50272-101

PB89-164693

REPORT DOCUMENTATION PAGE	1. REPORT NO.	2.	3.

4. Title and Subtitle: Industrial Hygiene Survey Report of the P. D. George Company, St. Louis, Missouri, Report No. IWS-143-22

5. Report Date: 88/11/00

6.

7. Author(s): Boeniger, M. F.

8. Performing Organization Rept. No.: IWS-143-22

9. Performing Organization Name and Address: Division of Surveillance, Hazard Evaluation and Field Studies, NIOSH, U.S. Department of Health and Human Services, Cincinnati, Ohio

10. Project/Task/Work Unit No.

11. Contract (C) or Grant(G) No.
(C)
(G)

12. Sponsoring Organization Name and Address

13. Type of Report & Period Covered

14.

15. Supplementary Notes

16. Abstract (Limit: 200 words): In an attempt to gather information related to employee exposure to 4,4'-methylenedianiline (101779) (MDA) in a batch type mixing operation, a visit was made to the P. D. George Company (SIC-3079), St. Louis, Missouri. At this site imide ester resin was manufactured for wire coating. The process was performed as a batch operation in which large amounts of pure MDA were used. The study indicated that airborne dust was generated during the dumping of MDA into the reactor's loading chute but that personal protection eliminated much of the respiratory hazard. Contamination of the workplace and poor work practices both probably resulted in dermal exposure, but this was not confirmed by actual measurement. Urine samples were all negative for MDA at the detection limits of 1.0 parts per billion, suggesting that exposures were not sufficient to be detected by this method. The authors recommend that decontamination procedures be implemented and performed after MDA is used. Dry cleanup should be performed with a vacuum installed with a HEPA filter and final decontamination should be performed with a methanolic solution of p-dimethylaminobenzaldehyde. Workers must wear full personal protective equipment while handling MDA. These garments must not be reworn or stored with street clothes. Workers should wash and shower after handling MDA.

17. Document Analysis a. Descriptors

b. Identifiers/Open-Ended Terms: NIOSH-Publication, NIOSH-Author, NIOSH-Survey, Field-Study, Region-7, IWS-143-22, Amines, Plastics-industry, Epoxy-resins, Skin-exposure, Urinalysis, Air-quality-monitoring, Carcinogens, Personal-protective-equipment

c. COSATI Field/Group

18. Availability Statement

19. Security Class (This Report)

21. No. of Pages: 16

22. Security Class (This Page)

22. Price

DISCLAIMER

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

Purpose of Survey:	The purposes of this survey were to 1) obtain information on the extent of exposure to 4,4'-methylenedianiline (MDA) in a batch type mixing operation, 2) obtain information on the elimination of 4,4'-MDA in the urine of exposed workers, and 3) identify deficiencies in the handling of 4,4'-MDA and to provide recommendations for improving the protection of the workers.
Employee Representatives Contacted:	Mr. Dennis M. Pivin, Q.A./Q.C. Manager and Environmental Chemist. Mr. Stephen George, Vice President, Production Engineering. Mr. Ray Miller, Resin Production
Employee Representative Contacted:	No union at the plant.
Standard Industrial Classification (SIC) Code Number for Plant:	3079 (Miscellaneous Plastic Products)

ABSTRACT

An in-depth assessment of potential for exposure to 4,4'-methylene dianiline was conducted during the manufacture of imide-ester resin for wire coating. The manufacture of this resin is performed intermittently in a batch operation, during which time large amounts of pure 4,4'-MDA are used. The purposes of this evaluation were to characterize the potential for exposure to the workers, gather information on the excretion of 4,4'-MDA given a singular exposure to the substance, and identify deficiencies in the handling of this material. Techniques used to determine the potential for exposure included the collection of air samples, wipe samples, and urine samples from the workers.

The results of sample analyses indicate that there is airborne dust generated during the dumping of 4,4'-MDA into the reactor's loading chute but that personal protection eliminates much of the respiratory hazard. Dermal exposure probably occurs because of contamination of the workplace and poor work practices, but this was not confirmed by actual measurements. The urine samples were all devoid of 4,4'-MDA at the detection limit of 1.0 part per billion indicating that the level and duration of exposure was not sufficient to be detected by this technique. Finally, improved work practices were recommended to further protect the workers in this sort of operation.

INTRODUCTION

Exposure to 4,4'-methylene dianiline (4,4'-MDA) has previously been associated with toxic liver damage, nausea, irritation of mucous membranes, and contact sensitization.(1-3) In 1982, the bioassay results from a National Toxicology Program study of 4,4'-MDA supported earlier bioassay findings that 4,4'-MDA is a carcinogen in rats and mice.(4) There is also some suggestive information that 4,4'-MDA is a human carcinogen. (5,6) NIOSH has reviewed the available information on 4,4'-MDA and concluded that occupational exposures to 4,4'-MDA should be controlled to the lowest feasible limit.(7) Recently, the Occupational Safety and Health Administration published the recommendations of a mediated rulemaking advisory committee for a health and safety standard for 4,4'-MDA (8).

PLANT DESCRIPTION

The P.D. George Company has been a producer of specialized paints, varnishes, lacquers, enamels and insulating materials for over 50 years. The company is located on a 16 acre site in an industrial area in St. Louis. The site is occupied by about two dozen 1- to 3-story buildings plus storage tanks. The resin production area, where 4,4'-MDA is used to make an ester-imide wire enamel resin, is located in a three story brick and concrete building. Within the building are two mixing/reactor units. On the top floor, raw dry materials are dumped into a loading chute. On the second floor are the mixing/reactor vessels and control room. Dispensing of the finished product is performed in the ground floor level.

DESCRIPTION OF WORKFORCE

The entire company's employment numbers about 175, of which 96 are in production. The number of production workers in the resins department is 27. All workers are males. Production departments operate over three work shifts. Employee turnover at the plant is reported to be low.

DESCRIPTION OF PROCESS

Imide type wire enamels are the only products made at this plant that contain 4,4'-MDA. These products are made intermittently and are only one type of many resins made in this department. During this survey, a large batch of the enamel was produced, to which about a ton of 4,4'-MDA was added. Several other organic components are automatically pumped into the mixing/reacting vessel. The chemical ingredients thermally "cook" for several hours at a temperature of between 400-500°F.

Historically, flaked technical grade 4,4'-MDA has been received from an overseas supplier, in plastic lined paper sacks. This material was used in the production of ester-imide wire enamel during this survey. A prilled material from another supplier is intended to replace the flaked 4,4'-MDA.

To produce the amide-imide wire enamel, 4,4'-MDA is loaded manually as a dry material through the top floor loading chute. Two workers are normally involved with the transfer of 20 Kg bags of 4,4'-MDA material into the loading chute. During the production of each batch of enamel, 4,4'-MDA is added to the reaction vessel in an identical manner. A proprietary chemical is added to terminate the "cooking" process. This is also expected to hydrolyze any residual 4,4'-MDA that had not already chemically reacted with the other ingredients in the vessel. The final product, reportedly devoid of free 4,4'-MDA, is piped to receiving tanks for rail or tank car shipment.

DESCRIPTION OF ENGINEERING CONTROLS

The reaction vessel and loading chute can be exhausted via a 15 inch duct to a roof fan. This fan is only operated during the loading operations, not during the "cooking" phase. Prior to exiting the building, the exhaust air passes through a venturi scrubber. Solvents are reclaimed in a condensation vessel and are later reused. During the cooking process, the vessel is kept at atmospheric pressure through a passive vent to the roof. Although the reaction vessel appeared tightly enclosed, the possibility of fumes escaping from the vessel into the work area cannot be excluded.

DESCRIPTION OF PERSONAL PROTECTIVE EQUIPMENT AND WORK PRACTICES

Worker contact with 4,4'-MDA is primarily limited to the loading operation on the top floor of the resins reactor building. Additional potential for exposure may occur during the movement of 4,4'-MDA to the loading area and during the disposal of the empty bags. The current practice during the loading of 4,4'-MDA into the loading chute is for the workers (usually two) to wear full body disposable coveralls (made of standard Tyvek® material), Tyvek foot covering, Tyvek hood, cuff-length rubber coated canvas gloves, and air supplied full face respirator. After the loading has been completed, the workers use the compressed air line to blow settled dust off their Tyvek clothing. The company's unwritten policy is for the coveralls to be disposed of after each use. Policy also dictates that full protection be worn when the several dozen empty 4,4'-MDA bags are moved over to the freight elevator and taken down to a trash dumpster. In practice, however, workers removed their personal protective equipment in the contaminated loading chute area without first disposing of the empty bags. Some workers also did not wear Tyvek foot coverings while loading 4,4'-MDA. In addition, workers kept their Tyvek coveralls and hoods and stored them in their personal lockers with their street clothes. Work shoes, provided biannually by the company, are either kept in or on top of the workers' lockers. The rubber coated gloves that are worn during the loading of 4,4'-MDA are used continually for general use until they are worn-out. This period of time typically ranges from several days to two weeks.

DESCRIPTION OF HEALTH AND SAFETY PROGRAM

This company employs an individual with an environmental chemistry background who has partial responsibility for addressing health and environmental

issues. Together with the company's management, policies on worker health and safety are formulated. However, executing administrative policies regarding personal protective equipment and work practices is the responsibility of the production manager in each department.

The environmental chemist has taken air samples for several organic solvents, lead, and total particulate mass. Chemically specific sampling and analysis for 4,4'-MDA had not been previously performed.

The company provides to the production workers a comprehensive medical examination through the the St. Louis University Hospital. Participation in this medical program, which includes surveillance and trend analysis, is voluntary. The examination includes an assessment of lung function, and blood and urine analysis.

Safety training is provided by the production supervisors to the new employees through on-the-job training. Showers are available but their use before leaving the plant is not mandatory.

SURVEY METHODS

This survey and the industrial hygiene sampling performed at this site was solely limited to the production of ester-imide wire enamel where 4,4'-MDA is loaded. Possible chemical interferences to the analysis of 4,4'-MDA were noted at the time of the survey. The survey consisted of collecting air samples during the loading operations which were performed on the day and evening work shifts. Occasionally, both 4,4'-MDA loading operations are performed on the same shift. Urine samples were obtained from the loading workers and reactor operator before exposure to 4,4'-MDA, during the loading day, and two days afterwards.

Air samples were collected on 37 mm acid-treated glass fiber filters, assembled with a paper O-ring support pad, in a three piece cassette. Sampling was performed open faced at a sampling flow rate of 2.5 liters per minute. Analysis was performed by a method developed within NIOSH (Memo to Director, DPSE, NIOSH, Method Development for 4,4'-Methylenedianiline. Sequence #4752. IWSB-85-544. November 3, 1986). This procedure involves use of a high performance liquid chromatograph (HPLC) for separation of the analyte. An ultraviolet detector and electrochemical detector are attached in series to monitor each chromatographic run. The UV detector is set at 254 nm wavelength. The filter samples are eluted from the acid-treated glass fiber filters with 4 mL 0.1 N potassium hydroxide in methanol. The base eluent converts all the salts of 4,4'-MDA back to the free amine. A direct injection of the eluent is made into the HPLC. Analyte recovery of spiked samples, samples spiked and stored for one month, and samples spiked with air drawn through, was performed. Recovery ranged from 94.5% at 3712 ng per filter to 77.8% at 9 ng per filter. Using a linear regression analysis of the calibration curve, an analytical Limit of Quantitation (LOQ) of 5.9 ng per mL and a Limit of Detection (LOD) of 1.8 ng per mL were established.

Wipe samples were collected on various work surfaces using cotton gauze pads which were either dry or moistened with methanolic potassium hydroxide solution. Samples were immediately placed in 10 mL of 0.1N methanolic potassium hydroxide solution to stabilize the 4,4'-MDA. Analyte recovery and long-term stability studies have shown the extraction efficiency is greater than 90 percent and stability is essentially unchanged when the analyte is in solution. Analysis was performed using the same analytical system described for air sample analysis.

Urine was collected from workers 1-3 (Table 1). Urine was not collected from workers 4 and 5 due to illness (of the surveyor). Workers 1-3 were instructed to collect urine voids at 4-hour intervals during work, upon retiring in the evening, and upon awakening in the morning for two days after having worked with 4,4'-MDA. Each worker was given a 500 mL high density polyethylene bottle to use to collect these samples. The urine volume was approximately determined by weighing the filled bottles. In addition, the refractive index and pH was checked on each sample. A primary aliquot of 50 mL was transferred to a 60 mL HDPE leak proof bottle and a backup aliquot of 30 mL was set aside for 4,4'-MDA analysis.

Urine analysis was performed by a method developed at NIOSH for the determination of 4,4'-MDA. First, 50 mL of urine was subjected to alkaline hydrolysis at 80°C for 2 hours. This step converts the acetylated and conjugated 4,4'-MDA to the free amine. A C18 Sep-Pak solid sorbent tube was then used to separate and collect the free amine in the urine. The amine was eluted from the Sep-Pak with 10 mL benzene and collected. This eluent was taken to dryness under a stream of nitrogen and gentle heat. The residue was redissolved in 1N potassium hydroxide in methanol, let sit overnight, and filtered through a 0.45-um filter. Detection and quantitation of 4,4'-MDA was performed on an HPLC equipped with an ultra-violet (UV) detector set at 245 nm as well as an electrochemical detector (ECD) in series. In laboratory evaluations of the method over a concentration range of 1.9 to 19 ug/L, the percent recovery was better than 90 percent with a percent relative standard deviation of 13.5 to 2.4, respectively. The LOD was 1.8 ug/mL urine and the LOQ equaled 5.9 ug/mL.

RESULTS

Six air samples (Table 1) were collected during the transfer of 4,4'-MDA into the reaction vessel and during the cooking operation. The breathing zone samples worn by the loading operators, all indicated concentrations of 4,4'-MDA ranging between 3 and 25 parts per billion (ppb). The higher air concentrations were measured on the workers who dumped the opened bags into the loading chute. All samples were short term samples which were worn only during this work task. The concentrations do not represent personal exposure because of the personal protection worn by the workers.

The air sample collected on the reactor operator represents personal inhalation exposure since no respirator was worn. This sample result was 1 ppb over a 305 minute period. During the second phase of the reactor cook,

only a stationary sampler was located near the reactor vessel. No 4,4'-MDA was detected in this sample. It is not known what the source of exposure to the reactor operator was during the first half of the cook.

The results of wipe samples are reported in Table 2. These results indicate a high degree of variability between like samples. Generally, 100 cm^2 were wiped unless the area of interest was smaller. These limited results do indicate that 4,4'-MDA was present from its last use in September and November, 1987, indicating its persistence and the lack of appropriate decontamination procedures.

The urine analysis results are not tabulated since none of the results were above the limit of detection. A total of twenty-four urine samples were submitted for the analysis of total 4,4'-MDA, after hydrolysis. All samples were regarded as normal, with respect to appearance, specific gravity, and pH. All samples were run in duplicate and each run was monitored with a UV detector and a ECD. The sensitivities of both detectors were comparable, but the addition of the ECD offered additional specificity. The LOQ and the LOD were calculated from the calibration curves of both detectors. The LOQ and LOD for the UV detector were 3.3 ppb and 1.0 ppb, respectively. The LOQ and LOD for the ECD were 7.8 ppb and 2.4 ppb, respectively. The presence of any detectable 4,4'-MDA would have been confirmed by the use of gas chromatography and mass spectrometry.

DISCUSSION AND CONCLUSIONS

It is well known that aromatic amines, as a class, are easily absorbed through the skin. Approximately 50 percent of a dilute dermal application in 4,4'-MDA has been shown to be unrecoverable from the skin of the rhesus monkey, rat, and guinea pig after 24 hours contact. Approximately 19 percent of the dermal dose in rhesus monkeys is eliminated as 4,4'-MDA or other products in the urine. The elimination period was very protracted, lasting several days. It was also determined that the percent absorbed will depend significantly on the dermal concentration, surface area covered and length of time the dose is present (1). Therefore, given the limitations of the current knowledge on dermal penetration, predictions of absorption among workers would be nearly impossible given all the variables involved.

Although work practices could be improved, it is likely that these workers had little exposure to 4,4'-MDA during this survey. But, because contamination of the work area was found and work practices could allow exposure to contaminants, it is likely that some skin contact with 4,4'-MDA occurs, although it is not known quantitatively how much. The respiratory exposure of one worker (reactor operator) was measured with confidence (i.e. no respirator was worn). If 50% of this dose was retained, this worker's absorbed dose was only about 42 ug, based on the sample duration and an average tidal volume of 1500 liters per hour. If about 20 percent of the absorbed dose were excreted, about 8 micrograms of 4,4'-MDA would be excreted if that were the primary metabolite. However, no 4,4'-MDA was detected in any of this workers' urine

voids. Because of the expected protracted excretion period, the excretion mass was probably too little to be detected when diluted in a large urine volume.

RECOMMENDATIONS

The following recommendations are offered towards minimizing potential exposures to 4,4'-MDA.

1. Decontamination procedures should be implemented and should be performed after 4,4'-MDA is used. Dry cleanup should be performed with a vacuum installed with a HEPA filter followed by washing with a dilute acidic solution. Final decontamination could be performed with a methanolic solution of p-dimethylaminobenzaldehyde. All concrete surfaces should be sealed with an impervious coating to facilitate decontamination procedures.(9,10)

2. Workers should continue to wear full personal protective equipment while handling 4,4'-MDA. However, these garments, including the gloves, should not be reworn or stored with street clothes. Continuous use of gloves after being used to handle 4,4'-MDA is strongly discouraged since permeation continues to occur after the gloves are removed and these gloves represent a repeated source of exposure every time the gloves are reworn.(11) Use of compressed air to blow off dust from the garments while still wearing them is not recommended because uncoated Tyvek material is porous to small particles and penetration would be facilitated by this procedure and would also lead to further unnecessary respiratory exposure. Use of compressed air to clean the outside of the loading chute also increases the distribution of the contamination. Empty bags or drums which are contaminated with 4,4'-MDA should be removed from the work area and properly disposed of while the workers are still wearing the personal protective apparel.

3. Workers should be required to wash and shower after handling 4,4'-MDA to remove contaminants on the skin and to reduce absorption of the chemical.

ACKNOWLEDGMENT

This survey could not have been conducted without the outstanding work of Mr. Charles Neumeister, Division of Physical Science and Engineering, NIOSH, who perfected the sampling and analytical methods used to detect 4,4'-methylenedianiline. Gratitude is also expressed to the company's management and its employees for their assistance during the performance of this survey.

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Table 1
Air Sampling Results for 4,4'-Methylenedianiline
P.D. George Company
St. Louis, Missouri
February 22-23, 1988

Sample Number	Worker Number	Sample Duration (min)	Location/Description	Air Concentration Result (ppb)	Air Concentration Result (ug/m^3)
1	1	40	Personal sample while loading 4,4'-MDA first loading	6	47
2	2	240	Personal sample while loading 4,4'-MDA first loading	3	25
3	3	305	Personal exposure to reactor operator during first half of cook	1	11
4	4	22	Personal sample while loading 4,4'-MDA second loading	7	57
5	5	17	Personal sample while loading 4,4'-MDA second loading	25	202
6		480	On operators desk, 8' from reactor vessel during last half of cook	ND[1]	--

1. The limit of detection and limit for quantitation were 0.06 and 0.11 ug/filter sample, respectively.

Table 2
Wipe Sample Results for 4,4'-Methylenedianiline
P.D. George Company
St. Louis, Missouri

Sample Number	Solvent Used[1]	Result Location/Description	ug/sample
The following samples were collected before 4,4'-MDA bags were opened:			
1.	No	On steam pipe behind loading chute	ND[2]
2.	Yes	Same as above	6
3.	No	On top of weight scale	9.7
4.	Yes	Same as above	0.6
5.	Yes	On pipe 10' from loading chute	1
The following samples were collected after 4,4'-MDA was loaded:			
6.	Yes	On pipe 10' from loading chute	(0.16)
7.	Yes	Yellow floor stain behind chute	2000
8.	Yes	Air hose line coupling	276

1. 0.1 N methanolic potassium hydroxide was used to wet the gauze.
2. The limit of detection and limit for quantization were 0.16 and 0.52 ug/wipe sample, respectively.