

Health Hazard Evaluation Report

HETA 81-133-1110 GERLINGER CASTING CORPORATION SALEM, OREGON

#### PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, medical, nursing, and industrial nygiene technical and consultative assistance (TA) to Federal, state, and local agencies; labor; industry and other groups or individuals to control occupational health hazards and to prevent related trauma and disease.

Mention of company names or products does not constitute endorsement by the National Institute for Occupational Safety and Health.

MAY 1982 GERLINGER CASTING CORP. SALEM, OREGON

#### SUMMARY I.

In January 1981 the National Institute for Occupational Safety and Health (NIOSH) received a request from the International Molders and Allied Workers, Local 139, to determine if a potential health hazard existed to chemicals used at the Gerlinger Casting Corp., Salem, Oregon. The request involved the chemicals in the phenolic urethane no-bake binder system used in mold making and the breakdown products of the binder system released during the pouring of the castings at the Gerlinger Casting Corp., Salem, Oregon.

On June 23 and 24, 1981, environmental air samples were collected to determine the workers exposure to acrolein, ammonia, aniline, benzene, carbon monoxide, dimethylamine, ethylamine, formaldehyde, hydrogen cyanide, methylamine, MDI (diphenylmethane diisocyanate), phenol, 4-phenyl propylpyridine, pyridine, toluene, triethylamine and xylene. A pre and post-shift medical questionnaire was administered to the workers in the molding and pouring departments.

Exposures to pyridine and 4-phenyl propylpyridine (two day average concentrations) in the molding area were 5.9 ppm and 1.1 ppm respectively with a combined average exposure of 7.0 ppm. The evaluation criteria for pyridine is 5 ppm. There is no criterion for 4 -phenyl propylpyridine; however, it is assumed that the criterion is the same as pyridine (5 ppm). When two or more compounds are present that have similar health effects, as with pyridine and 4-phenyl propylpyridine, the exposures have to be considered as additive. The combined pyridine and 4-phenyl propylpyridine exposure in the molding area was 140% of the evaluation criterion of 5 ppm and in the pouring area it was 70% of the criterion. The benzene concentration in the pouring area was 0.24 ppm or 24% of the criterion of 1 ppm. All samples collected for acrolein, amines, formaldehyde, hydrogen cyanide, MDI, phenol, toluene and xylene were less than 6% of the appropriate criteria, Carbon monoxide concentrations ranged from 1 to 7 ppm or less than 20% of the criterion.

One pourer developed a cough during the day. This was the only symptom he experienced. The other pourer had a had cold so symptoms related to work could not be determined. The employees conducting the molding experienced burning and itching of the eyes during the times they made the large gears. At the end of the shift, one had a dry throat, watery eyes and a slight cough. The employee who cleaned the mixer had burning and itching of the eyes, a cough and a dry throat. The core maker had a dry throat and felt lightheaded.

On the basis of the data collected for this investigation, NIOSH determined that the molders and other molding area employees are occupationally exposed to toxic concentrations of pyridine and 4-phenyl propylpyridine as used and found while conducting operations in the molding area. The molders' and casters' exposure to airborne acrolein, ammonia, aniline, benzene, carbon monoxide, dimethylamine, ethylamine, formaldehyde, hydrogen cyanide, methylamine, MDI, phenol, toluene, triethylamine and xylene were not toxic as measured. Recommendations involving local exhaust ventilation and personal protective clothing have been included in this report to further reduce exposure to these compounds.

KEY WORDS: SIC 3221 (Gray Iron Foundries) benzene, 4-phenyl propylpyridine, pyridine, phenolic urethane no-bake binder systems.

### II. INTRODUCTION

In January 1981 the National Institute for Occupational Safety and Health (NIOSH) received a request from the International Molders and Allied Workers, Local 139, to determine if a potential health hazard existed to chemicals used in the phenolic urethane no-bake binder system, in mold making and in the breakdown products of the binder system released during the pouring of the castings at the Gerlinger Casting Corp., Salem, Oregon. An initial survey was conducted on January 22, 1981 and an environmental survey on June 23-24, 1981. An interim report including the environmental and questionnaire results and recommendations was submitted to the company and the union.

### III. BACKGROUND

Gerlinger Casting Corp. is a gray iron foundry. This evaluation involves only the molding and pouring departments. A phenolic urethane no-bake binder system is used in the mold making process. Phenolic urethane no-bakes are high speed chemical binder systems. Using this system, molds can be ready to strip within 1-15 minutes after filling a pattern. The phenolic urethane usually comes in 3 parts. The phenolic urethane chemicals are mixed with sand in a mixer immediately preceding the molding operation. The mixed molding sand is placed in the mold at which time the mold begins to cure. This curing takes place in a matter of minutes. The excess sand is placed in an open bin next to the molding station. Some excess sand is inadvertently spilled on the floor. After the molds have cured the flasks are removed and the molds transferred to the pouring area. The large molds, such as the large gears, have a lot of surface area. The molders lean over the mold to do their work. This results in a higher short term exposure to the released gases and vapors. There is one sand mixer and molding station using this process. There is no local exhaust ventilation on this process. The molders wear rubber gloves as several of the chemicals can be absorbed through the skin. During the morning and afternoon breaks, lunch time and at the end of the shift, one worker cleans the resin-sand mixture from the mixer.

The potential exposures include airborne vapors and gases of the chemicals used in the resin formulation, the breakdown products as a result of the curing process, and the potential skin contact with the wet resin-sand mixture prior to curing. The molds are lined up in the pouring area and poured in place. The airborne vapors, gases and fumes include the chemicals in phenolic urethane sand binder systems and the chemical breakdown products resulting from the hot molten metal being poured into the molds. There is no local exhaust ventilation at the pouring station. The pouring area is in the high bay section of the building and general ventilation is accomplished in warmer weather by leaving the mearby overhead doors open. There were 5 employees in the molding area and 3 in the pouring area. The plant was working one shift per day.

# IV. EVALUATION DESIGN AND METHOD

#### A. Environmental

Area air samples were collected at a location 4 feet from the molders and at a second location in the middle of the pouring floor. Several samples were also collected in the breathing zone of the molder and pourers. Area samples were selected in lieu of breathing zone samples since there was only one molder and two pourers and 10 different pieces of sampling equipment were required to obtain the samples at each location.

Listed below are the sampling and analytical methods used in this evaluation.

Substance	Collection Method	Flow Rate	NIOSH Analytical Method
acrolein	bubbler 1% Na HSO <sub>3</sub> hexylresorcinol	1.0 1pm	P&CAM 211
amines (aliphatic)	silica gel	50-100 cc/min	P&CAM 221
amm on i a	long term detector tubes	20 cc/min	-
aniline	silica gel	50-100 cc/min	P&CAM 168
benzene, toluene, xylene	charcoal	50-100 cc/min	P&CAM 127
carbon monoxide	long term detector tubes	20 cc/min	-
formaldehyde	treated charcoal	1.0 1pm	P&CAM 318
hydrogen cyanide	bubbler 0.1N KOH	1.0 1pm	P&CAM 116
MDI	treated filter	1.0 1pm	P&CAM 326
pheno1	bubbler 0.1 N NaOH	1.0 1pm	P&CAM S-330
pyridine and 4-phenyl propylpyridine	charcoal tube	50-100 cc/min	P&CAM S-161

# B. Medical

The molders and pourer were privately interviewed during which time they stated the adverse symptoms they experienced in the past. A short pre and post-shift questionnaire was administered which elucidated the employees' symptoms of dry or sore throat, burning or itching eyes, tearing of the eyes, stuffy or runny nose, headache, dizziness or lightheadness, coughing, tight chest, wheezing, nausea, skin rash or irritation, and blurred vision or halo effect.

# V. EVALUATION CRITERIA

#### A. Environmental

The environmental criteria for exposure to toxic substances used in this evaluation are based on the following; l. NIOSH Criteria Documents, Recommended Standards for Occupational Exposures; 2. Threshold Limit Values (TLV) of the American Conference of Governmental Industrial Hygienists (ACGIH); 3. The Oregon State Occupational Health Standards; and 4. The U.S. Department of Labor (OSHA) Occupational Health Standards.

<i>y</i>	NIOSH (or ACGIH) RECOMMENDED CRITERIA	OSHA & OREGON STANDARDS
SUBSTANCE	10 hr TWA*	8 hr TWA
acrolein	0.1 ppm (ACGIH)	0.1 ppm
ammon i a	50 ppm (5 min. ceiling) 25 ppm (ACGIH)	50 ppm
aniline	2 ppm -S**-(ACGIH)	5 ppm
benzene	<pre>1 ppm (5 ppm ceiling)</pre>	10 ppm (25 ppm ceiling)
carbon monoxide	35 ppm	50 ppm
dimethylamine	10 ppm (ACGIH)	10 ppm
ethylamine	10 ppm (ACGIH)	-
formaldehyde	0.8 ppm 30 minutes	3 ppm ceiling
hydrogen cyanide	5 ppm -S	10 ppm
methyl amine	10 ppm (ACGIH)	10 ppm
MDI (diphenylmethane diisocyanate)	0.2 mg/cu m ceiling	0.2 mg/cu m ceiling
phenol	5 ppm -S	5 ppm
4-phenyl propylpyridine		<u>.</u>
pyridine	5 ppm (ACGIH)	5 ppm
toluene	100 ppm -S	200 ppm
tri et hylami ne	25 ppm (ACGIH)	25 ppm
xylene	100 ppm -S	100 ppm

<sup>\*</sup> TWA - time weighted average \*\* S - Skin absorption a factor

# B. Toxicology

Only those substanced which were present in potentially toxic concentrations are discussed below.

PYRIDINE - "Irritation of the conjunctiva of the eye and comea and mucous membranes of the upper respiratory track and skin may occur. It occasionally causes skin sensitization, and photosensitization has been reported. Very high concentrations may cause narcosis. Repeated, intermittent, or continous low level exposure may lead to transient effects on the central nervous system and gastrointestinal tract. The symptoms include headache, dizziness, insomnia, nervousness, anorexia, nausea, vomiting, and diarrhea. Low back pain and urinary frequency with no changes in urine sediment or liver or renal function and complete recovery have been reported to follow exposures to about 100 ppm." (1)

4-PHENYL PROPYLPYRIDINE - There is very little information in the existing literature. Animal studies in mice indicate that it is irritating to the skin and eyes. The LD-50 is about the same as pyridine and males are more suceptable than females. (2)

# VI. RESULTS AND DISCUSSION

### A. Environmental

All samples collected for acrolein, amines, formaldehyde, hydrogen cyanide, MDI, phenol, toluene and xylene were either not detectable or were less than 6% of the appropriate evaluation criteria. (Tables 1-4) The carbon monoxide concentrations ranged from 1 to 7 ppm which is 20% or less of the criteria of 35 ppm. (Table 2) One benzene sample collected in the pouring area was 0.24 ppm which is 24% of the criteria of 1 ppm. (Table 3) Benzene is not present in the original formulation but is a breakdown product of the heat in the casting operation.

4-phenyl propylpyridine is present in the sand binder as a catalyst. A portion of this is converted to pyridine during the sand mixing and molding process. The pyridine concentrations on the pouring floor were 2.5 and 2.8 ppm, which is 50% of the evaluation criteria, and the 4-phenyl propylpyridine concentrations were 0.7 ppm and less than 0.5 ppm. (Table 3) At the molding area the pyridine concentrations were 6.0 and 5.7 ppm, which is 120% of the criteria of 5 ppm, and the 4-phenyl propylpyridine concentrations were 1.0 and 1.2 ppm. There is no evaluation criteria for this compound, however if it is assumed that the evaluation criteria is the same as pyridine (5 ppm), then these concentrations would then be 20% of this criteria. When 2 or more compounds are present that have similar health effects, as in this case with pyridine and 4-phenyl propylpyridine, the exposures have to be considered as additive. The combined pyridine and 4-phenyl propylpyridine exposures would then be 140% of the evaluation criteria during the 2 days of sampling. Breathing zone concentrations of the molder would probably be higher than those measured as he is working directly over the molds. These samples were collected on warms days with the large overhead doors near the process open (except for a portion of the afternoon on the second day). This produced a breeze through the molding area. It is anticipated that on days when the doors are closed all or most of the day, as in the winter, that the pyridine and 4-phenyl propyl pyridine concentrations would be higher than those measured.

#### B. Medical

The past and present symptoms reported by the workers from the molding area were burning and itching of the eyes, throat irritation, cough, headaches, blurred vision. constipation, skin rash, chest tightness, diarhea and lack of appetite. Several stated that some of the symptoms had not been present since they started wearing rubber gloves in December of 1980. The past and present symptoms reported by the workers from the pouring area were burning eyes and difficulty in breathing during the pour.

A short pre and post-shift medical questionnaire was administered which asked if the employees had symptoms of dry or sore throat, buring or itching eyes, tearing of the eyes, stuffy or runny nose, headache, dizziness or lightheadedness, coughing, tight chest, wheezing, nausea, skin rash or irritation, and blurred vision or halo effect.

One pourer developed a cough during the day. This was the only symptom he experienced. The other pourer had a bad cold so symptoms related to work could not be determined. The employees conducting the molding experienced burning and itching of the eyes during the times they made the large gears. At the end of the shift, one had a dry throat, watery eyes and a slight cough. the employee who cleaned the mixer had burning and itching of the eyes, a cough and a dry throat. The core maker had a dry throat and felt lightheaded.

# VII. CONCLUSIONS

It is determined that the molders and other molding area employees are exposed to concentrations of pyridine and 4-phenyl propylpyridine that are toxic as used and found while conducting operations in the molding area. This is based on airborne samples that showed exposures to these compounds were 140% of the evaluation criteria, and that molding of the large gears and cleaning of the mixer produce short term exposures which resultes in the employees experiencing intermittent burning and itching of the eyes, cough and dry throat.

#### VIII. RECOMMENDATIONS

- Provide local exhaust ventilation where the molds are made. A suggestion is the use of slot ventilation on one side near the mold which would not interfere with the molding operation.
- 2. Provide local exhaust ventilation on the mixer.
- Cover and ventilate the excess molding sand bin located next to the molder.
- 4. Install an exhaust system on the floor under the molding location to capture the vapors released form the spilled mixed sand lying on the floor.

- 5. Avoid physical contact with the resin. Use protective clothing such as rubber gloves and aprons as these chemicals can be absorbed through the skin.
- 6. Clothing contaminated with the resin or catalyst should be removed and washed before wearing again.
- 7. Clean work clothes should be used daily.
- 8. Pending adequate engineering controls, if feasible, the person cleaning the mixer should wear a NIOSH approved full face respirator with cartridges for use with organic vapors or with an air cap similar to those used in other operations in the plant.
- 9. Pending adequate engineering controls, if feasible, the employees working in the molding area should wear an air cap or an approved respirator with cartridges for use with organic vapors. The molder should wear an air cap or a full face respirator especially when making large gears.
- Consider installation of local exhaust ventilation at the point where the castings are poured.
- ll. Monitor the molding area workers exposure to pyridine and 4-phenyl propylpyridine under various conditions and jobs in order to prioritize the installation of controls.
- 12. Keep searching the market for less toxic chemicals that would perform the same functions as those currently used in the molding operations.

#### IX. REFERENCES

- 1. OCCUPATIONAL DISEASES A GUIDE TO THEIR RECOGNITION National Institute for Occupational Safaety and Health DHEW (NIOSH) publication No. 77-181.
- 2 FICHE TOXICOLOGIQUE No. 155 INRS 30, Rue Olivier Noyer 75680 Paris Cedex 14th Paris, France.

# X. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this complete Determination Report are currently available upon request from NIOSH, Division of Standards Development and Technology Transfer, Information Resources and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After ninety (90) days, the report will be available through the National Technical Information Service (NTIS), Springfield, Virginia. Information regarding its availability through NTIS can be obtained from NIOSH Publications Office at the Cincinnati address.

Copies of this report have been sent to:

- 1. Gerlinger Casting Corp., Salem, Oregon
- International Molders and Allied Workers Local 139 Portland, Oregon
- U.S. Department of Labor, Occupational Safety and Health Administration, Region X, Seattle, Washington
- 4. Ore gon State Accident Prevention Division, Salem, Ore gon

For the purpose of informing the 8 affected employees, the employer shall promptly post this Determination Report in a prominent place(s) near the work area of the affected employees for a period of thirty (30) calendar days.

# XI. ACKNOWLEDGEMENTS

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TABLE 1 ACROLEIN, FORMALDEHYDE & PHENOL AIR CONCENTRATIONS

# GERLINGER CASTING CORPORATION Salem, Oregon

HHE 81-133

			ACROLET	IN .		FORMALDEH	TDE	PHENOL			
LOCATION	DATE	SAMPLE NUMBER	TIME MINUTES	ppm	SAMPLE NUMBER	TIME MINUTES	ppm	SAMPLE NUMBER	TIME MINUTES	ррп	
Middle of pouring floor (GA) (on edge of raised portion)	6-23-81	9	430	0.001	5	430	0.05	11	370	0.06	
Middle of pouring floor (GA) (on edge of raised portion)	6-24-81	79	435	0.001	75	435	0.03	81	435	0.23	
4 ft. from molder (GA)	6-23-81	29	425	<0.0005	25	425	0.05	31	380	0.11	
4 ft. from molder (GA)	6-24-81	49	425	0.002	45	425	0.03	51	300	0.17	
Attached to front of the sand mixer in the molders breathing zone.	6-24-81				62	410	0.03	63	400	0.29	

Limits of detection: acrolein - 0.045 ug

formaldehyde - 6 ug phenol - 0.03 mg

TABLE 2

AMMONIA, CARBON MONOXIDE, HYDROGEN CYANIDE AND DIPHENYLMETHANE DIISOCYANATE (MDI)

AIR CONCENTRATIONS

# GERLINGER CASTING CORPORATION Salem, Oregon

HHE 81-133

		AM	MONIA		CA	RBON MONO	IDE	НУ	DROGEN C	YANIDE	MDI			
LOCATION	DATE	SAMPLE NUMBER	TIME MINUTES	S ppm	SAMPLE NUMBER	TIME MINUTES	ррт	SAMPLE NUMBER	TIME MINUTES	mg/cu m	SAMPLE NUMBER	TIME MINUTES	ug/cu t	
Middle of pouring floor (on edge of raised portion)	6-23-81	6	430	< 0.5	7	430	2	10	430	<.0.01	. 8	430	<0.6	
Middle of pouring floor (on edge of raised portion)	6-24-81	76	435	<0.5	77	435	7	80	435	<0.01	48	405	<0.6	
4 ft from molder	6-23-81	26	425	<0.5	27	425	1	30	425	< 0.01	28	425	<0.6	
4 ft from molder	6-24-81	46	425	<0.5	47	425	2	50	425	<0.01				
Attached to front of the sand mixer in the molders breathing zone.	6-23-81	-			-		-	-	·		32	400	<0.6	
Attached to front of the sand mixer in the molders breathing zone.	6-24-81	-	***			***	-		***		64	410	<0.6	
Breathing zone - pourer	6-23-81				12	380	3	-						
Breathing zone - pourer	6-24-81	-			82	435	4	-						

Limits of detection - Ammonia - 0.5 ppm
Carbon Monoxide - 0.5 ppm
Hydrogen Cyanide - 5 ug
MDI - 0.3 ug

TABLE 3

BENZENE, TOLUENE, XYLENE, PYRIDINE, AND 4-PHENYL PROPYLPYRIDINE
AIR CONCENTRATIONS

# GERLINGER CASTING CORPORATION Salem, Oregon

HHE 81-133

LOCATION		-		BENZENE	TOLUENE	XYLENE	entrance i	PYRIDINE		1-PHENYL PROPYLPYRIDINE		
	DATE	NUMBER MI	TIME MINUTES	ppm	ppm	ppm	SAMPLE NUMBER	TIME MINUTES	ррт	SAMPLE NUMBER	TIME MINUTES	ppm
Middle of pouring floor (on edge of raised portion)	6-23-81						4	430	2.5	4	430	<0.5
Middle of pouring floor (on edge of raised portion)	6-24-81	73	435	0.24	<0.1	<0.1	74	435	2.8	74	435	0.7
4 ft. from molder	6-23-81	23	425	0.05	<0.1	<0.1	24	425	6.0	24	425	1.0
4 ft. from molder	6-24-81	43	425	0.05	<0.1	<0.1	44	425	5.7	44	425	1.2

Limits of detection: benzene - 0.001 mg

toluene, xylene - 0.01 mg

pyridine - 0.02 mg

4-phenyl propylpyridine - 0.1 mg

TABLE 4

ALIPHATIC AMINES (DIMETHYLAMINE, ETHYLAMINE, METHYLAMINE, TRIETHYLAMINE) AND ANILINE AIR CONCENTRATIONS

# GERLINGER CASTING CORPORATION Salem, Oregon

HHE 81-133

		ALIPHATIC AMINES							ANILINE			
LOCATION	DATE	SAMPLE NUMBER	TIME MINUTES	DIMETHYL- AMINE mg/cu m	ETHYL- AMINE mg/cu m	METHYL- AMINE mg/cu m		SAMPLE NUMBER	TIME MINUTES	mg/cu m		
Middle of pouring floor (on edge of raised portion)	6-23-81	1	430	<2.5	<1.5	< 2.5	<2.5	2	430	< 0.5		
Middle of pouring floor (on edge of raised portion)	6-24-81	71	435	<1.4	<1.0	<1.4	<1.4					
4 ft from molder	6-23-81	21	425	<2.5	<1.5	<2.5	<2.5	22	425	<0.5		
4 ft from molder	6-24-81	.41	425	<1.5	<1.0	<1.5	<1.5	42.	425	< 0.3		
Attached to front of the sand mixer in the molders breathing zone.	6-23-81	33	400	<2.5	<1.5	<2.5	<2.5					
Attached to front of the sand mixer in the molders breathing zone.	6-24-81	61	410	<1.2	<1.0	<1.2	<1.2					

NOTE: No aromatic amine peaks greater than 0.01 mg relative to analine were observed.

Limits of detection - Dimethylamine, methylamine, triethylamine - 0.05 mg
Ethylamine - 0.03 mg
Aniline - 0.01 mg