PRELIMINARY PLANT VISIT
INDUSTRIAL HYGIENE REPORT

Formaldehyde Production Facility
E. I. DuPont de Nemours & Company
Grasselli Plant
Linden, New Jersey 07036

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PREPARED FOR:
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Cincinnati, Ohio 45268

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1. BACKGROUND

The National Institute for Occupational Safety and Health (NIOSH) and the U.S. Environmental Protection Agency (EPA) have entered into an interagency agreement to perform a study that will determine the levels of pollutants to which workers in the formaldehyde production industry are exposed and that will evaluate the effectiveness of control technologies currently used to minimize exposures. A similar study of the semiconductor industry is being conducted simultaneously. The findings of both studies will be presented as reports summarizing the results of these assessment.

EPA has 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 is being assisted in the study by personnel from GEOMET Technologies, Inc. (GTI).

The study of the formaldehyde industry is being directed toward a cross-section of production facilities. Of principal importance are 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 will examine all agents associated with formaldehyde production processes. Process agents of concern and the workforce exposed to such agents will be identified, concentrations evaluated, and the operations and process parameters of the worksite will be characterized.

A limited number of volunteers will be selected from the workers at a few selected sites for the determination of total (24-hour) exposure to air contaminants, including those found in the workplace, in-transit, and in residence. This portion of the study will be designed in such a way that it can be used to estimate the total average daily exposures of worker populations to air contaminants. These contaminants will be measured by personal and/or area monitors and will include those contaminants found in the workplace as well as others commonly found in the ambient and residential environments.

The focus of the workplace control technology study will be the assessment of control technology currently in use or available for minimizing worker exposure to harmful chemical or physical agents. The assessment will include examination of processes and process equipment. Control effectiveness will be 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. The costs of controls versus their effectiveness will also be examined.

The following sections briefly describe the objectives of the two segments of this project: the industrial hygiene/control technology assessment segment includes two phases, a preliminary walk-through survey (the subject of this report) and a detailed survey. The 24-hour exposure profile segment, is designed to study the exposures of formaldehyde production workers and office workers in the workplace, the residence, and the in-transit environments.

1.1 OBJECTIVES OF THE INDUSTRIAL HYGIENE/CONTROL TECHNOLOGY ASSESSMENT (IH/CTA) STUDY SEGMENT

The objectives of the IH/CTA segment are to:

- identify potential hazards to workers,
- evaluate the effects of these potential hazards on workers,
- evaluate the effectiveness of industrial hygiene control programs to control these potential hazards,

- assess current formaldehyde production technology with respect to control of potential exposures of workers,
- identify the best available means to control emissions and potential exposures,
- evaluate the state-of-the-art of control technology in the formaldehyde production industry,
- assist the transfer of control technology inter- and intra-industry, and
- 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.

This segment is divided into two phases, preliminary surveys and detailed surveys. Objectives of these phases are presented below.

1.1.1 Objectives of the Preliminary Industrial Hygiene/Control Technology Survey Phase

The objectives of the preliminary surveys are to:

- identify potential exposures to hazardous agents in formaldehyde processes and operations,
- identify control technology currently used by the formaldehyde industry to eliminate or control potential exposures,
- prepare a series of preliminary plant visit reports detailing findings from the first two objectives, and
- select 4-5 candidate plants from the original 12 plants for later detailed surveys, based upon the findings from the first two objectives.

1.1.2 Objectives of The Detailed Industrial Hygiene/Control Technology Survey Phase

Detailed plant visits comprise the second phase of the study. The objectives of these visits are to:

- observe operator work practices,
- conduct quantitative personal sampling,
- evaluate engineering control techniques used by the industry to reduce exposures, and
- prepare a series of detailed plant visit reports, detailing worker practices and evaluating the engineering controls used by the plant.

This part of the IH/CTA segment will be coordinated with the 24-hr exposure profile at four selected plants.

1.2 OBJECTIVES OF THE 24-HOUR EXPOSURE PROFILE SEGMENT

The objectives of the 24-hour exposure profile segment are to:

- determine the exposure of selected formaldehyde production and office workers to five selected pollutants on a 24-hour basis,
- evaluate these results and identify potential areas of concern due to high exposure, and
- determine the need for further indoor air studies.

1.3 SUMMARY OF ACTIVITY

The plant visit team met the plant personnel and held an extended conference during which the process, operations, and control technology described in this report were discussed. The group then walked through the plant operation following the process flow and discussing various aspects of the operation. Information from the walkthrough survey was then further discussed. Union and employee representatives were then introduced, the management personnel departed, and the project objectives and preliminary findings were discussed. A final closing conference was then held with management.

Prior to the plant visit, the OSHA area office had been contacted. Mr. Palmieri indicated that no industrial hygiene inspections of the formaldehyde unit had been carried out. Safety inspections had not indicated any problems with this unit.

1.4 PEOPLE CONTACTED

The plant visit described in this report was carried out by John Pate (GTI), Kathleen Rabbitt (MRC), and William McKinnery (NIOSH) on July 30, 1981. Personnel contacted in connection with the visit included:

Plant Personnel

R. H. Akins, Plant Manager
H. W. McDowell, Environmental Coordinator
Pat Gilby, Environmental Associate, Wilmington
Donald R. Carr, Senior Supervisor of Health & Environmental Control
James R. Koterski, Production Superintendent
P. J. Costello, Senior Supervisor of Production

Union and Employee Representatives

Thomas Stefanick, Union President (Mechanic/Instrument Mechanic)
John Williams, Union Vice-President (Mechanic/Electrician)
Jimmy Barber, Production (not formaldehyde)

OSHA Area Office

Richard Palmieri, Area Director

2. DESCRIPTION OF PLANT

The Grasselli plant is a 210-acre area in a heavily industrialized section of Union County, in Linden, New Jersey. Formaldehyde production takes place in a unit separated (more than 50 feet) from other operating units of the plant. This unit consists of the formaldehyde production section and a contact sulfuric acid production section. These two sections are separated by a road (Figure 1).

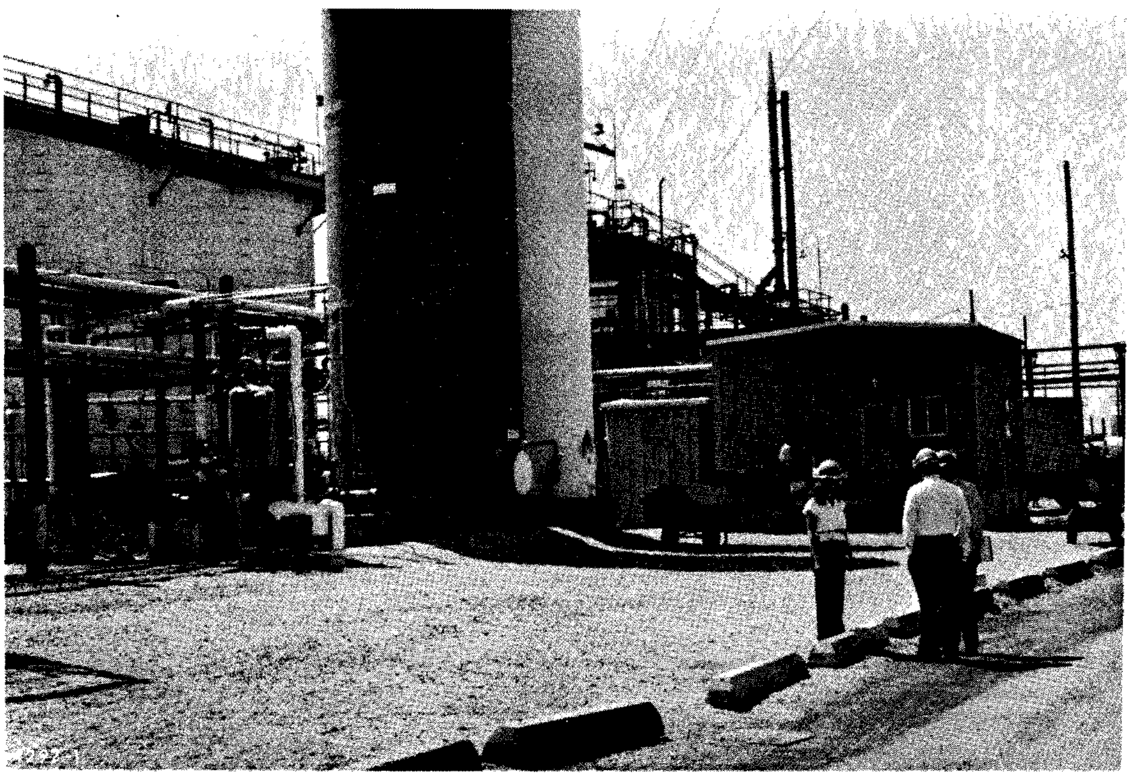

Figure 1. Road separating formaldehyde (on left) and sulfuric acid units. Formaldehyde storage and blending area.

The formaldehyde unit produces four grades of formaldehyde (aqueous solutions). Two grades are low methanol content, and the other two grades are U.S.P. grade (higher methanol content). The plant has a rated capacity of 160 million pounds per year (on a 37 percent basis).

The production facility is a tri-level, open-air chemical complex. The unit was started in 1971 and operates as a continuous process 24 hours a day, 7 days a week.

The workforce covers two production areas (formaldehyde and sulfuric acid) consists of seventeen employees: two supervisors, five chief operators, four formaldehyde operators, five service operators, and one shipper. The chief operators also work the sulfuric acid plant, only an estimated 30 percent of their time being devoted to the formaldehyde operation. They are licensed boiler operators and spend the major portion of their time in the control room.

The formaldehyde operators' duties include turning valves and other general operational duties as well as loading tank trucks. The service operators are involved in miscellaneous service work and clean-up. Service operators spend most of their time on duties with the sulfuric acid plant.

Formaldehyde operators devote 100 percent of their time, and service operators about 20 percent, to formaldehyde production. In addition, the area has a shipper who is a clerk with minimal field (outside) responsibility in formaldehyde. The shipper, as the service operator, is shared with the sulfuric acid plant.

The maintenance group consists of a supervisor and 8 to 10 persons. They cover a large area and are estimated to spend no more than 20 percent of their time in the formaldehyde area.

3. PROCESS DESCRIPTION

Formaldehyde is made in this plant by a combination oxidation-dehydrogenation process, using silver oxide as a catalyst:

$$CH_3OH + \tfrac{1}{2}O_2 \text{ (air)} \xrightarrow{\text{catalyst}} CH_2O + H_2O$$
$$CH_3OH \longrightarrow CH_2O + H_2$$

Figure 2 is a block flow diagram of the process used in this plant. As shown in the figure and the equations above, methanol and air are the raw materials for the process. Air is brought in with a positive displacement blower and passes through a scrubber, which conditions and cleans the air prior to entering the reactor.

Methanol is brought from off-site in tank trucks (Figure 3) and stored onsite in a tank. It is piped into the vaporizer, mixed with air and enters the reactor (Figure 4). The preheated mixture is not in the explosive limit envelope for methanol-air mixtures.

The temperature of the reaction is controlled to optimize yields. Since the oxidation reaction is exothermic, waste heat is recovered as shown in the block diagram. The reactor system contains the silver catalyst. The product gas contains a considerable amount of hydrogen and unreacted methanol.

The product gases are passed directly to a series of countercurrent scrubbers that comprise the absorber. This cools the gases and dissolves the formaldehyde in water (Figure 5).

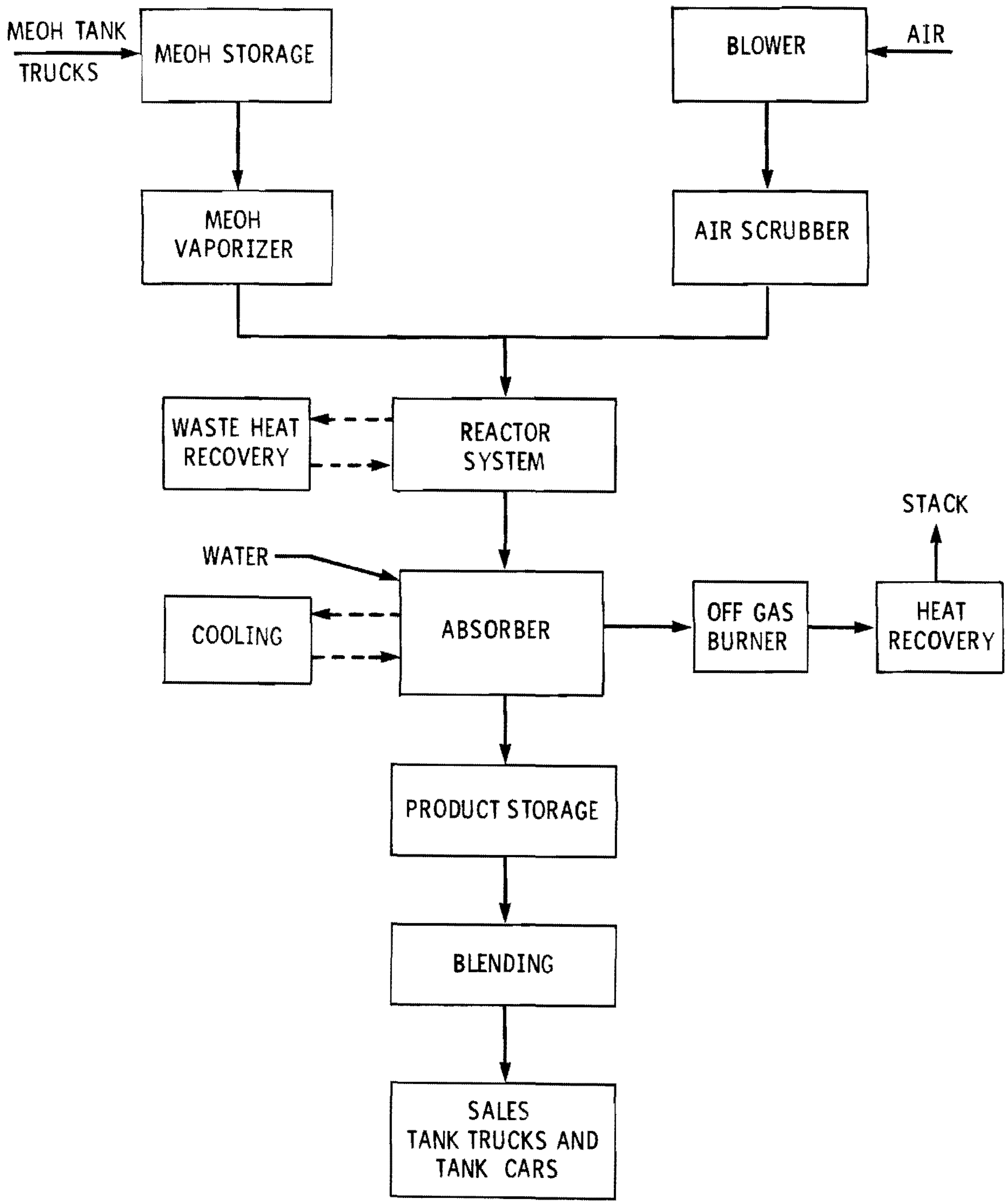

Figure 2. Formaldehyde process - block flow diagram.

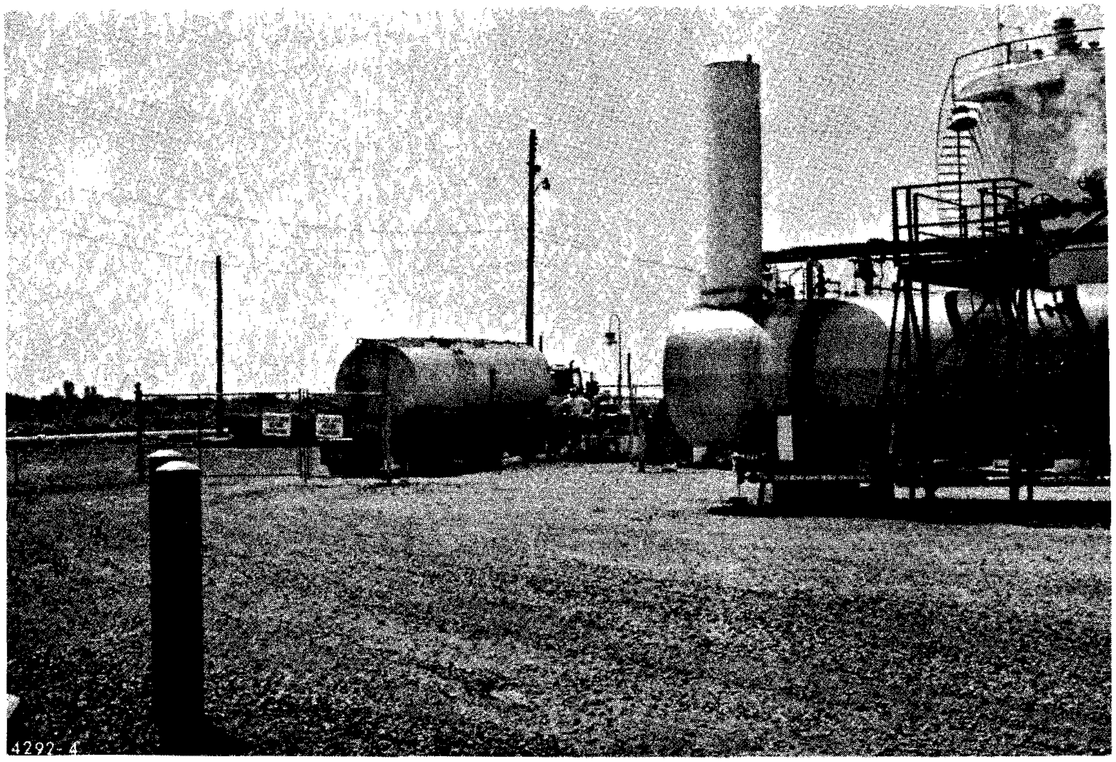

Figure 3. Methanol unloading area.

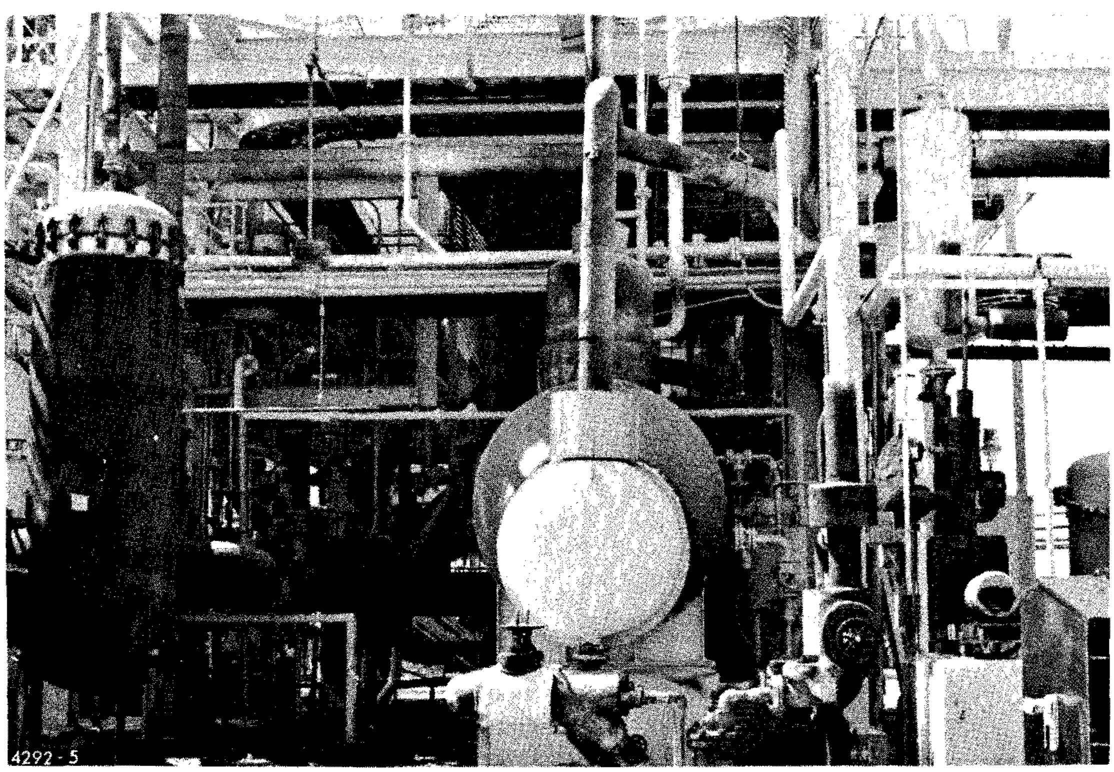

Figure 4. West end of reactor.

Figure 5. Absorber tower.

The off-gas from the absorber contains hydrogen and nitrogen with traces of formaldehyde and methanol. This is burned and the heat recovered (Figures 6 and 7) and used in the process (vaporizer). The effluent gas from the burner is primarily nitrogen, water vapor, and carbon dioxide. The burner is designed to give a 99 percent combustion efficiency.

The product stream from the absorber is an aqueous solution of formaldehyde (up to 50 percent, as desired). It also contains some methanol and formic acid.

Products of varying strength are blended to create products required for specific sales. The blended products are loaded into tank trucks (95 percent) (Figures 8 and 9) or railroad tank cars (5 percent).

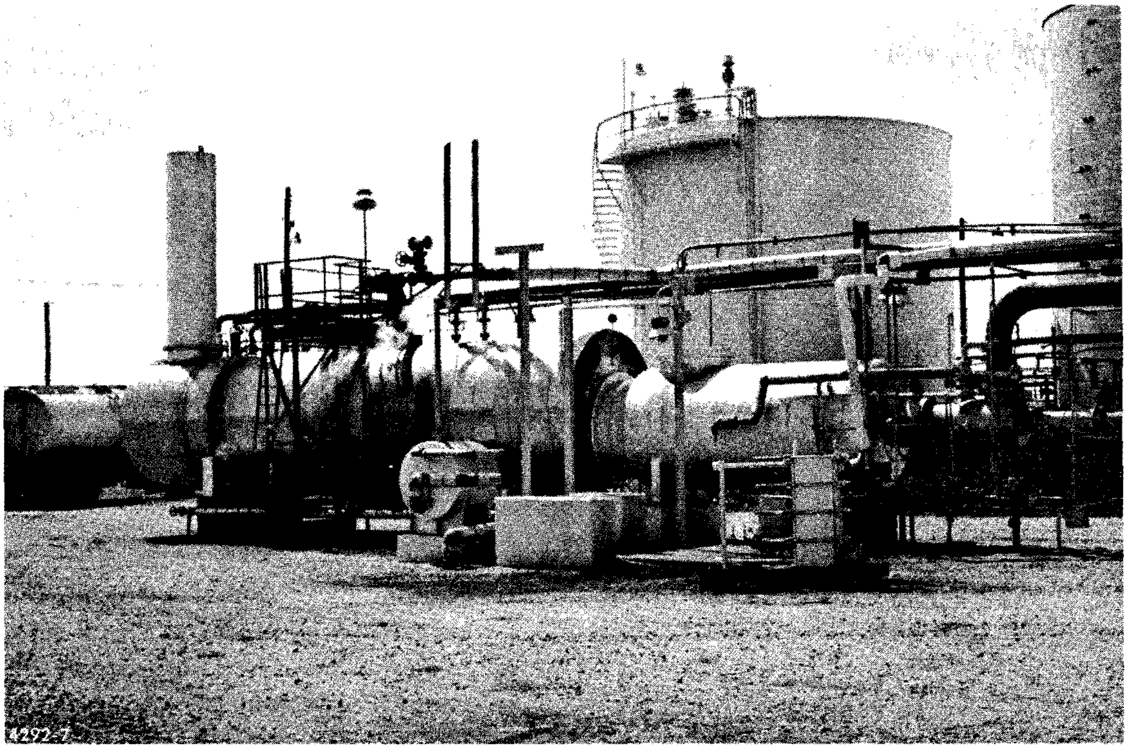

Figure 6. Incinerator for waste gas.

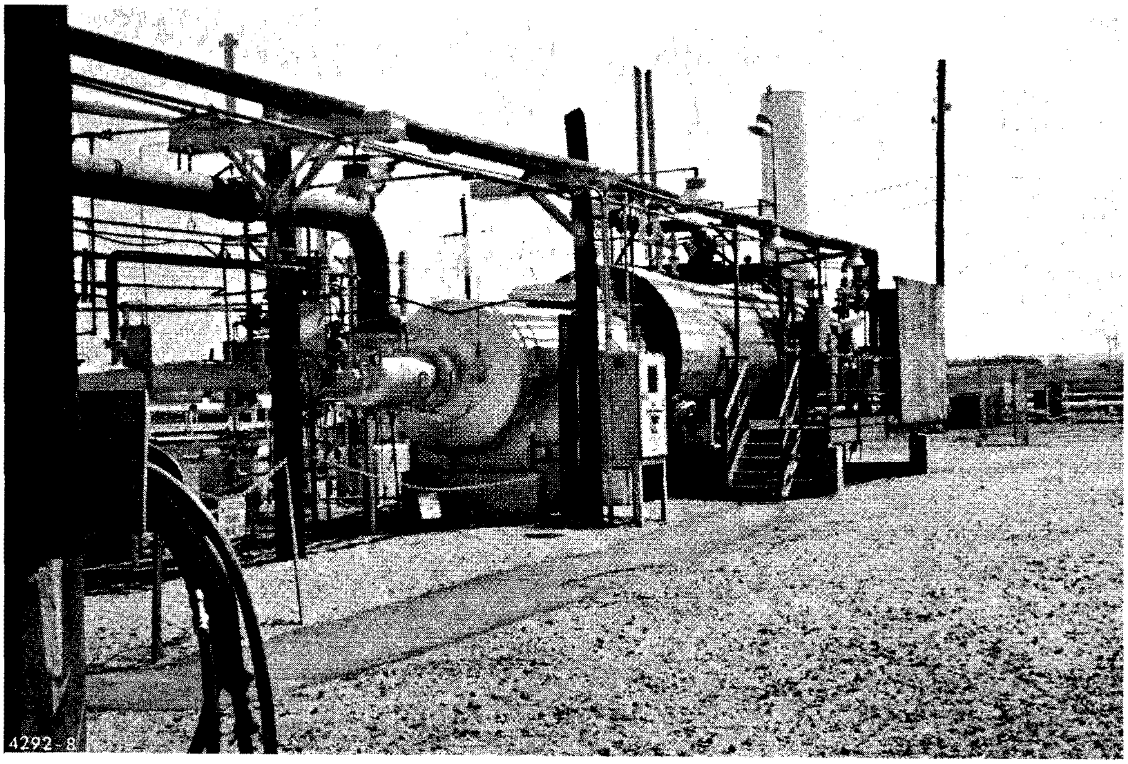

Figure 7. Incinerator for waste gas.

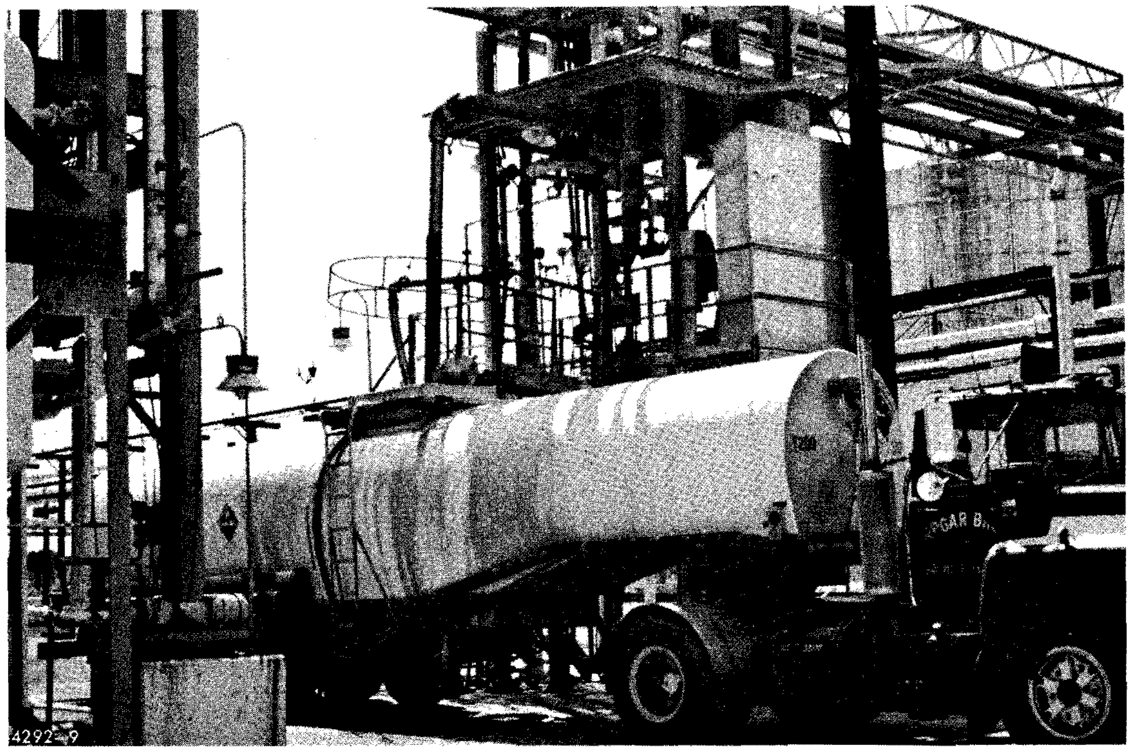

Figure 8. Truck loading area.

Figure 9. Truck loading area.

4. DESCRIPTION OF PROGRAMS

4.1 INDUSTRIAL HYGIENE

The environmental coordinator at the plant is responsible for safety, industrial hygiene, and environmental concerns. In addition to the corporate industrial hygiene group and external consulting groups which may be used as resources, the laboratory supervisors and chemists carry out monitoring as recommended by the coordinator.

An occupational safety and health committee consisting of supervisors and health personnel serves for review, coordination, and program development functions. Information is reviewed and passed along to the site employees. Supervisors must document that such information has been reviewed by them.

The independent union which represents the employees has no formal safety and health committee, but maintains an active interest in safety and health questions. For example, recent information on formaldehyde provided by the occupational safety and health committee was reviewed by the union.

Contingency plans for emergencies are well-defined. The nearest fire station is within several blocks, and the plant is a member of the Linden Industrial Mutual Aid Council (LIMAC) which provides for mobilization of private sector assistance in the case of fire, explosion or other emergencies.

Safety precautions have been and continue to be integrated into the operating procedures covering each phase of operation in the plant.

Formal "lockout" procedures (isolation of personnel from danger) are used for any operation which involves "breaking" a line or using a "fire" (welding, torching, etc.).

Safety equipment (showers, eyewashes, protective clothing, self-contained breathing apparatus, fire extinguishers and blankets, and first aid kits) are located at numerous points in the plant, and are well marked (Figures 10 and 11).

4.2 OCCUPATIONAL SAFETY AND HEALTH (OSH) TRAINING

A formal employee training program is required for new employees. OSH training is incorporated in the on-the-job training provided by the supervisors and operators for new employees or employees assuming new duties. Safety retraining is scheduled every 2 years and includes fire protection and first aid.

Spill control procedures are provided for each chemical found in the plant. Training in these include use of the appropriate and specified personal protective equipment and handling procedures.

Job-cycle checks are performed every 2 years. In these, elements of a specific aspect of the job are reviewed with the employee (e.g., tank car loading). Thus, the formaldehyde operator's job will include about 20 separate job cycles to be reviewed.

Use of respirators is an element of the training program. If operators' duties may require use of negative-pressure respirators, they are retrained once a year.

4.3 PERSONAL PROTECTIVE EQUIPMENT (PPE)

Training in use of respirators is an integral part of the overall training program. The safety department is responsible for cleaning and maintenance of the respirators. All full-face respirator users are fit-tested (qualitative) once a year.

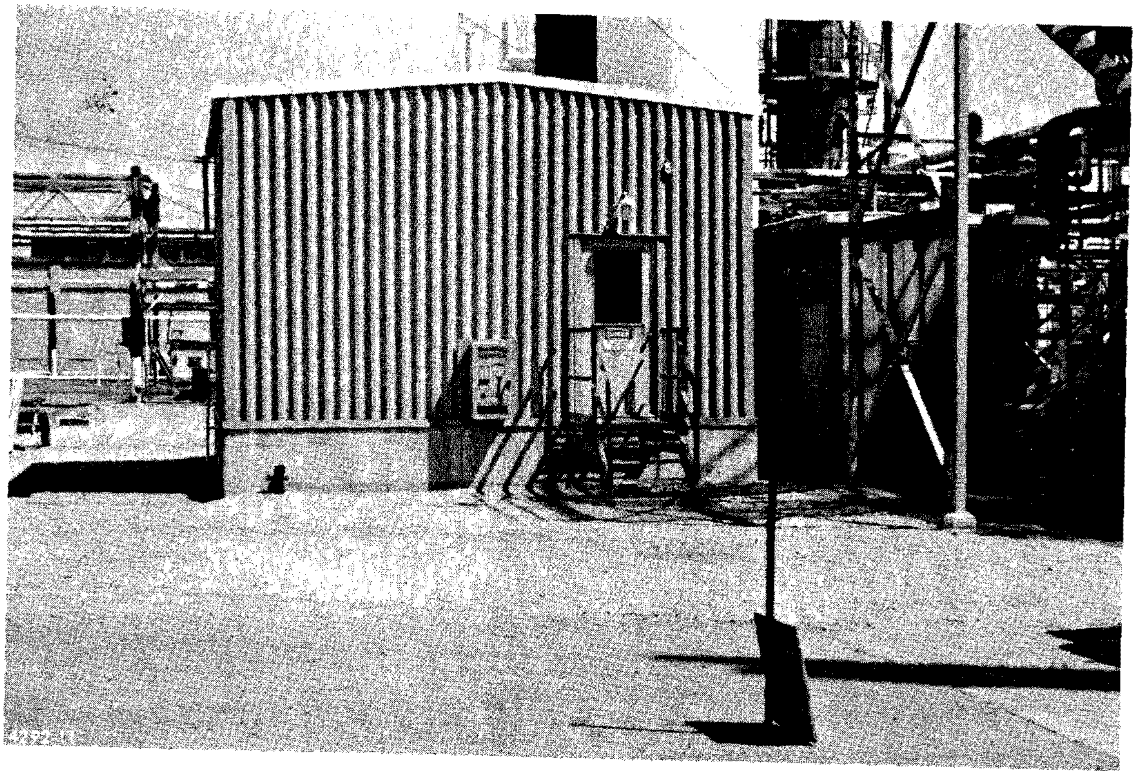

Figure 10. Self-contained breathing apparatus on control room.

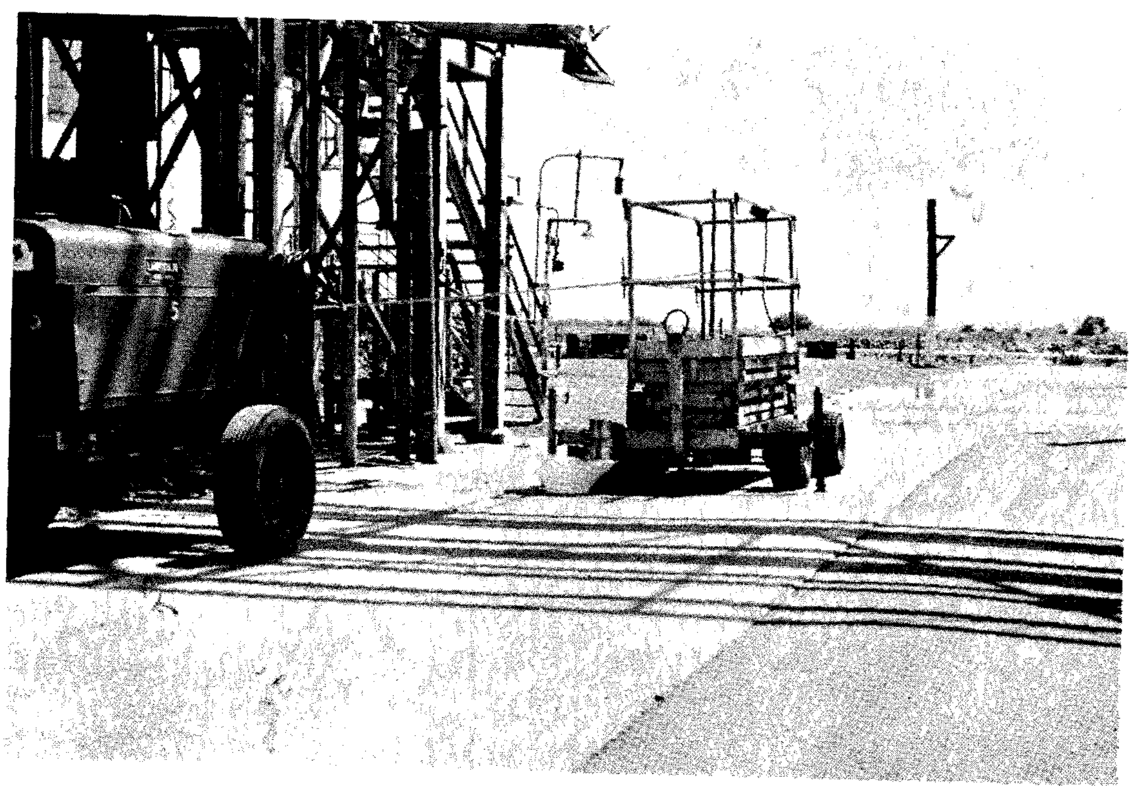

Figure 11. Eyewash and shower station.

Specific PPE is required as follows:

<u>All formaldehyde operations</u>

Hard hats and side-shield safety glasses

<u>Startup operations</u>

Full-face respirators

<u>Loading operations</u>

Rubber gloves
Coverall goggles
Full-face respirator during hookup

<u>Opening blocked piping</u>

Supplied air mask

<u>Operating overhead valves</u>

Overall goggles

4.4 MEDICAL PROGRAM

An occupational physician is available at the plant site four afternoons per week. A full-time registered nurse is employed onsite and is on call.

No compensation claims or work-related illness or dermatitis have been reported from this unit.

5. SAMPLE DATA

An active monitoring program for workplace pollutants has been carried out and is continuing in conjunction with engineering controls which are being developed (see Section 6). The results of the sampling for formaldehyde are shown in Table 1. The method used for these samples was the NIOSH method involving collection on silica gel, desorption with water, and analysis with chromotropic acid. Currently, samples are collected using two impingers in series.

TABLE 1. FORMALDEHYDE SAMPLING RESULTS

Job assignment/area	Sample type	Exposure concentration range, ppm[a]	Comments
Loader	Personal - 8 hr TWA	0.02 - 1.02	Loading HCHO by tank truck
HCHO operator	Personal - 8 hr TWA	0.12 - 0.50	Routine operation
Shipper	Personal - 8 hr TWA	0.01 - 0.06	Most time spent in shipping office
Chief operator	Personal - 8 hr TWA	0.01 - 0.13	Most time spent in control room
HCHO operator	15 min TWA	0.05 - 0.68	Highest result while loading tank truck
Chief operator	15 min TWA	None found	Control room
HCHO operator-start up	15 min TWA	4.1 - 22.4	All samples taken while operator making adjustments to process
Start up	Area sample - 4 hr TWA	0.32	10 ft downwind of primary reactor (4 hours)
Start up	Area sample - 3 hr TWA	0.89	6-10 ft west of interstage filter-ground level (3 hours)
Tank truck loading	Area sample - 5 hr TWA	0.71	Downwind of loading rack (5 hours)
Sump	Area sample - 5 hr TWA	0.56	Downwind of sump (5 hours)

[a]DuPont has adopted a 1 ppm (8 hr time weighted average) and a 2 ppm ceiling as acceptable exposure limits (AEL) for formaldehyde.

6. CONTROL STRATEGIES FOR INDIVIDUAL OPERATIONS

The operations identified as providing potential exposures to hazardous materials are discussed below with respect to applicable control technology.

In most of the operations described, some potential exists for spillage of formaldehyde (or methanol). The appropriate "spill control procedure" for the material is incorporated as a referenced part of the appropriate operating procedure.

6.1 STARTUP

As shown in Table 1, the highest short-term exposures for operators occur during startup. Malfunctions, power outages, line blocks, and process modification may cause shutdown with an ensuing startup, although the unit is designed for continuous operation.

A project is currently underway to design engineering controls (vent-scrubber system) to collect and scrub the vapors which escape while operators are making adjustments to the process.

During the interim period, potential exposures are controlled by requiring the appropriate operating procedures to be rigorously followed, which includes wearing full-face respirators during startup and adjustment operations. Monitoring (personal sampling) is carried out during startup operations.

6.2 MAINTENANCE

Leaking valves, joints, and pumps were not specific problem areas. Depending on the maintenance operation, lockout procedures and full protective equipment including supplied air respirators may be required. This is specifically required when opening piping blocked by paraformaldehyde.

6.3 METHANOL UNLOADING

Specific operating procedures, which incorporate safety precautions, use of personal protective equipment, and other control measures, are relied upon to minimize exposures. Potential exposures are related to those discussed for loading products (Section 6.6) except that the comparatively high vapor pressure of methanol (compared to the partial pressure of formaldehyde over aqueous solutions) contravenes the safety factor of the considerably higher potential exposure level of methanol.

6.4 OPERATIONS

Exposures during normal operations are minimal as shown by the ranges of concentrations for normal operation in Table 1. Only in the case of the formaldehyde operator during the startup procedure were any relatively high exposures measured.

The absence of exposures during normal operations is inherent in the nature of formaldehyde production, not of specific control technology. The process is a typical, continuous, closed, chemical system. Operators are not required to spend considerable time at the system itself, and if the integrity of the closed system is maintained, resulting exposures will be minimal. The highly automated operation further ensures that the chief operator's work station is the control room, which is not an area with any appreciable exposure potential.

6.5 PROCESS SAMPLING AND ANALYSIS

Samples are collected in glass containers by opening sample valves (spigots) located strategically throughout the unit. The samples are then carried to the control laboratory (a small building within the unit) and analyzed.

A laboratory hood was recently added to the control laboratory. Samples are stored and analyzed in this hood. When the analysis is completed, samples are grouped outside the hood while awaiting disposal (sample containers are closed).

6.6 LOADING PRODUCT

Tank trucks are pulled into the loading area, the dome opened, the delivery boom inserted, and the appropriate amount of product loaded. As shown in Table 1, the loader can receive an appreciable exposure if he is not wearing his respirator.

The loading area and delivery arm have a vapor collector and exhaust ventilation to minimize exposure. A new system, a variation of the truck-loading arm, is in the final stages of installation. This includes cover pods.

Finally, operating and spill control precautions are in effect. In part, these require rubber gloves, coverall goggles during loading operations, and full-face respirators during hookup.

6.7 PROCESS WASTE

All liquid process waste (primarily water with some methanol, formaldehyde and ammonia) is brought by pipe to a waste sump from which it is transferred to a storage tank.

Area samples immediately downwind of the sump show low ambient levels of formaldehyde. Since this is not a work station, only occasional exposures to maintenance workers and transients can occur.

6.8 TANK ENTRY

Cleaning and repair of tanks can require tank entry on infrequent occasions. Operating procedures prescribe a rigid tank entry protocol to be followed, including testing, clearing, ventilation, and use of supplied-air respiratory equipment.

7. CONCLUSIONS

The plant shows awareness and support by management of an effective hazard control program. The program is implemented by using engineering and operating controls to eliminate unacceptable exposures, and using work practices to minimize exposures already ordinarily below existing standards. Engineering controls include use of a closed-piped process and a layer of oil over the waste sump which appears to be effective in minimizing fugitive emissions of methanol and formaldehyde. Monitoring is used to validate effectiveness of control measures. The plant is responsive to current additional hazard information. Several additional engineering controls are being installed to further decrease workers' exposures.

Until several plants have been visited, suitability of this DuPont plant as a candidate plant for an extended visit cannot be determined. However, this plant would provide specific information on these aspects:

- Potential exposures in loading product in rail and truck tank cars, with examples of up-to-date engineering control,
- Methanol unloading,
- Process sampling and analysis.

The plant personnel specifically mentioned that the absence of standardization of truck domes was hindering their efforts to provide control devices for the loading operations.

Leaks from valves and joints are currently not a problem. The plant was very clean and well-maintained, with very little evidence of any leaks of formaldehyde (no paraformaldehyde buildups). Any odors of formaldehyde were faint and concentrations in the ambient air were not sufficiently high to be detected using Dräger tube samplers. No samples were taken.