FINAL REPORT

MERCURY CONTROL TECHNOLOGY ASSESSMENT STUDY

Cosan Chemical Corporation Carlstadt, New Jersey

Preliminary and Indepth Survey Report for the Site Visits of July 16, 1981 and June 16-17, 1982

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DISCLAIMER

Mention of company name or product in this report does not constitute endorsement by the National Institute for Occupational Safety and Health.

FOREWORD

A Control Technology Assessment (CTA) team consisting of members of the Dynamac Corporation Enviro Control Division met with representatives of the Cosan Chemical Corporation in Carlstadt, New Jersey on July 16, 1981, to gather preliminary information and June 16-17, 1982, to conduct an indepth survey on the techniques used to control worker exposure to mercury. Participants in the survey were:

Dynamac Corporation

Donato Telesca, Program Manager David D'Orlando, Engineer Robert Reisdorf, Industrial Hygienist Andrew Reyburn, Industrial Hygienist

Cosan Chemical Corporation

Albert Eilander, Vice President of Research and Development Stuart Cooper, Manager of Production

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The indepth CTA was completed in two days. The study included a process tour, review of mercury controls. The local exhaust ventilation units were studied in detail.

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INTRODUCTION

CONTRACT BACKGROUND

The Mercury Control Technology Assessment Study has been initiated to assess the current technology used to protect the worker from exposure to mercury. The objective is to identify and evaluate the methods employed by industries in controlling worker exposure to elemental mercury and mercury compounds. A result of the study will be the publication of a comprehensive document describing the most effective means of controlling emissions and exposures. This report will be available to companies that handle mercury in order to transfer technology within the major mercury using industries. The study will also determine where additional research is necessary.

JUSTIFICATION FOR SURVEY

Cosan Chemical Corporation was selected for an indepth survey in order to study the local exhaust ventilation units used in controlling mercury vapor concentrations in the work areas.

SUMMARY OF INFORMATION OBTAINED

An opening meeting was held during which the objectives of the survey were discussed. Information on the work place air monitoring, biological monitoring, work practices, engineering controls, and personal protective equipment used at the facility was obtained. Area and personal sampling for mercury vapor and particulate was conducted. Ventilation measurements were made on the local exhaust ventilation units.

PLANT DESCRIPTION

The Cosan Chemical Corporation manufactures additives for the paint and coatings industry and catalysts for the plastics industry. The paint additives are fungicides and bactericides which contain phenyl mercuric acetate (PMA). Cosan has manufactured these products for 17 years, 9 of which have been at the Carlstadt plant. The Cosan facility consists of an excutive office building, an engineering research and development building, and two production plants. One of the plants (Building #5, PMA plant) houses all the operations involving mercury (Figure 1). Building #5 covers approximately one-third of an acre and is constructed of block wall with a wood roof. The interior of the plant has been continuously renovated section by section to accomodate new process equipment and mercury controls.

Cosan employs a total of 50 people, 14 of whom work in the PMA plant.

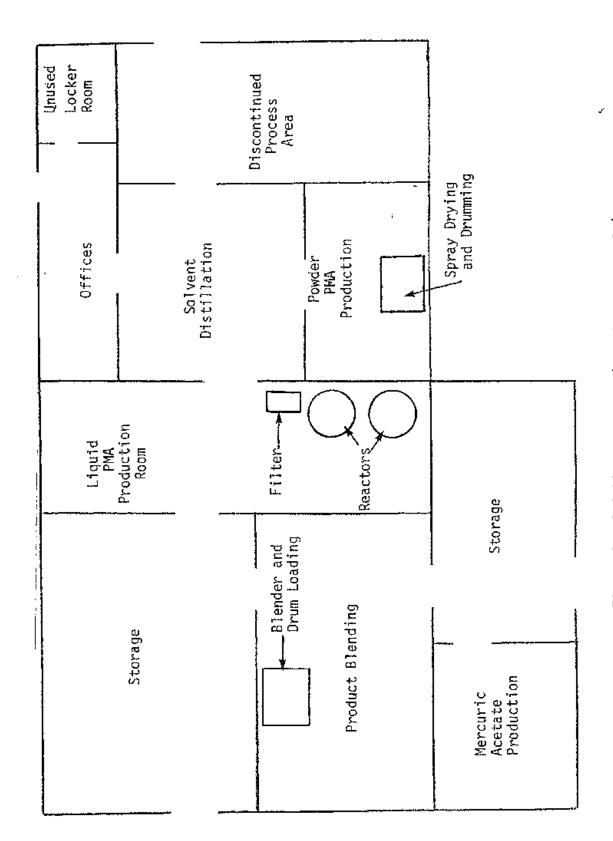


Figure 1. PMA Plant Layout (not drawn to scale)

PROCESS DESCRIPTION (Figure 2)

Phenyl mercuric acetate is produced by reacting mercuric oxide or mercuric acetate with benzene and acetic acid at reflux. Solvents in the resulting product are stripped leaving a slurry of PMA. This slurry can be used to make either a liquid or powder form of PMA.

RAW MATERIAL PROCUREMENT

Mercuric oxide for use in PMA production is purchased from an outside vendor in 50-pound plastic bag-lined cardboard drums.

MERCURIC ACETATE PRODUCTION

Mercuric acetate is manufactured on-site. Elemental mercury purchased from Placer-Amex is transported in 2,200 pound super flasks by fork truck to the mercury addition area. It is drawn out of the flask by a vacuum pump and into storage tanks. From the storage tank it is pumped to a head tank located above a 1,500 gallon stainless steel reactor. The reactor is charged with mercury by opening a valve. Mercuric acetate is produced in this reactor through a proprietary process, and is pumped to storage tanks.

PMA PRODUCTION

PMA is produced at Cosan in 2,000 gallon glass lined reactors. Mercuric acetate is pumped from storage tanks to the reactors where it is combined with benzene and acetic acid, and refluxed at 176 F (80 C) to form the phenyl compound. Additional benzene and acetic acid are added to the reactor as needed.

If mercuric oxide is to be used instead of mercuric acetate, it is added to the reactors manually by emptying fifty pound bags into a manhole through a specially designed exhaust hood.

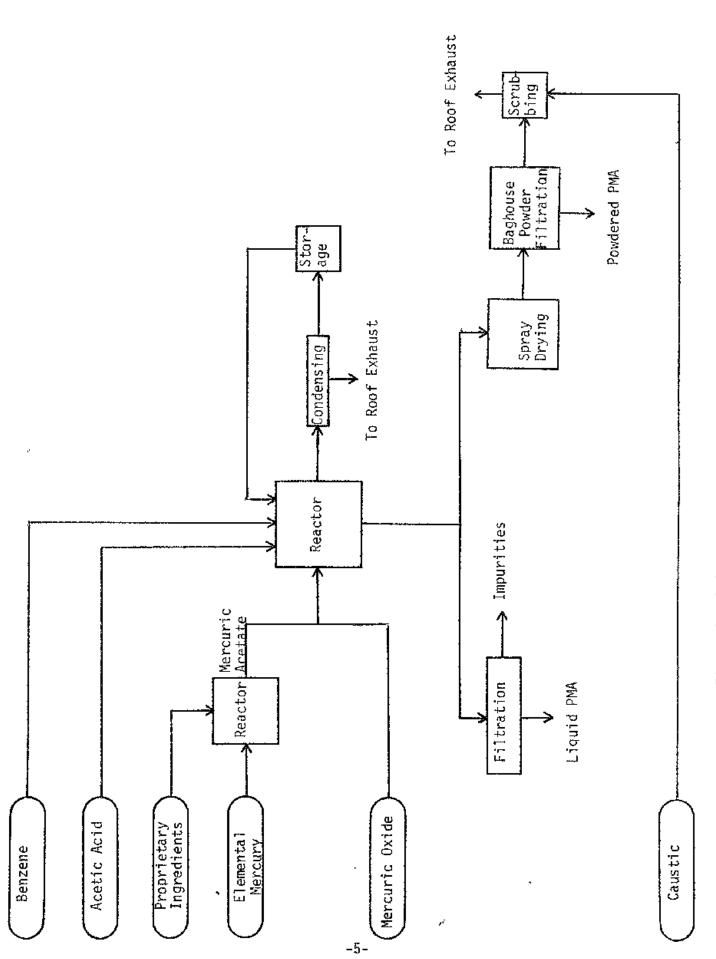


Figure 2. PMA Manufacturing Process Flow Diagram

The excess solvents, stripped from the product in the reactor, are condensed, and pumped to storage tanks for use in subsequent batches.

The resulting PMA slurry is further refined into either a powder or a liquid.

PRODUCT REFINEMENT

Powder.

Relatively pure PMA powder is produced by spray drying the PMA slurry. Dried powder from the spray drier is separated from the airflow in a 36 bag Mikro Pul Model 36S-8-30 baghouse. Air and powder are blown through six sets of six 16-ounce NOMEX fabric bags. The bags have wire mesh cages inside of them to keep them from collapsing. A Pulsair unit in the baghouse blows the powder down from the bags. An automatic timed knocker is used to shake the powder down to the bottom of the baghouse into a rotary valve. The rotary valve turns continuously releasing the PMA powder through a drop chute into a drum below. Airflow from the baghouse passes through a caustic scrubber which controls acetic acid emissions and prevents accidental release of PMA into the air stream in the event of bag breakthrough.

Liquid

Liquid is manufactured by mixing the PMA with low molecular weight glycol and adding ammonia to raise the pH to 8. The resulting liquid is an ammonium complex containing approximately 30% PMA, 20% alcohol, 25% ammonium acetate, and 25% water. Impurities which may contain mercury are removed from the liquid in a ventilated filter press and the product is stored in 55-gallon drums.

DILUTE PRODUCT BLENDING

A fine textured, more dilute form of PMA powder is also produced at Cosan. This product is manufactured by blending powdered PMA with calcium silicate to form a powder containing approximately 20% PMA. This is used as a

biocidalingredient in wall board sealing compounds. The blending is done in a Patterson-Kelly V blender which has a disc-type distributor and an intensifier bar which prevents the formation of clumps. Each ingredient is added to the blender by a closed system. The calcium silicate is drawn into the blender by a vacuum system. PMA is added to the blender from a head tank located above.

MERCURY CONTROL STRATEGY

ENGINEERING CONTROLS

Mercury Enclosed Transfer System

Elemental mercury used to produce mercuric acetate is transfered under vacuum from the one-ton mercury flask to a mercury storage tank. A schematic drawing of this system is presented in Figure 3. Mercury is first drawn into a tank where it is washed with water. It is then drawn off of the bottom of the wash tank and flows into the storage tank. The vacuum line from the storage tank leads to a Busch R5-series single stage rotary vane vacuum pump powered by a 3-housepower motor. The pump has a free air displacement of 20 cubic feet per minute (cfm).

A Calgon Vent-sorb filter is used to remove mercury vapor from the discharge of the vacuum pump. It consists of activated charcoal filter media housed in a 55-gallon drum. Pump exhaust air enters the drum at the bottom and is exhausted from the top of the drum to the roof. The filter exhaust is monitored monthly using a Bacharach MV-2 mercury vapor detector to insure that breakthrough has not occurred.

Mercuric Oxide Charger Hood

When mercuric oxide is used to produce PMA, it is added to the reactor through an opening where a specially designed removable exhaust hood is situated (Figure 4). Dimensions of the hood components are illustrated in Figure 5. The hood is used in the following manner:

- the reactor manhole is opened, vacuum is applied to the reactor, and the hood is put in place over the opening.
- a flexible exhaust duct is connected to an opening on the top of the hood.

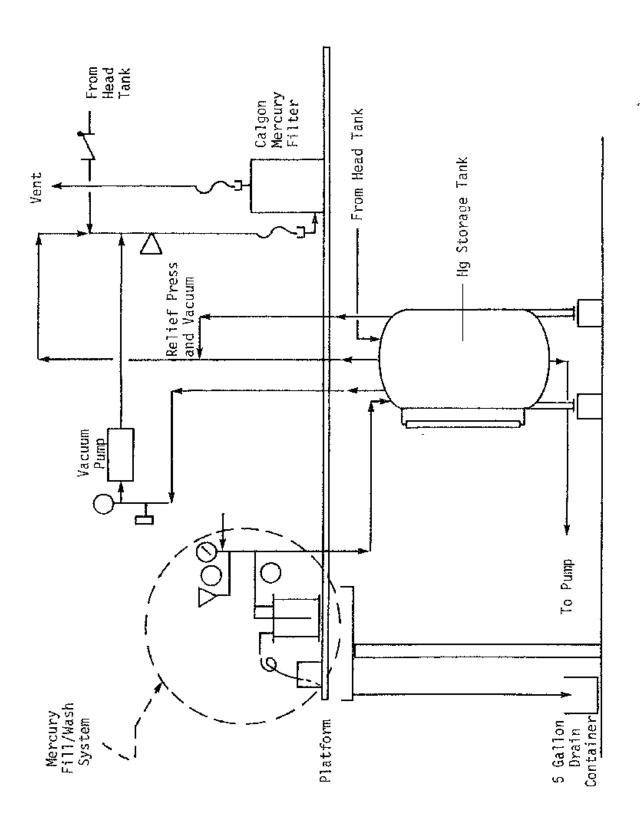


Figure 3. Mercury Transfer System

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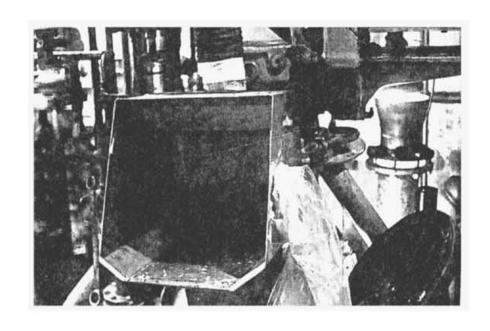


Figure 4. Mercuric Oxide Charger Hood

- 1. All 304 stainless steel/fiberglass
- Shelf must support repeated loading with 50 lb. weight (8 3/8" dia. X 7-1/4" high container)
 1-1/2" ring around elipse is to secure unit to reactor manhole

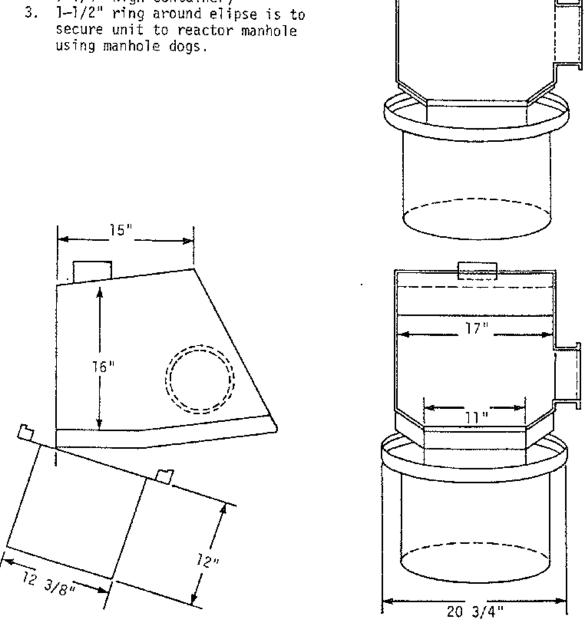


Figure 5. Mercuric Oxide Charger Hood Design Reference: Cosan Chemical Corporation Drawing

- a plastic refuse bag is connected to an opening on the side of the hood.
- the worker opens the plastic liner of the 50-pound mercuric oxide container and empties the bag into the manhole.
- the empty bag is put into the refuse bag on the side of the hood. The refuse bag is sealed and disposed of in a drum for hazardous waste.
- the exhaust duct is disconnected, the hood is removed from the opening, the reactor is vented, and the manhole is closed.

The exhaust hood is removable so that it can be used at any reactor being charged with mercuric oxide. The exhaust duct leads to a roof exhaust fan which draws approximately 210 cfm (measured). A HEPA filter is used to remove the particulate mercury from the exhaust air stream.

Seals and Gaskets

Teflon gaskets are used at flange connections. Single or double mechanical pump seals are used depending on the application. Double mechanical seals are used for hazardous process flows where it would be permissible for seal water to leak into the process streams.

Baghouse Powder Fill System

Powdered PMA is packaged in plastic lined drums underneath the rotary valve and delivery chute on the baghouse. The plastic liner is connected to the chute so that the powder will not disperse into the air while a drum is being filled.

Spray Dryer Scrubber

A Heil Model 722 venturi scrubber is used to remove acetic acid from the baghouse exhaust air stream. It is a caustic recirculation unit designed to maintain pH above 12. The scrubber acts as a secondary mercury control because it reduces PMA emission to the atmosphere in the event of a bag breakthrough. The scrubbing solution is checked on an hourly basis to

insure that PMA powder has not leaked through the baghouse. This is performed by a qualitative visual check for PMA powder on the surface of the scrubber reservoir. Airflow through the scrubber is vented to the roof.

Room Exhaust Fans

Table 1 shows the exhaust fans in the PMA production area.

TABLE 1
Description of Exhaust Fans in PMA Production Area

Location	Rated Capacity (CFM)	Description
Liquid PMA room	4890	roof & floor exhaust
Liquid PMA room	1390	roof & floor exhaust
Powdered PMA room	3390	roof & floor exhaust
Mercuric acetate room	6000	roof exhaust
Blending room	10000	wall exhaust

Drum Loading Exhaust Hood

Dilute PMA powder produced in the V-Blender is loaded in drums under a specially designed exhaust ventilation unit (Figure 6 and 7). The unit consists of a plastic dust hood (Figure 8) which is hydraulically lowered over the empty drum for filling. Three flexible exhaust air ducts are attached to the hood. Before loading the drum, a flexible chute is connected from the hood to the blender discharge. This helps to enclose the fill system and reduces powder dispersion. The exhaust air flow through the hood was measured to be 410 cfm.

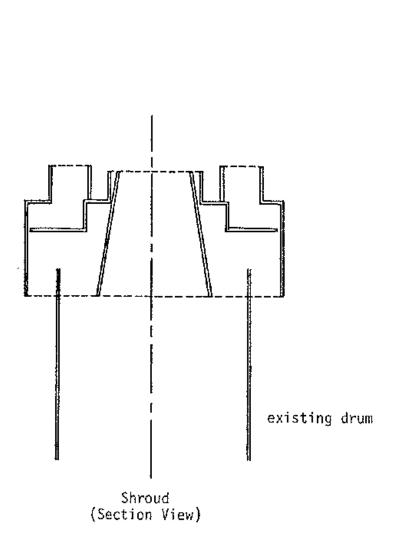
The exhaust air from the flexible ducts is drawn into a Mikero Pul baghouse. The filter bags are automatically shaken down periodically using a reverse compressed air pulse. The particulate from the baghouse falls through a



Figure 6. Drum Loading Dust Hood Showing Exhaust Air Ducts



Figure 7. Drum Loading Dust Hood Covering Chemical Drum



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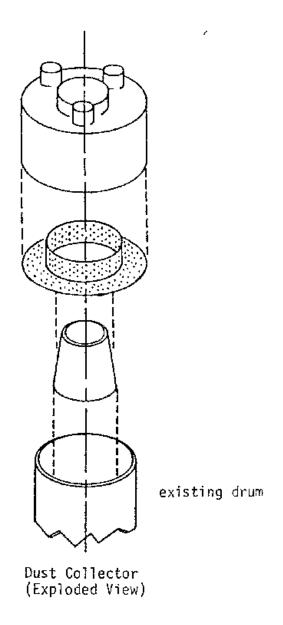


Figure 8. Schematic Drawing of Drum Loading Dust Hood Reference: Cosan Chemical Corporation Drawing # G-1-109

chute into a 55-gallon drum. When the drum is full, the material is put through the blender again. The vacuum used to draw calcium silicate into the blender is created using an air eductor connected to an outside wall fan. Particulate is removed from the vacuum air stream using a knock-out drum.

Filter Press Exhaust Hood

A 2-1/2 by 5 feet exhaust hood (Figure 9), balanced by a counter weight, is lowered over the filter press when liquid PMA is being filtered. The hood has a large baffle inside of it so that a 0.75-inch slot is maintained around the periphery of the hood to increase exhaust air velocity.

A 12 inch exhaust duct connects the hood to a roof exhaust fan. The measured flow of the exhaust air through the hood was 455 cfm.

PERSONAL PROTECTIVE EQUIPMENT

- Respirators (MSA Comfo II^R) are worn during certain operations where there is a high potential for exposure to mercury (either mercury vapor or particulate). These operations include PMA blending and cleaning filter presses. The respirators are equipped with a chemical cartridge designed to protect against mercury vapor (Mine Safety Appliances, MSA-Mersorb Indicator Cartridge #466204), and MSA type F dust filter approved for respiratory protection against dusts and mists.
- Supplied air respirators are worn when cleaning baghouses.
- Cloth uniforms and jackets are provided by the company. These are changed daily. Laundry service is provided by an outside company.
- Gloves (latex/nitrile) are used when handling mercury compounds. These are changed daily or more often if visibly contaminated.
- Disposable Tyvek^R coveralls are worn when exposure potential is high (e.g., cleaning baghouse).
- Work shoes are provided by the plant. They may not be worn home by the worker.

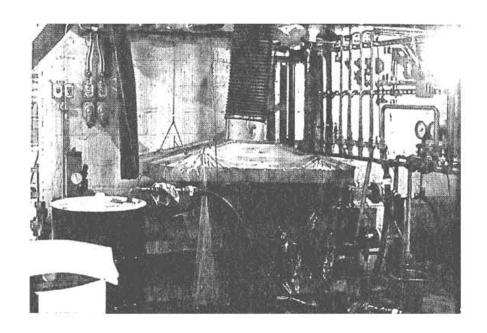


Figure 9. Filter Press Exhaust Hood.

Prior to 1979, most of these practices were in use at the facility; however, the program was not strictly enforced. Plant representatives feel that the enforcement of the housekeeping program since 1979 resulted in reduced employee exposure to mercury.

WORK PRACTICES

- Workers are required to shower at the end of the work day. Time is provided by the company for this activity.
- Consumption of food or beverages is not permitted in work areas.
- Job rotation is practiced within job grades.
- Smoking is not permitted in production areas.
- Workers are required to wash their hands before breaks.

HOUSEKEEP ING.

- Weekly cleaning of floors with ZEP^R Flash (non-caustic alkali industrial cleaner).
- Monthly cleaning of all equipment and work stations with ZEP^R Super Flash.
- Daily floor cleaning using hose and water.
- Immediate spill cleanup using 3M Adsorbent Pads (for aqueous and non aqueous materials).
- Contracting with an outside firm for removal of mercury containing waste.

MONITORING PROGRAMS

Biological Monitoring

Biological monitoring is an important part of the company's medical program. Monitoring consists of both blood and urine analysis to determine levels of mercury. Samples are taken twice per year. Spot samples are collected for urinalysis, and blood samples are collected the same day. The comprehensive biological monitoring program was initiated in 1973. It involves the monitoring of both biological and physical parameters on all production workers. A less stringent program had been in effect since the inception of the company in 1965.

The current acceptable level at the facility for mercury in blood is 5 micrograms per 100 milliliter of blood. At levels between 5 and 10 micrograms per 100 milliliters, reinforcement of the proper use of personnel protective equipment and procedures are undertaken by management personnel with the individiual. Where a level is greater than 10 micrograms per 100 milliliter the work assignment is adjusted so as to preclude further potential exposure to mercury vapor. If after 30 days of nonmercury production assignment, the level remains above 10 micrograms per 100 milliliters, the case is referred to outside industrial hygenists who are experts in the field of mercury toxicology. All action programs were developed by consulting physicians.

Air Contaminant Monitoring

Monthly monitoring is conducted to determine the concentrations of mercury vapor associated with various operations. This involves use of a direct reading mercury vapor detector (Bacharach MV-2). In addition, occasional sampling for airborne levels of PMA is conducted. The collection device for PMA consists of an impinger with potasium permanganate as the absorbing solution.

SURVEY DATA

VENTILATION MEASUREMENTS

The airflows through the local exhaust units studied were determined using an Alnor velometer (Model P-6000). The results of these measurements are illustrated in Table 2.

TABLE 2

Local Exhaust Unit	Effective Area (ft ²)	Average Velocity (fpm)	Airflow (cfm)
Mercuric Oxide Charger Hood	2.25	93	210
Drum loading Exhaust Hood	2.02	206	416
Filter Press Exhaust Hood	0.91	500	455

AIR SAMPLING RESULTS

Sampling was conducted for mercury vapor and phenyl mercuric acetate to evaluate the control methods used at Cosan. During the preliminary survey, a limited amount of sampling was used to determine the nature of the work environment. This preliminary sampling utilized a direct-reading instrument for mercury vapor (Jerome #401). The results of this sampling are presented in Table 3.

Subsequent indepth sampling used the aforementioned direct-reading instrument and sorbent tubes (Hopcalite) for mercury vapor. Sorbent tubes were used with low-flow sampling pumps operating at approximately 120 milliliters of air per minute. These time-weighted average (TWA) samples were taken for several hours during the workday. Laboratory analysis of the Hopcalite was conducted with flameless atomic absorbtion spectrophotometry.

TABLE 3

Direct Reading Mercury Vapor Sampling Results
(7-16-81)

Sample Location	Concentration (mg/m^3)		
	Range	Average	
Solids Room (spray drying)	0.025-0.045 (3)*	0.038	
Liquid PMA Production		0.052	
Acetate Production	0.050 (3)	0.050	

^{*}Number in parentheses indicate number of samples taken.

During the course of the survey, corresponding instrument readings were taken with the company's mercury vapor detector (Bacharach MV-2). These readings were consistently higher than those of the Jerome Instrument by about 30 percent. No immediate explanation was available for this; however, the Jerome is the more accurate, as confirmed by by time-weighted average results.

Time-weighted sampling for particulate phenyl mercuric acetate utilized high-flow air pumps operating at 2 liters per minute. Air was drawn through filter cassettes containing Whatman glass microfiber filters. Cellulose filters were not used because of possible absorbtion of mercury vapor on the cellulose. Analysis of the glass filters was conducted using EPA Method 245.5 for organic mercury. The final quantitation for this method is by flameless atomic absorbtion spectrophotometry.

Results of direct-reading instrument analysis from the indepth survey are presented in Table 4. These are generally comparable to the results of preliminary survey sampling of July 19, 1981, although somewhat higher.

TABLE 4

Direct Reading Mercury Vapor Sampling Results
(6/16/82-6/17/82)

	Concentration (mg/m ³)		
Sample Location	Range	Average	
Stîll Room	0.036-0.044 (3)*	0.040	
Solids Room (spray drying)	0.028-0.060 (8)	0.045	
Liquid PMA Room (near filter)	0.070-0.150 (4)	0.094	
Liquid PMA Room (reactors)	0.085-0.180 (5)	0.120	
Liquid PMA Room (floor)		0.350	
Blending Room	0.026-0.067 (3)	0.042	

^{*}Numbers in parentheses indicate number of samples taken.

Results indicate that area workplace concentrations are generally below the OSHA permissible exposure limit of 0.10 mg/m 3 and the NIOSH limit of 0.05 mg/m 3 , with the exception of the liquid PMA room. Direct-reading sample results show that the reactor room floor was a major source of mercury vapor.

Time-weighted sampling results are presented in Table 5. These results agree with the grab sample results. Exposures of the liquid PMA room operators were also high. Respirators are worn by all employees while in the reactor room. Grab samples did not indicate a significant difference between the filter area and other areas of the liquid PMA room, indicating that the filter press may not be a major source of contamination.

Other employees sampled also had exposures that were not consistent with the area samples taken near their work stations. This was the case with the reactor operators (i.e., their samples were higher than the corresponding area samples). This possibly reflects "microenvironmental" exposure (e.g., clothing contamination). This type of exposure is common in mercury-using industries and should be the subject of increased attention.

TABLE 5
TWA Mercury Vapor Area and Personal Sampling Results

Lecation or Worker Sampled	Concentration (mg/m ³)	
	Range	Average
Liquid PMA Room/Filter Press	0.063-0.180 (4)*	0.123
Blending		0.023
Reactor Operator (Liquid PMA)	0.180-0.200 (2)	0.190
Solids/Still Room Operator	0.095-0.100 (2)	0.097

^{*}Numbers in parentheses indicate number of samples taken.

Particulate sampling results (Table 6) showed low concentrations of phenyl mercuric acetate throughout most of the facility. The only exception was the solids room where solid PMA is produced. The TWA area sample concentrations in this room averaged approximately half of the OSHA PEL of 0.10 mg/m³. Although the PMA bagging operation is a carefully conducted procedure at this plant, this operation is probably contributing to the PMA concentration in this area. Normally workers spend less than 1 hour/day in the solids room; respirators are worn during this time.

TABLE 6
TWA Particulate Phenyl Mercuric Acetate Sampling Results

	Concentration (mg/m ³)	
Sample Location	Range	Average
Blending Room	<0.001-0.002 (3)*	0.001
Blending Room (during PMA drumming)	0.003-0.008 (2)	0.005
Solids Room (spray drying room)	0.035-0.049 (2)	0.042
Liquid PMA Room	<0.001-0.002 (2)	0.002
Still Room	<u></u>	0.002

^{*}Numbers in parentheses indicate number of samples taken.

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

Mercury vapor concentrations in excess of the OSHA PEL (0.1 mg/m³) were detected in the reactor room. In this room, control methods appeared to be effective in minimizing exposures from filtering and mercuric oxide charging. However, other emission sources appear to be responsible for the elevated concentrations.

The solids room had concentrations of PMA at approximately 0.05 mg/m³. The bagging operation at the spray dryer has a control that was effective in reducing PMA emissions, However, significant amount of PMA was being generated in conjunction with the operation.

RECOMMENDATIONS

- More thorough cleaning in the reactor room to minimize mercury vapor concentrations should be considered.
- Source emission testing from the reactors and spray drying should be investigated to determine the areas to apply controls.
- Continue use of respirators for those activities where levels approach or exceed the NIOSH exposure limit.