can be withdrawn from the tank in case a leak develops. One plant also uses a side agitator with a modified seal to keep the solution well stirred to minimize paraformaldehyde formation and to minimize the needs for seal maintenance.

Safety is stressed in a formaldehyde tank storage area. The tanks are grounded to prevent any spark discharge. The tanks are surrounded by dikes which prevent the escape of any large spills. The ground around the tanks is often cemented to prevent seepage into the ground. Safety showers and eye washer stations are located in this area. The large amount of liquid transferred and the long time necessary for its transfer makes the formaldehyde shipping area the most hazardous in terms of exposure. The ultimate solution to this problem would be a closed tank system under vacuum that would remove the potential for liquid spills or gaseous emissions during loading. None of the plants surveyed had such a system in place.

One plant, however, did use a modified closed dome system and a passive ventilation system to remove gaseous emissions. Tank cars have permanent connections to which the operator attached the delivery boom and the ventilation duct. The truck loading was similar, but required the operator to insert some of the connections. This system worked well except that no automatic sampling system was installed and the automatic delivery and level control system were inaccurate, requiring the operator to open the hatch to check the level and to take a sample.

Another plant had an active ventilation system without a closed dome. This system was not as effective as the closed dome system because vapors can escape along the edge of the hatch where the ventilation duct is inserted. Tests showed that this system did not generate a sufficient vacuum to prevent this from occurring.

All of the plants visited had automatic delivery systems that should allow the operator to set the required load then leave the area, thus preventing exposure during loading. This system also prevents overfilling, which often results in spills.

All of the plants visited had the capability of loading formaldehyde solution into either tank trucks or rail cars. As the liquid fills the tank, vapors from them are forced out through the vent. At some of the plants the vent goes to a scrubber similar to those used on the storage tanks. The formaldehyde is scrubbed out from them and returned for reuse in the plant via the absorber. The level indicator in the filling system tells when the tanks are full.

For this potentially hazardous operation, personal protective equipment is provided. Respirators, goggles, and gloves were always available.

6.6 LABORATORY AREAS

6.6.1 Potential Problems

The analysis of process samples is often done in the control room in a hood. Analysis offer the possibility of direct contact with the liquid. Any liquid or vapor which escapes can contaminate the control room, an area in which the operators spend up to 70% of their time.

6.6.2 Control Technology

The samples are generally kept sealed during their transport to the laboratory hood. The laboratory hoods are usually designed to have a 100 foot per minute inlet velocity across the face of the hood, but in some cases the flows were not uniform across the hood and fell well below this level. The presence of a laboratory hood for analysis, therefore, is no guarantee that formaldehyde exposure will be low. In some cases hoods were not turned on, and in other cases they were not large enough for all of the analyses to be conducted inside of them. In some cases they were not used when samples were discarded. Also, they were subject to poor clean-up. Sinks are generally available inside the hood for sample discard. This liquid often goes to the waste water treatment plant, but it can also be sent to the absorber. The vent from the laboratory hood usually has no emission controls. It is usually vented to the atmosphere directly above the control building in which it is located.

6.7 MAINTENANCE

6.7.1 Potential Problems

Maintenance personnel have the potential of direct contact with formaldehyde solution for extended periods of time. Many of the repairs that they make, such as repacking valves or pumps or putting new gaskets into reactors, involve opening equipment which contains formaldehyde vapor or solution. Although the maintenance forces normally are assigned to the plant as a whole, rather than to the formaldehyde production facility only, they are familiar with it and the hazards involved.

6.7.2 Control Technology

The maintenance personnel typically lock out rotating machinery to prevent the possibility of restarting the process while they are repairing equipment. Wash-down procedures have been well established to remove formaldehyde solution encountered when lines or pieces of equipment are opened. The maintenance personnel at the sites visited were well-schooled in the use of personal protective equipment and had respirators, gloves, and goggles available anytime they were working on the formaldehyde process.

7. SAMPLING AND ANALYSIS

Formaldehyde and methanol sampling were conducted during the surveys to determine time-weighted average (TWA) long-term and short-term exposure levels (STEL) for personnel and areas associated with formaldehyde production. Operators, chief operators, and production supervisors were sampled for formaldehyde and methanol exposure during eight-hour shifts to determine their normal 8-hour shift exposure. Process operators were also sampled during potentially high exposure activities for short-term exposure levels. Areas associated with formaldehyde production and frequently attended by the operators, were sampled over an 8-hour shift for formaldehyde and methanol to determine area concentration levels and to possibly pinpoint areas of concern.

7.1 SAMPLING TIME

The survey objectives dictated that two types of samples be collected. Long-term samples, collected over periods of 120 minutes or longer, were used to determine the time-weighted average exposures. Short-term samples, collected over periods of between 15 and 120 minutes, were used to determine the exposures from certain, but typically short, events occurring during the normal regular shift hours. Personal long-term samples generally were comprised of two, approximately 240 minutes long, consecutive sampling periods and were used to determine an eight-hour, time-weighted average according to the following formula [24]:

$$TWA = \frac{T_1X_1 + T_2X_2}{T_t}$$

where
TWA = time-weighted average
T_1, T_2 = sampling times for long-term samples
X_1, X_2 = concentrations of long-term samples
T_t = total time

This same formula was applied to personal as well as area samples. Long-term samples were repeated on a second day to enhance the survey results and to evaluate day-to-day variations in reproducibility.

Short-term samples were taken during operator activities where peak exposures might be expected, but possibly not be shown in the long-term samples. The short-term samples were also to indicate where controls may be more cost-effective, if the exposure concentration levels need to be reduced. Short-term samples were taken at flow rates of about 200 cm^3/min (as compared with 100 cm^3/min for long-term samples) to assure collection of pollutant volume sufficient for reliable analysis.

7.2 SAMPLING METHODS

Sampling for formaldehyde was conducted using an active dosimeter method developed by the research department of Monsanto Agricultural Products Company [25] and approved by the NIOSH project officer, Mr. W. N. McKinnery, Jr. The method uses sampling tubes packed with 2,4-Dinitrophenylhydrazine (2,4-DNPH)-coated silica gel to absorb formaldehyde from the sampled gas. To draw the gas through the tubes, MRC used DuPont Model P200 portable sampling pumps set and calibrated to deliver a constant flow rate (±5%) of approximately 100 cm^3/min (actual pumps ranged from 92.0 to 115.5 cm^3/min) for a long-term samples as suggested by Mr. David Haile, supervisor of the MRC industrial-hygiene certified laboratory. Short-term samples were collected using the sample pumps set and calibrated at a constant flow rate (±5%) of approximately 200 cm^3/min (actual pumps ranged from 180.7 to 203.4 cm^3/min). Pumps were generally checked for significant (greater than ±5%) deviation after use, and the samples were discarded where a significant deviation was observed.

To assure quality of results, formaldehyde sample blanks and spikes were used and all samples were analyzed and reported in accordance with standard MRC Quality Assurance/Quality Control procedures. Additional details on formaldehyde sampling and analysis methods are provided in the detailed industrial hygiene reports on this contract [14-17]. All of the formaldehyde samples taken were refrigerated after they were collected, stored under refrigeration, shipped cold in insulated containers, and refrigerated upon receipt at the analysis laboratory to preserve them and protect them from degradation.

Sampling for methanol was conducted using a NIOSH-approved active dosimeter method, NIOSH S59. Silica gel tubes were used in conjunction with DuPont Model P200 pumps which were set and calibrated at a constant flow rate (±5%) of approximately 50 cm^3/min (actual pumps vaired between 47.5 and 56.8 cm^3/min) for personal, source, and area sampling. Pump flowrates were checked after sampling to ensure constant flow.

To assure quality of results an unexposed silica gel tube was collected as a blank during each sampled shift. In addition, methanol samples were collected in duplicate, and one of the duplicates was spiked during sampling with either 0.8 or 1.2 times the PEL to check on recovery and precision of sampling and analytical procedures. All methanol samples and blanks were analyzed and the results reported according to MRC Quality Assurance/Quality Control Procedures. Additional details on the methanol sampling and analysis procedures used in these surveys are included in the detailed industrial hygiene survey reports on this contract.

8. RESULTS

The following tables and figures present the analytical results for samples taken by the MRC survey team at the formaldehyde plants visited as a part of this project. All volumes and concentrations have been corrected to standard temperature and pressure (20°C and 760 torr or 68°F and 29.92 in. Hg).

Table 1 presents the long-term personal sample analytical results for formaldehyde. The ranges of these data are also shown in graphical form in Figure 5. Relative to the OSHA time-weighted average permissible exposure limit of 3.0 ppm for formaldehyde, this graph shows that all of the measurements made are well below the OSHA standard. NIOSH recommends a 1.0 ppm ceiling on formaldehyde exposures.

Short-term formaldehyde personal sample analytical results are presented in Table 2. The ranges of these data are also shown in graphical form in Figure 6. Relative to the OSHA short-term exposure limit of 5.0 ppm for formaldehyde, the graph shows that all of the measurements made are well below the OSHA standard.

Area sample results for formaldehyde exposure are shown in Table 3. The ranges of these results are also shown graphically in Figures 7 and 8. While most of these results are low, the higher values given do show that there are places within formaldehyde plants where the potential exposures do exceed the current OSHA limits for formaldehyde.

Table 4 shows the long-term personal sample analytical results for methanol. The ranges of these results are also shown graphically in Figure 9. It is easily seen that all of the measured values are far below the OSHA time-weighted average permissible exposure limit of 200 ppm for methanol. The NIOSH recommended permissible exposure limit for methanol is also 200 ppm, with 800 ppm being allowable for 15 minutes. No short-term personal samples were taken for methanol.

The area sample results for methanol are presented in Table 5. The ranges of these results are also shown graphically in Figures 10 and 11. It can readily be seen that unlike the formaldehyde results, none of the methanol area concentrations are even close to exceeding the OSHA standards for personnel exposure.

TABLE 1. LONG-TERM PERSONAL SAMPLES - FORMALDEHYDE

Sampler Location	Number of samples	8-Hr TWA range,[a] ppm	8-Hr TWA median, ppm	8-Hr TWA mean, ppm	Standard deviation
OPERATOR					
Plant A	4	0.38-0.68	0 58	0.55	0.125
Plant B	6	0 09-0 36	0 18	0 23	0 108
Plant C	5	0.11-0.56	0 39	0.31	0.178
CHIEF OPERATOR					
Plant C	3	<0.13-0 24	0 22	<0 19	0 059
PRODUCTION SUPERVISOR					
Plant C	2	0.30-0.32	0.31	0 30	0.016
MAINTENANCE WORKER					
Plant A	6	<0.05-0.32	0.14	<0.15	0.093
Plant B	4	0 09-2.22	0 35	0 61	0 999

[a] < Sign indicates concentration is below lower detection limit for formaldehyde, which varies with the total amount of gas sampled.

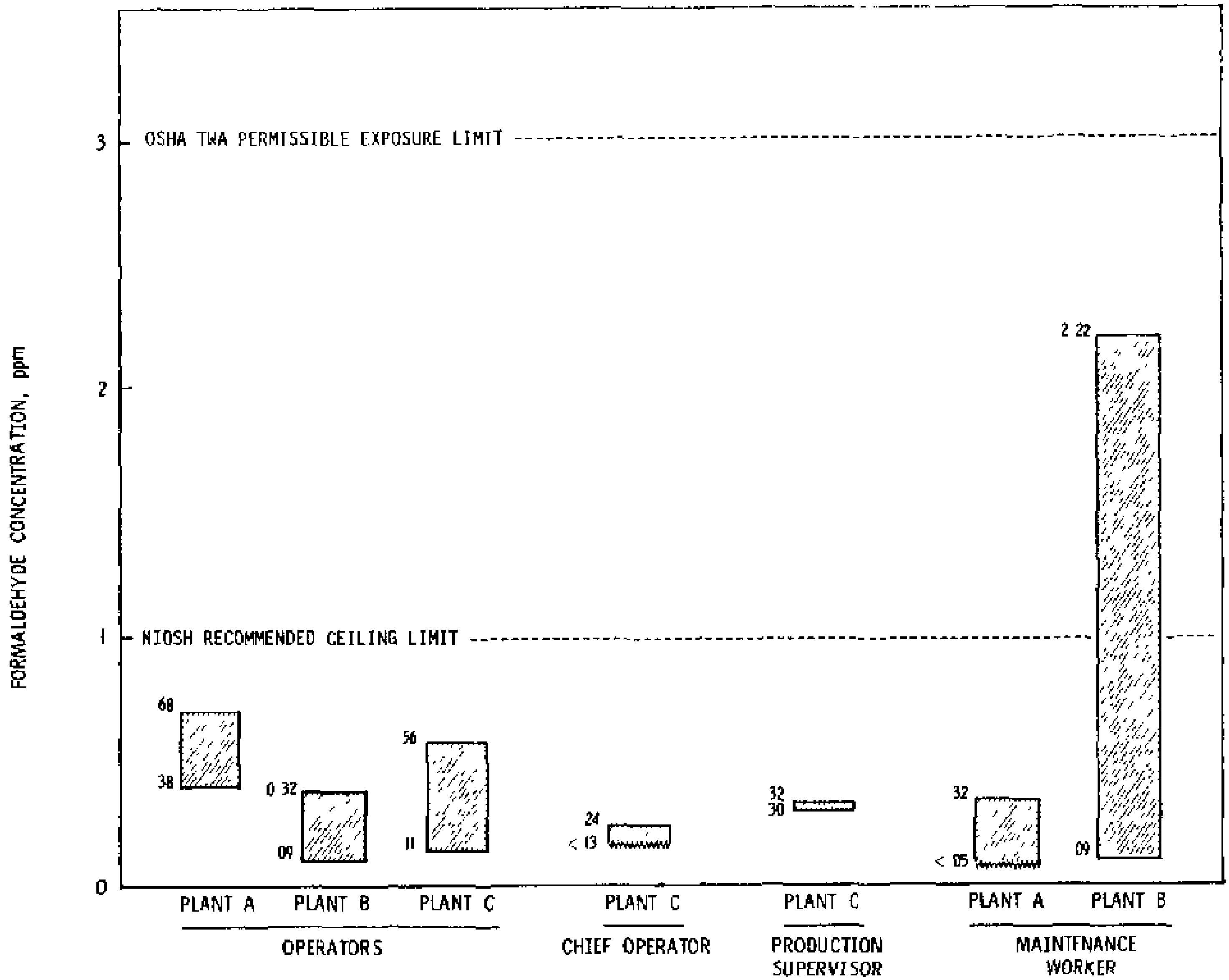

Figure 5. Long-term personal samples - formaldehyde.

TABLE 2. SHORT-TERM PERSONAL SAMPLES - FORMALDEHYDE

Sampler Location	Number of samples	TWA range,[a] ppm	TWA median, ppm	TWA mean, ppm	Standard deviation
PROCESS SAMPLING AND ANALYSIS					
Plant A	6	0.31-1 89	0 58	0.87	0 604
Plant B	11	<0.05-0.64	0.15	<0 27	0.160
Plant C	6	<0.05-1.76	1 10	<1.02	0 667
PRODUCT LOADING					
Plant A	2	0.19-0 55	0 37	0 32	0 264
Plant B	3	0 86-1.07	1 04	1 00	0.114
Plant C	2	0.96-1 79	1.22	1.22	0.627
AFTERCOOLER SAMPLING					
Plant B	1	1 34	1 34	1.34	-

[a] <Sign indicates concentration below minimum detection limit

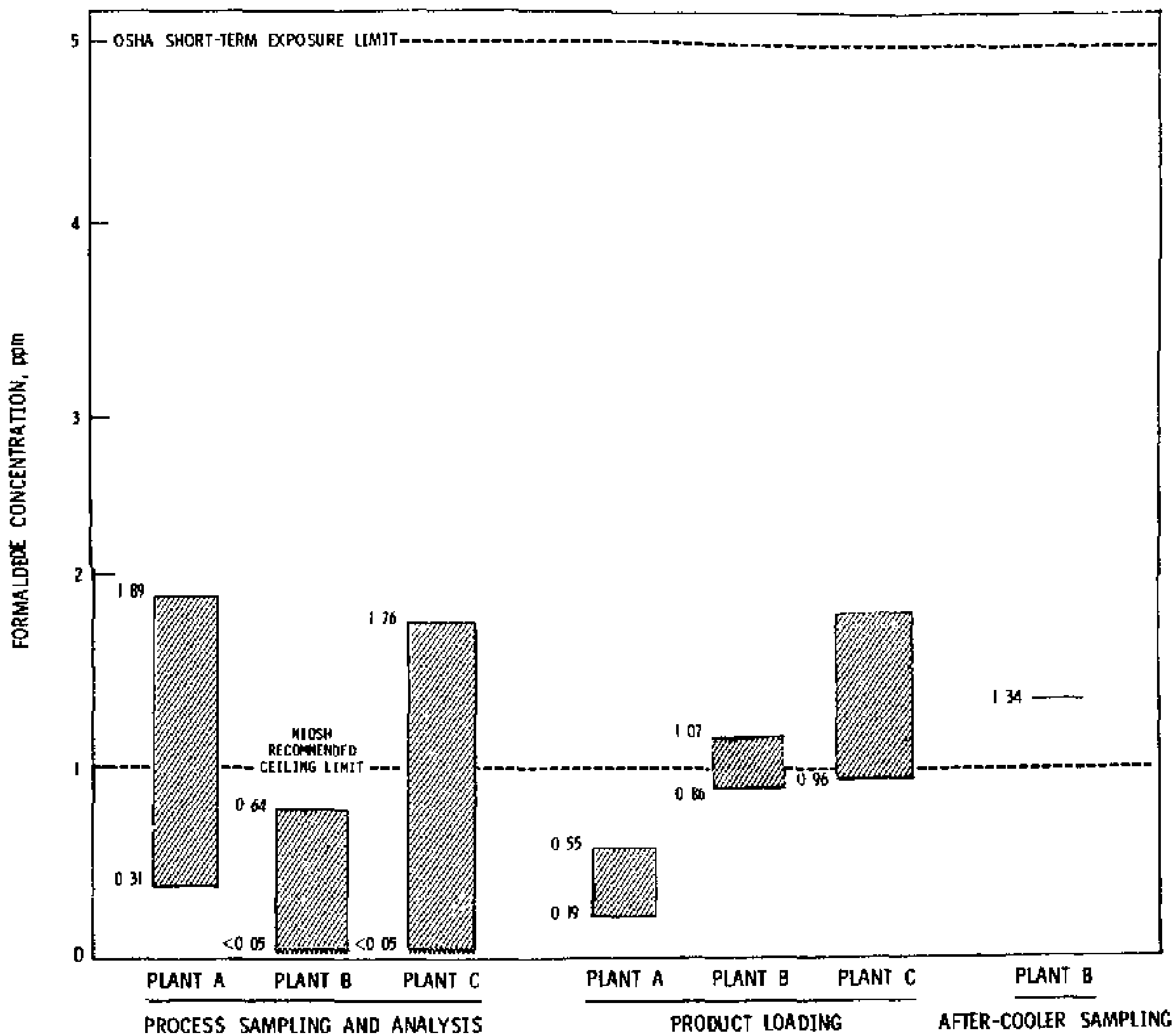

Figure 6. Short-term personal samples - formaldehyde.

TABLE 3. LONG-TERM AREA SAMPLES - FORMALDEHYDE

Sampler Location	Number of Samples	Concentration Range,[a] ppm	Concentration Median, ppm	Concentration Mean, ppm	Standard Deviation
METHANOL STORAGE					
Plant A	1	0.12	0 12	0.12	-
Plant B	2	0 32-0 55	0.44	0 45	0.164
PRODUCTION AREA (REACTOR-ABSORBER)					
Plant A	14	0.05-1 38	0.18	0 27	0 330
Plant B	14	0.01-0 64	0.12	<0.18	0.167
Plant C	11	<0.06-3.63	0.16	<0.61	1 055
FORMALDEHYDE STORAGE					
Plant B	4	0 56-1.06	0.78	0 78	0.205
Plant C	4	0.17-0.35	0 22	0.24	0.077
FORMALDEHYDE BLENDING					
Plant A	3	0 27-1 02	0.40	0 69	0.428
Plant C	2	0.11-0.16	0.14	0.13	0 035
FORMALDEHYDE LOADING					
Plant A	2	0 28-8 62	4.45	4 32	5.90
Plant C	3	<0.05-1.55	<0.05	<0.37	0.893
CONTROL LAB-GENERAL					
Plant A	6	0 38-0.69	0 52	0 50	0 113
Plant C	6	0.13-0.69	0.36	0.39	0.218
CONTROL LAB-HOOD AREA					
Plant A	4	<0.01-1 14	0 54	<0 58	0.435
Plant C	4	0.53-2 60	1.70	1.46	0 886

[a] < Sign indicates concentration below minimum detection limit.

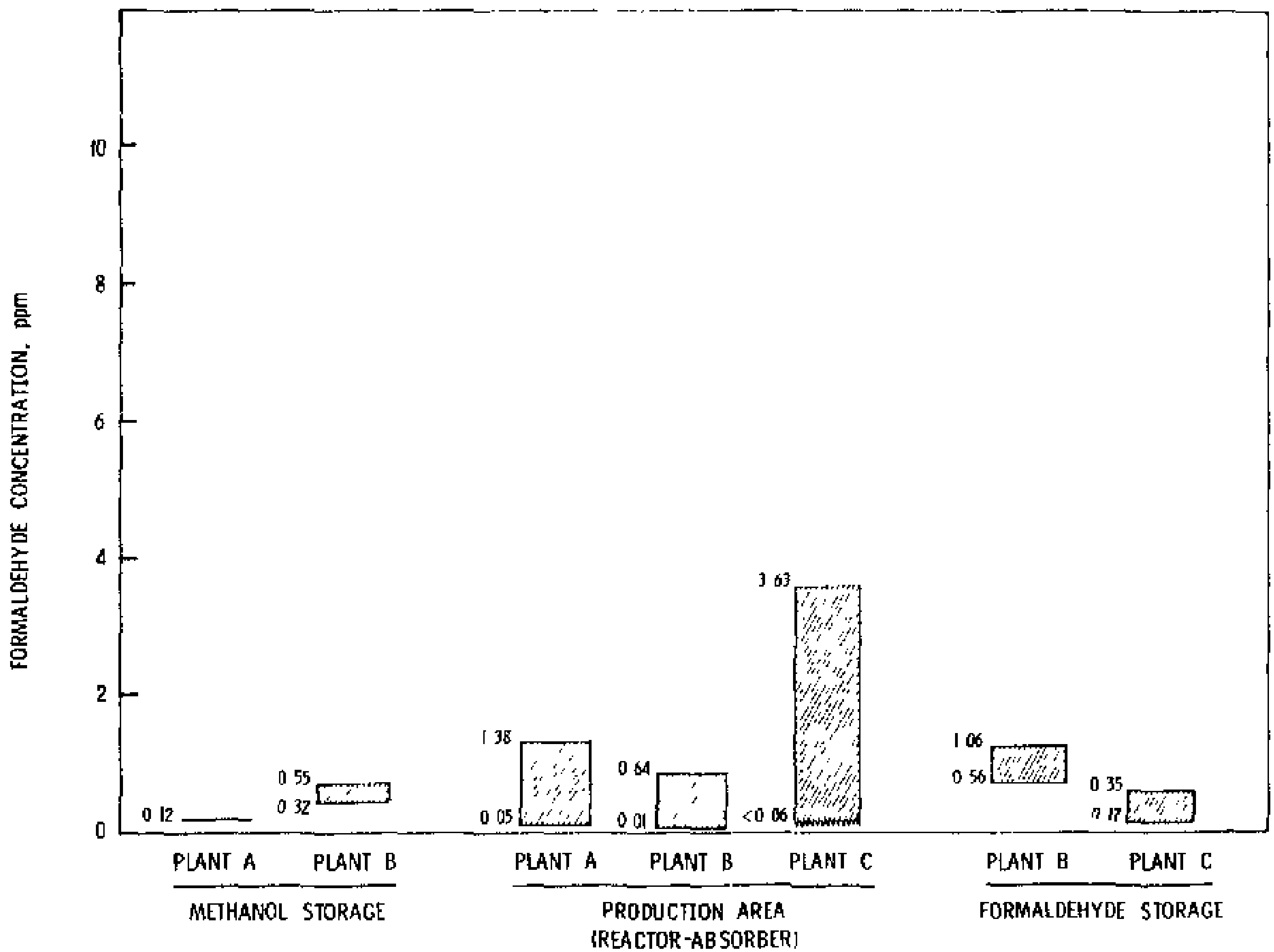

Figure 7. Long-term area samples - formaldehyde.

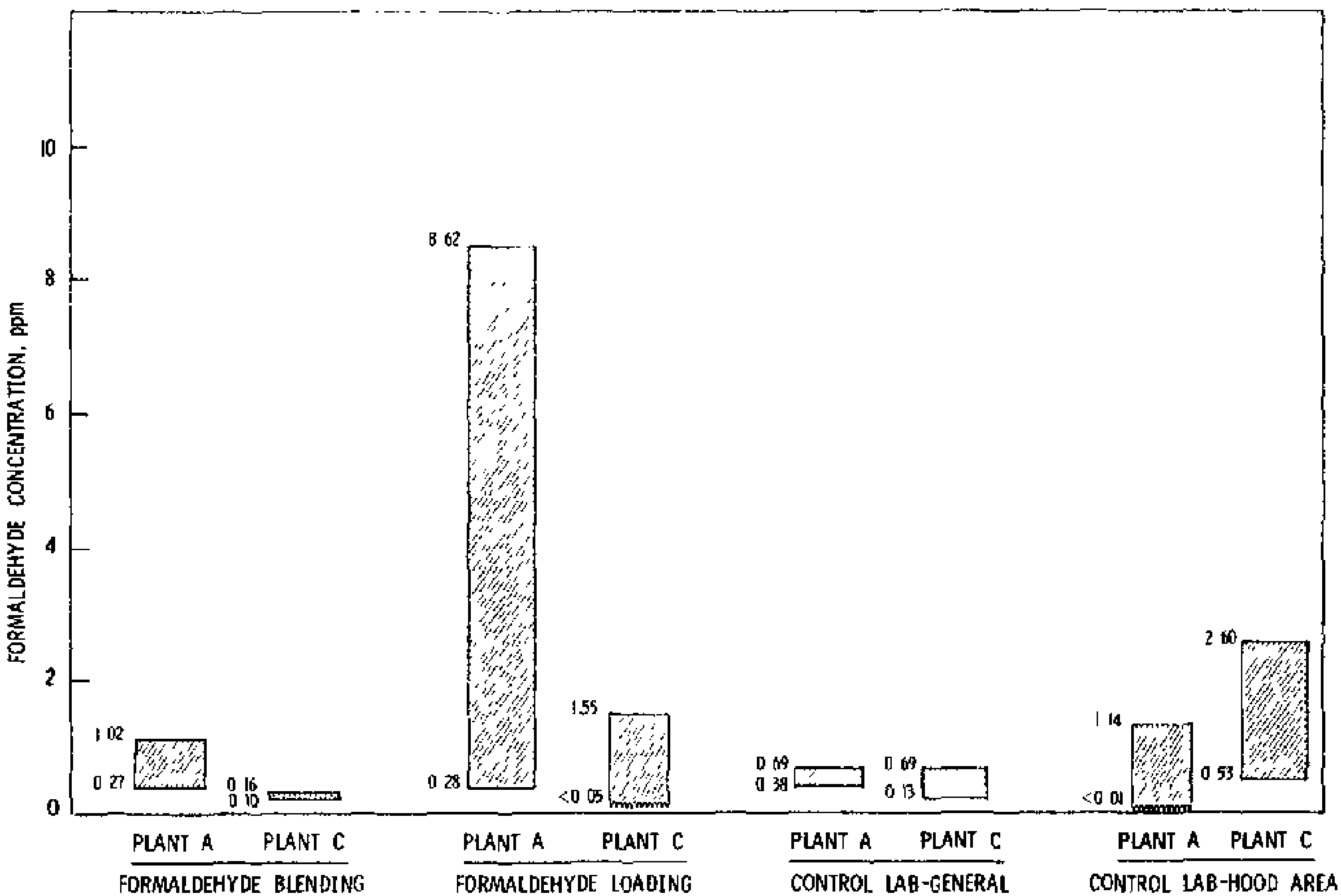

Figure 8. Long-term area samples - formaldehyde (continued).

TABLE 4. LONG-TERM PERSONAL SAMPLES - METHANOL

Sampler Location	Number of Samples	Concentration Range,[a,b] ppm	Concentration Median, ppm	Concentration Mean, ppm	Standard Deviation
OPERATOR					
Plant A	4	<1 0->9.75	>6.58	>5.69	3 73
Plant B	6	<3.0-12.09	<3.0	<3.49	0 712
Plant C	4	<0.3->2 02	0.31	>0.84	0.563
Plant D	3	<1.0-5.04	<1 0	3 01	1 79
MAINTENANCE WORKER					
Plant A	4	<1.0-1.66	<1.0	<1 14	0.265
Plant B	4	<3.0-3 38	<3 0	<3 03	0 062
Plant D	2	<1 0->8.34	>4 3	8.05	11.14
CHIEF OPERATOR					
Plant C	1	<0.3-0.35	<0.32	<0 32	-
PRODUCTION SUPERVISOR					
Plant C	2	<0.3->10.57	<0.3	>3.07	3 78

[a] <Sign indicates concentration below minimum detection limit.

[b] >Sign indicates breakthrough occurred on sample.

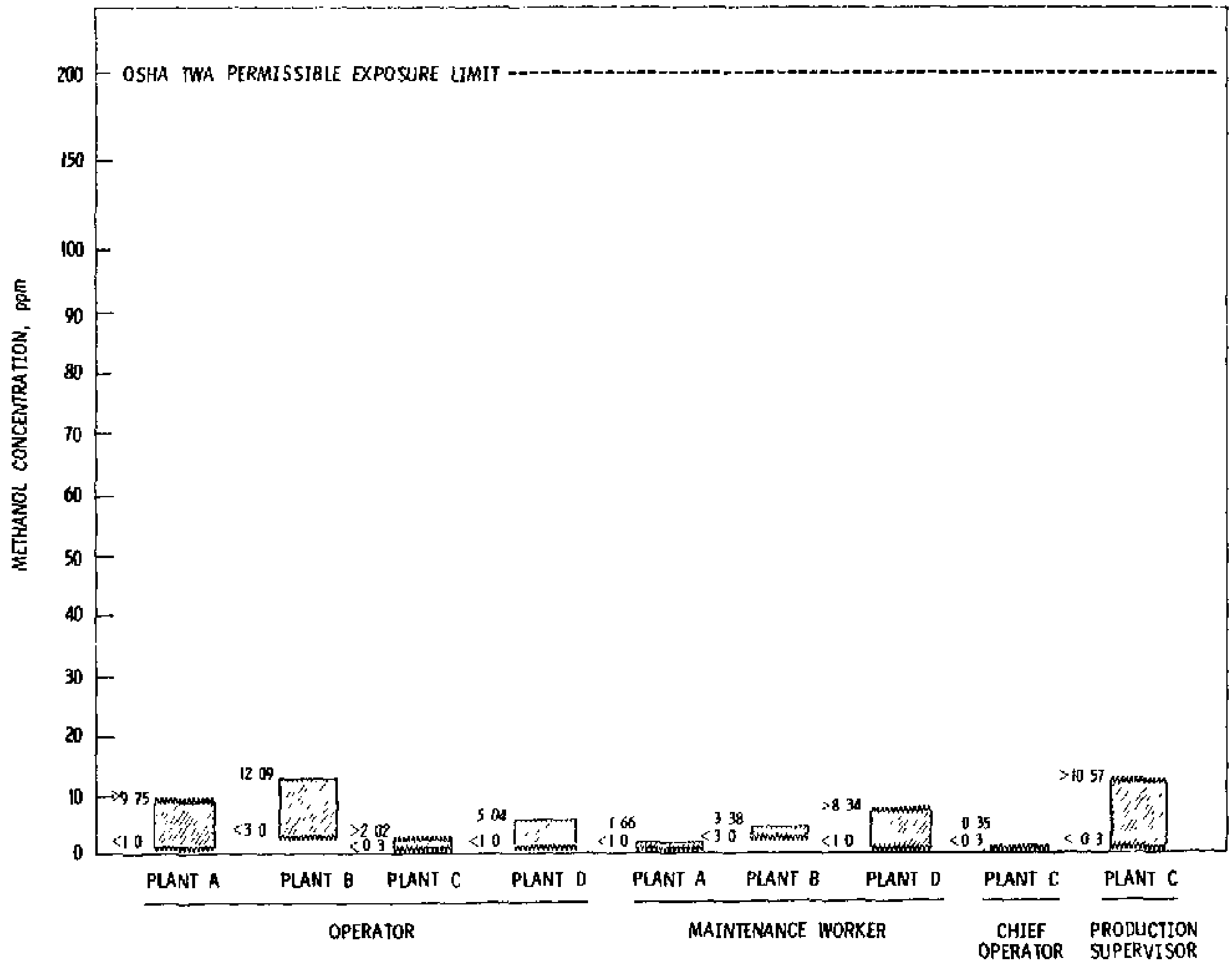

Figure 9 Long-term personal samples - methanol.

TABLE 5. LONG-TERM AREA SAMPLES - METHANOL

Sampler Location	Number of Samples	Concentration Range,[a,b] ppm	Concentration Median, ppm	Concentration Mean, ppm	Standard Deviation
METHANOL UNLOADING AREA					
Plant A	1	<1.0	<1.0	<1.0	-
Plant B	3	<3.0	<3.0	<3.0	-
Plant C	6	<0.3-5.7	>3.6	>2.12	2.58
Plant D	3	<1.0-3.40	2.08	<2.27	1.21
METHANOL STORAGE AREA					
Plant B	2	<3.0	<3.0	<3.0	-
PRODUCTION AREA					
Plant A	14	<1.0-1.53	<1.0	<1.04	0.142
Plant B	15	<3.0-22.7	<3.0	>6.28	6.64
Plant C	6	<0.3->13.70	0.68	>3.03	5.37
Plant D	10	4.72-125.6	7.84	25.92	37.12
BLENDING BUILDING					
Plant A	2	<1.0	<1.0	<1.0	-
Plant C	3	<0.3-0.53	<0.3	<0.38	0.133
FORMALDEHYDE STORAGE AREA					
Plant A	1	<1.0	<1.0	<1.0	-
Plant B	4	<3.0	<3.0	<3.0	-
Plant C	2	0.85-1.37	1.11	1.12	0.368
CONTROL LAB GENERAL					
Plant A	3	<1.0-8.65	5.5	<4.73	3.86
Plant C	4	<0.3->0.86	0.3	>0.42	0.284
CONTROL LAB - HOOD					
Plant A	1	51.4	51.4	51.4	-

[a] <Sign indicates concentration below minimum detection limit

[b] >Sign indicates breakthrough occurred

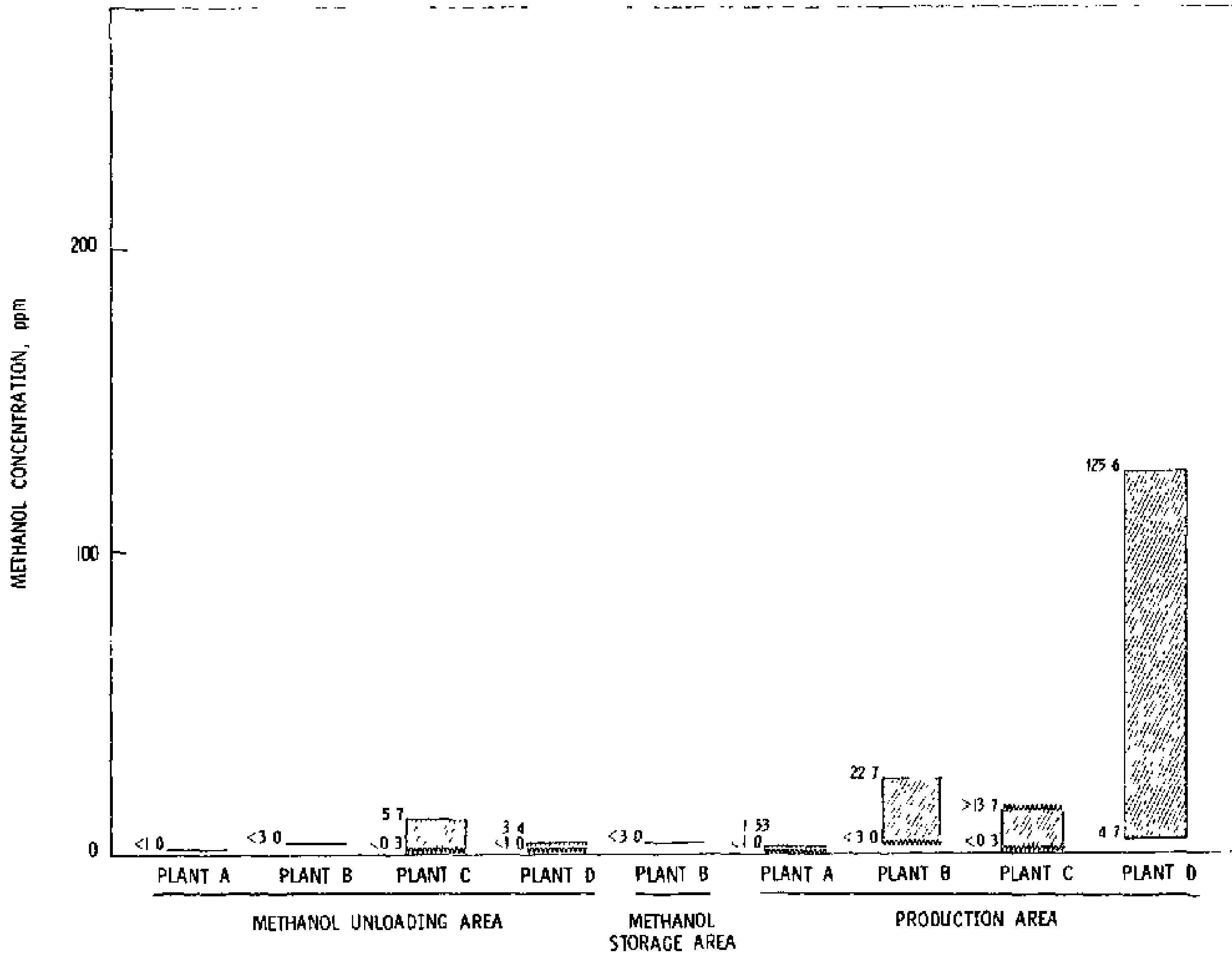

Figure 10. Long-term area samples - methanol.

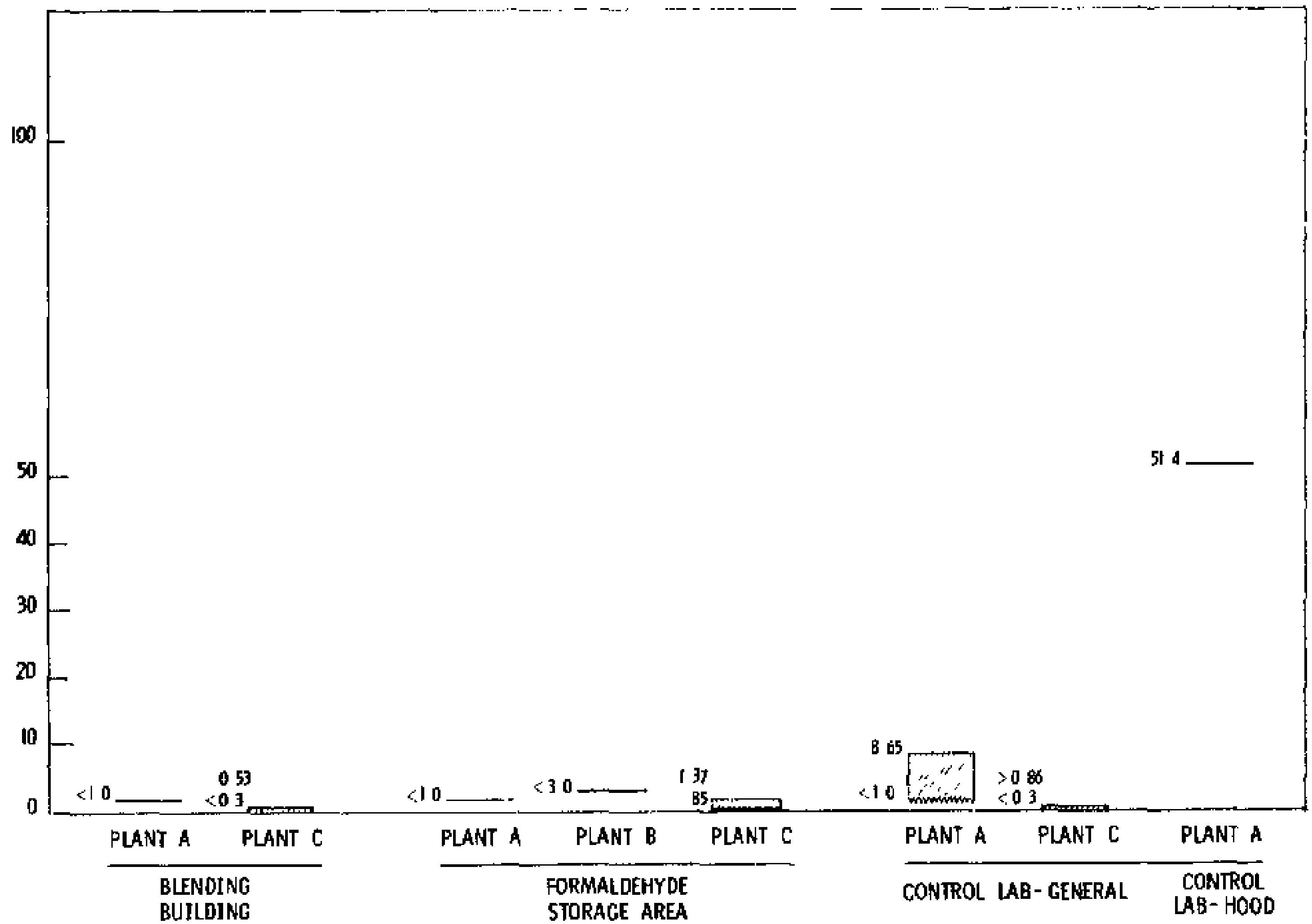

Figure 11. Long-term area samples - methanol.

9. CONCLUSIONS

As a result of the plant visits made during this study, conclusions have been reached by the project personnel concerning formaldehyde exposure, methanol exposure, and the engineering controls used in formaldehyde production facilities. These conclusions are listed below:

9.1 FORMALDEHYDE EXPOSURE

- All long-term samples taken on operators resulted in formaldehyde concentrations less than either the OSHA TWA PEL of 3.0 ppm, or the NIOSH recommended ceiling level of 1.0 ppm. These results indicate good control of the formaldehyde exposure for these workers.

- Long-term samples taken on production supervisors and chief operators also resulted in formaldehyde concentrations less than either the OSHA TWA PEL of 3.0 ppm or the NIOSH recommended ceiling, level of 1.0 ppm. These results also indicate good control of the formaldehyde exposure for these workers.

- The operator exposure when loading a rail car or tank truck where loading is not provided with local exhaust ventilation control could exceed OSHA limits, depending on weather conditions such as wind direction and speed.

- Sample results indicate that the concentrations of formaldehyde to which the operators are exposed during process sampling and analysis are less than the OSHA STEL of 5.0 ppm. However, several of these concentrations did exceed the NIOSH recommended ceiling level of 1.0 ppm.

- Nine long-term sample results for maintenance workers indicated non-excessive exposures less than the OSHA TWA PEL of 3.0 ppm. However, one maintenance worker did have an exposure which exceeded the NIOSH standard. None of the maintenance workers were repairing formaldehyde leaks or working on the formaldehyde process. Exposure sampling is needed to estimate the exposure when repairing major leaks.

9.2 METHANOL EXPOSURE

- Sampling indicates that operators, production supervisors, and chief operators were not exposed to methanol concentrations above the OSHA TWA PEL of 200 ppm or the NIOSH recommended standard PEL of 200 ppm, with an 800 ppm, 15 minute ceiling.

- The major exposure caused during methanol unloading does not appear to present a hazardous exposure.

- Sampling indicates maintenance workers are not exposed to excessive methanol, based upon the OSHA TWA PEL of 200 ppm, the ACGIH STEL of 250 ppm, or the NIOSH recommended standard.

9.3 ENGINEERING CONTROLS

The following engineering controls were found to be effective for preventing or reducing formaldehyde and methanol exposure:

- Single or double mechanical seals on pumps.

- Reuse of Absorber emissions

  a) recycle to process - metal oxide catalyst systems
  b) waste heat recovery - silver catalyst systems

- Purge collection systems - air pressurized return to the absorber - water rinsed.

- Water scrubber on storage tank emissions - return water to absorber.

- Water scrubber on loading ventilation system - return water to absorber.

- Automatic loading.

- Condensing loop on methanol storage tank emissions.

- Enclosed process.

The passive closed dome system is currently the most progressive control for formaldehyde loading. A closed dome loading system with active ventilation would be expected to be even more effective.

Many of the plants in the formaldehyde production industry are built in the open rather than being enclosed in buildings, allowing natural ventilation to assist in keeping ambient levels of formaldehyde and methanol low.

Some control room laboratory hoods at formaldehyde plants are ineffective and are not operating with a minimum average face velocity of 100 fpm.

The HCHO production industry has the necessary control technology to control formaldehyde and methanol concentrations to the levels currently acceptable to OSHA. However, it appears that some additional controls would be needed to meet the NIOSH recommended standard for formaldehyde.

10. RECOMMENDATONS

10.1 RECOMMENDED WORK PRACTICES

10.1.1 Formaldehyde Exposure

10.1.1.1 Process Sampling and Analysis

- The samples should be collected over a water-rinsed catch basin which directs purges and over-fills to an enclosed system away from the sample point.

- The sample should be immediately covered once the sample container is filled.

- All of the analyses should be performed within an adequate locally exhaust ventilated laboratory hood. A minimum recommended average face velocity of 100 fpm should be adequate to control the formaldehyde gas exposure during analysis.

- All analytical wastes should be discarded in a sink located within the laboratory hood which directs waste to a treatment facility.

- The possible use of an indirect sampler and a sample enclosure to minimize operator contact with the samples should be investigated.

10.1.1.2 Loading

- A local exhaust ventilation system should be used during loading. The local exhaust ventilation system should be turned on prior to loading. The system should be kept in operation until all duties at the loading site have been completed.

- The truck samples should be closed immediately after filling.

- Automatic loading and metering should be used, so as to eliminate the need for manual depth gauge readings.

- All truck samples should be analyzed within a laboratory fume hood. The recommended minimum average inward face velocity of 100 fpm is recommended to control formaldehyde exposure. Periodic measurements should be made to insure that the hood is working properly. The ACGIH Industrial Ventilation Manual should be used as a guide for installation and operation of laboratory fume hoods for this purpose [26].

- If a flexible delivery line is used, any formaldehyde solution trapped in it after loading should be directed back into the tank truck or rail car to prevent its being spilled on the ground or on personnel. Then any residual solution should be flushed back into the tank truck or rail car so that there is no exposure to residual formaldehyde after removal of the line from the tank truck or railcar.

- After loading, any formaldehyde contaminated material or equipment should be hosed off and any spills should be washed down a drainage sump which directs waste to a treatment facility.

10.1.2 Methanol Exposure

- A sample container positioned at the end of a dip stick should be used to collect samples from trucks.

- Once the sample bottle is filled, it should be closed immediately.

- Methanol samples should be analyzed in a laboratory fume hood. A minimum average face velocity of 100 fpm is recommended so as to control any methanol vapor. The ACGIH Industrial Ventilation Manual should be used as a guide for the installation and operation of these facilities [26].

- Residual solutions from chemical analyses for formaldehyde or methanol should be disposed of in such a way that no additional exposure results. Pouring these solutions down a sink inside of the laboratory fume hood is a recommended method for accomplishing this.

- In order to minimize exposures, personnel should spend as much of their time as is feasible within the requirements of their jobs away from unloading sites.

10.2 RECOMMENDED PERSONAL PROTECTIVE EQUIPMENT

- Maintenance personnel should be required to wear gloves and either a NIOSH-approved self-contained breathing apparatus or a NIOSH-approved supplied-air respirator when repairing major formaldehyde leaks. A full-face organic vapor cartridge respirator should be adequate when repairing major methanol leaks.

- Operators should be required to wear gloves and a NIOSH-approved full-face cartridge respirator designed for organic vapor protection, when loading a rail car or tank truck which are not exhaust ventilated.

- Operators should be required to wear gloves and chemical goggles when withdrawing a formaldehyde process sample or a sample from a storage tank.

- An operator should be required to wear gloves and a NIOSH-approved full-face cartridge respirator designed for organic vapor protection when collecting a formaldehyde gas sample.

10.3 RECOMMENDED ENGINEERING CONTROLS

10.3.1 General Production Operations

The formaldehyde production facility should be a closed process to the extent possible. Welded pipes, gasketed reactors, and tightly packed valves should be used to minimize leakage. Floor surfaces in and around processing equipment should be constructed of an impervious material (such as concrete) to facilitate spill cleanup. The system should be constructed for automatic shutdown in case of emergencies. Rupture discs should be in place to prevent system overpressure. The use of heat exchangers to control temperatures and to recover heat is recommended. The use of open air structures to prevent the build up of flammable or hazardous fumes is recommended.

10.3.2 Methanol Handling

The use of personal protective equipment while connecting hoses to tanks in which methanol is delivered is recommended. Single mechanical seal centrifugal pumps should be used to transfer methanol, and they should be automatically primed, if possible. Underground piping is advantageous in preventing mechanical damage to these systems. The storage tanks should be diked and grounded. A condenser for methanol emissions which returns them to the system is preferred. If a condenser is not used, then a flame arrester should be installed to prevent possible ignition of the highly volatile methanol. An external level gauge should be present to prevent the necessity of opening the tank for gauging.

10.3.3 Absorber Area

The absorber emissions should be reused. Those from the silver catalyst process should be burned for heat recovery. Those from the metal oxide catalyst process can be reused as a diluent for air in the inlet stream to the reactor. The use of double mechanical seals with an inert liquid to flush the seal faces appears very desirable. The sampling ports should have catch basins for purge collection and should be equipped with a water wash of the purge. The collected purge should be returned to the absorber for secondary contact. Capped flasks should be used for sample collection and transport. Personal protective equipment should be available when this operation is performed. At some future time, an automatic purge and sampling device may be developed which would reduce the potential exposure of this operation still further.

10.3.4 Centrifugal Pumps

The use of double mechanical seal centrifugal pumps with inert liquids to seal and flush the faces is recommended, even though they may cost more. Single mechanical seal pumps that use a formaldehyde solution from recycle to seal and flush the face, and the use of steam jackets to heat and prevent paraformaldehyde buildup are also acceptable practice.

10.3.5 Formaldehyde Storage and Loading

Formaldehyde storage tanks should be diked and grounded. Water scrubbers should be installed on the breathing ports of the tanks. In order to minimize the exposure of maintenance workers during the repair and formaldehyde storage tank heating systems, it is recommended that the heaters be installed externally (with recycle used to heat the fluid) or internally in an easily-removable configuration (such as the fastening of steam coils on a manhole cover). External level gauges are definitely preferred. Surfaces around storage and loading areas should be sealed with impervious material to assist in the cleanup of any formaldehyde spills.

The use of a closed dome system on the tank trucks or rail cars while loading formaldehyde solution is recommended. A passive system involving a passage of the displaced gases through a water scrubber for formaldehyde condensation recovery is an effective way to control emissions. An active vent system where the vapors are pulled through such a scrubber might be preferable. Automatic filling control is definitely preferred, as is quick-connect ductwork to minimize the amount of time operators spend in making connections to the receiving tank. Personal protective equipment, including respirators, goggles, and gloves, must be available.

Sample analysis should be done in a laboratory hood with a face velocity of at least 100 feet per minute. Provisions should be made for the discharge of waste liquids to a drain inside of the hood so that they don't contaminate the control room in which the hood is located.

10.3.7 Maintenance

Effective lock out procedures and proper washdown procedures need to be established and used. Personal protective equipment including respirators, goggles, and gloves must be available for such operations.

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