I. TOXICITY DETERMINATION

It has been determined that employees in the resinoid mixing department are experiencing toxic effects of an irritant nature from exposure to excessive levels of furfural. This determination is based upon (1) environmental measurements, obtained on August 21-23, 1973, December 5-6, 1973 and March 19, 1974, in excess of existing standards; (2) medical interviews substantiating appropriate symptoms in a high proportion of employees; and (3) a review of the toxicologic properties of furfural. It should be emphasized that the type of symptomatology being experienced by employees (eye and upper respiratory tract irritation) is transient in nature and is not known to result in serious or permanent physical impairment.

Based upon air sampling results and medical evidence, it is also concluded that lead, fluoride, phenol, total dust, and silica dusts are not toxic as used or in the concentrations found.

II. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this Determination Report are available upon request from the Hazard Evaluation Services Branch, NIOSH, U.S. Post Office Building, Room 508, 5th and Walnut Streets, Cincinnati, Ohio 45202.

Copies have been sent to:

b. Authorized Representative of Employees
c. U. S. Department of Labor - Region X
d. NIOSH - Region X
e. Washington Department of Labor and Industry

For the purposes of informing the approximately 16 mixers and mixer helpers, the employer will promptly "post" the Determination Report in a prominent place(s) near where affected employees work for a period of 30 calendar days.
III. INTRODUCTION

Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S. Code 669(a)(6) authorizes the Secretary of Health, Education, and Welfare, following a written request by 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 National Institute for Occupational Safety and Health (NIOSH) received such a request from a representative of employees regarding exposure to compounds used in the formulation of grinding wheels in the Mixing Department of Pacific Grinding Wheel Co., Marysville, Washington.

IV. HEALTH HAZARD EVALUATION

A. Plant Process

The Pacific Grinding Wheel Co. manufactures both resinoid and vitrified grinding wheels. This request involved only the mixing operation connected with the production of the resinoid wheels. Each type of wheel manufactured has its own formulation, so the entire mixing operation consists of formulating numerous small batches (several hundred pounds or less). Although each batch has a different formulation, the same compounds are frequently used in each mix with only a change in the ratio of the ingredients.

The compounds used include:

Solids - Olivine sand, synthetic cryolite, quicklime, litharge, activated charcoal, silicon carbide, aluminum oxide, chalk and powdered resins which consist of phenolic resins, thoric acid, potassium sulfate and iron pyrite.

Liquids - Furfural, creosote, and liquid resins which consist of polymerized phenol-formaldehyde resin, free phenols and a small amount of caustic catalyst (NaOH).

The employees are exposed to these compounds in the form of dusts (both inhalation and skin contact), vapor (inhalation) and liquid (skin contact).

The Mixing is accomplished in vertical and tumbling mixers. Screening of the mixed materials is done using a riddle screen. The mixers, screens and storage bin outlets are all equipped with local exhaust ventilation.
B. Evaluation Design and Progress

1. Environmental Evaluation

The environmental air concentrations of the various materials were collected in the general air and in the breathing zone of the workers exposed. Many sampling difficulties were encountered during this evaluation resulting in five plant visits occurring between August 8, 1973 and March 19, 1974. The sampling for furfural revealed numerous technical problems.

The sampling method recommended by NIOSH involved collection on charcoal tubes with subsequent analysis by gas chromatography. This method was used during the first sampling session. At the same time, furfural concentrations were measured using a portable infrared analyzer and recorded on a strip chart. When the results of the two methods were compared, the charcoal tube results were about 40% of the corresponding infrared values. The infrared unit was recalibrated and all vapors that could be present were checked to see if they interfered and produced a falsely high result. None of the other vapors present interfered, thus it was concluded that valid measurements were obtained via the infrared method. Two additional days of sampling were performed. At this time, charcoal tube samples and infrared measurements were made side by side. Again the charcoal tube samples were approximately 40% of the infrared results. One thought was that polymerization was taking place on the tube. Additional charcoal tube samples were then collected and analyzed by the Washington Industrial Safety and Health Agency. Even at best, desorption was incomplete with carbon disulfide and ranged from approximately 20 to 70%. Additional research work is being conducted on the use of charcoal tubes for use with furfural. For this Health Hazard Evaluation, only the results obtained with the infrared analyzer will be reported.

2. Medical Evaluation

The medical evaluation conducted by the NIOSH physician on March 19, 1974 consisted of personal interviews and in some instances limited physical examination of the exposed employees. Interviews were all begun in a non-directed manner to elicit past and current complaints or symptoms which the individual attributed to his work and the temporal relationship of such symptoms to the job, free time, vacation periods, etc. Specific questions were then asked concerning the presence of and frequency of headaches, symptoms of eye irritation, throat irritation, ptyalism (excessive flow of saliva), cough, nasal irritation, nausea, vomiting, diarrhea, dizziness, giddiness, sensation of intoxication, skin problems, weight loss, and liver or kidney problems. Urine samples were collected on a prior visit, August 21-23, 1973 to aid in evaluation of employees exposure to lead, phenol and fluoride.

C. Evaluation (Sampling and Analytical) Methods

A Wilks Miran Portable Infrared Analyzer was used to sample for furfural. Sampling was continuous and the results were recorded on a strip chart. The
phenols were collected in 0.1 N NaOH in midget impingers with subsequent analysis using the gas chromatograph. Total dust (respirable dust plus non-respirable dust), free silica, fluoride and lead particulate samples were collected on 37 mm filters at a flow rate of 2.0 liter/minute. The total dust concentrations were measured by pre and post sample weighing of the filters. Free silica determinations were made on the same filters using the colorimeteric method. Fluoride samples were analyzed by the fluoride electrode method and lead was analyzed by the atomic absorption method. Furfural and phenol samples were collected in the general vicinity of the mixer, which approximated the breathing zone exposures, and the dust, fluoride and lead samples were collected in the breathing zone and in the general vicinity of the mixers.

Pre- and post-shift urine samples were collected from the mixers for fluoride and lead determinations. The fluorides were analyzed by the fluoride electrode method and the lead by the atomic absorption method. Post-shift urine samples were collected from the mixers and a selected number of press operators for phenols. The phenol test was a qualitative test using ferric chloride and was performed by the medical officer at the plant on freshly collected urine.

D. Evaluation Criteria

The evaluation criteria applicable to the individual substances of this evaluation are as follows:

The occupational health standards as promulgated by the U.S. Department of Labor (Federal Register, October 18, 1972, Title 29, Chapter XVII, Subpart G., Table G-1, G-2, G-3).

<table>
<thead>
<tr>
<th>Substance</th>
<th>8-hour time weighted average</th>
</tr>
</thead>
<tbody>
<tr>
<td>fluoride, as. dust</td>
<td>2.5 mg/m³ *</td>
</tr>
<tr>
<td>furfural (skin) ***</td>
<td>5 ppm **</td>
</tr>
<tr>
<td>phenol (skin)</td>
<td>5 ppm</td>
</tr>
</tbody>
</table>

1973 Threshold Limit Values for chemical substances and physical agents in the workroom environment as published by the American Conference of Governmental Industrial Hygienists.

<table>
<thead>
<tr>
<th>Substance</th>
<th>8-hour time weighted average</th>
</tr>
</thead>
<tbody>
<tr>
<td>inert dust (total)</td>
<td>10 mg/m³</td>
</tr>
<tr>
<td>lead</td>
<td>0.15 mg/m³</td>
</tr>
<tr>
<td>silica (total dust)</td>
<td>30 mg/m³ + % free SiO₂</td>
</tr>
</tbody>
</table>

* mg/m³ - milligrams of substance per cubic meter of air.

** ppm - parts of vapor or gas per million parts of air by volume at 25°C and 760 mm Hg pressure.

*** skin - refers to the potential contribution to overall exposure by the cutaneous route including mucous membranes and eyes, either by airborne or more particularly by direct contact with the substance.
Biological criteria for the toxicity determination of lead exposure is based on a urine lead level in excess of 0.20 mg per liter of urine and the fluoride exposure is based on a urine fluoride level in excess of 5 mg per liter of urine. The ferric chloride test on urine is sensitive at 1:1000 in detecting phenol, creosote, and other phenolic compounds.

E. Toxic Effects of Substances

**Fluoride** Acute poisoning from inhalation of the dusts of fluoride salts has rarely been recorded. Irritant effects upon the eyes and upper respiratory passages and nausea are noted at air levels of 5 mg/m³. Higher levels commonly result in nosebleeds. Exposure to excessive levels over very protracted time periods can result in mottling of tooth enamel and chronic bone changes (fluorosis) which may lead to severe crippling.

**Furfural** The physiologic effects of furfural are generally regarded as relatively mild. Furfural air concentrations of 1.9 to 14 ppm are reported to cause headaches, and throat and/or eye irritation in some individuals. The present TLV of 5 ppm probably is not sufficiently low to ensure the freedom of all persons from irritation. On rare occasions respiratory sensitization has occurred.

**Inert Dust** Inert or nuisance dusts produce little adverse effect upon the lungs and do not result in significant organic disease or toxic effects if kept under reasonable control. When inhaled, such dusts may provoke some cellular response, but the reaction is potentially reversible and progressive lung disease does not ensue.

**Lead** Lead is a well known toxic substance and its effects have been observed and documented for several centuries. Common signs and symptoms include loss of appetite, constipation, anemia, weakness, insomnia, headache, nervous irritability, muscle and joint pain, tremor, encephalopathy, and abdominal colic. In lead colic, the abdominal pain may be very severe. In workers who have had repeated attacks of colic, there is a tendency towards weakness of extensor muscle groups resulting in progressive paralysis most frequently manifested as wrist or foot "drop". Both ingestion and inhalation are important routes of absorption. Biologic monitoring is essential to assure that workmen exposed to inorganic lead are not absorbing unacceptable amounts. Unacceptable absorption of lead posing a risk of lead poisoning is demonstrated at levels of 0.080 mg/100 gms of whole blood or greater, or at levels of 0.20 mg/liter for urine.

**Phenol** Due to a relatively low volatility, phenol does not frequently constitute a serious respiratory hazard in industry. Vomiting, dizziness, delirium, convulsions, collapse, loss of consciousness, and oliguria are common signs and symptoms in severe cases of poisoning, which usually occurs through ingestion. An early sign of mild poisoning is dark colored urine. Phenol is readily absorbed through the skin producing an initial numbness and blanching. Later the skin becomes reddened and necrotic. Cresols and creosote have similar effects although they are regarded as being somewhat less toxic.
Silica. In contrast to inert or nuisance dusts, the inhalation of excessive crystalline free silica results in permanent lung damage which may be progressive even when exposure is stopped (silicosis). However, usually many years of exposure are required to initiate silicosis, unless massive exposure has occurred. The symptoms are progressive shortness of breath and cough. Tuberculosis and other respiratory diseases are frequently associated with silicosis during its chronic course.

F. Evaluation Results and Discussion

1. Environmental Results

Furfural results are shown in Table 1. The furfural concentrations were measured for 1390 minutes (23 hours 10 minutes) during four working shifts. These measurements were made in the general vicinity of workers to approximate the breathing zone levels. During this sampling time, the furfural concentrations were between 3.5 and 5.0 ppm for 150 minutes, 5 to 7.5 ppm for 530 minutes, 7.5 to 10 ppm for 400 minutes, 10 to 12.5 ppm for 160 minutes, 12.5 to 15 ppm for 30 minutes, and 15 ppm to 20 ppm for 120 minutes. Thus, air levels in excess of the evaluation criteria were present in nearly 90% of the total sample period.

Nine phenol samples were collected during three work shifts. Each sample was at least six hours in length. The average phenol concentrations during each of the shifts was 0.75, 0.95, and 0.53 mg/m\(^3\), which are all less than 10% of the evaluation criteria.

Litharge is used only occasionally during only one shift. The lead concentrations in the breathing zone of the worker using litharge in his mix was less than 0.0075 mg/m\(^3\) or approximately 5% of the evaluation criteria.

The four fluoride samples were all 0.02 mg/m\(^3\) or less which is less than 1% of the evaluation criteria (Table II).

Five samples were collected for total dust and free silica (Table III). The highest level measured was 4.4 mg/m\(^3\). All the samples were less than 60% of the inert dust evaluation criteria and the appropriate free silica evaluation criteria.

The local exhaust ventilation systems used to collect the vapors and dust from the mixers and storage bins was found to be recirculating 100% of the exhausted air. The air was passed through a cyclone, a bag house and then was recirculated back into the mixing room about 15 to 20 feet from the mixers. The dust collectors removed the dust, but were ineffective in removing vapors. In January of 1974, the re-entry of vapors was corrected. The Company changed the ventilation system so that vapor-contaminated air is now exhausted outside the building. The air is now exhausted directly by a fan located approximately 10 to 15 feet above the ground. Under certain atmospheric conditions the exhausted vapors could presently re-enter through a side door which is left open during nice weather.
2. Medical Evaluation Results

A total of 15 workers were interviewed. The average age was 34.6 years (range 26-68 years) and the average duration of employment with the Company was 6.4 years (range 1-27 years). An average of 1.6 years had been spent in the Resinoid Mix Area (range 1 week - 10 years).

Worker responses were determined by individual interview and confirmed where possible by physical examination. The majority of men had symptoms of eye and upper respiratory tract irritation which is consistent with the effects known to occur with exposure to furfural.

Eye irritation manifested by itching, burning, tearing and/or redness was reported by 11 of 15 workmen. In eight individuals it was noted at least twice weekly and usually was experienced daily by those men in greatest proximity to furfural spraying. Several individuals habitually use proprietary eye drops to help control their symptoms. Definite redness of the conjunctiva was noted in two workers although the majority of men were interviewed during the early portions of their shifts when such findings would be probably rather minimal.

Ten individuals noted frequent (usually daily) nasal irritation resulting in symptoms of stuffiness (plugging), dryness, or soreness. One of these, noted an occasional bloody nasal discharge. Dryness of the mouth or throat was reported by seven individuals and several workers chew gum in an attempt to alleviate this symptom.

NIOSH personnel (3) experienced similar symptoms (eye irritation, nasal stuffiness, and dryness of the mouth) during the course of the investigation. In one instance, when half-shift furfural concentrations averaging 13.5 and 16 ppm occurred, these symptoms were of rapid onset even though the investigators were not continuously in the environment. Similar symptoms were reported to be present in a majority of night shift workmen when average furfural values of 5.9 and 5.1 ppm occurred for the first and second halves of the shift, suggesting that the present standard may not be adequate to protect most individuals from irritative symptoms.

Thirteen of 15 workers reported one or more skin complaints. The most common symptoms (11/15) related to excessive dryness and a yellowish discoloration of the skin of the forearms and hands. This was confirmed by examination. Two individuals had noted phototoxic type reactions in the form of excessive sunburn responses from minimal exposure. These symptoms are thought to be the result of skin contact with creosote although furfural exposure undoubtedly contributed to the excessive dryness observed.

Cloth gloves are presently being used and by the end of the day they are moist with the liquids being used. This provides ample contact resulting in the cutaneous problems observed. A change to impervious gloves should alleviate these problems.
No other symptoms were noted with a frequency suggesting any causal relationship to the work environment.

Pre- and post-shift urine samples collected from the mixers for lead and fluoride were all in the normal range and similar to values found in the general population. The results are shown in Table IV. Qualitative tests made for the presence of phenol in the urine of the mixers were all negative.

Based on the air results and urine samples, it is concluded that lead, fluoride, phenol, total dust and silica dusts are not toxic in the concentrations found.

V. RECOMMENDATIONS

The following recommendations should aid in reducing the furfural concentrations in the general atmosphere in the mixing rooms.

1. Covers could be placed on the pans containing the mixed batches of materials prior to the pressing operations.

2. Local exhaust ventilation could be installed over the resin and furfural dispensers.

3. Avoid using compressed air to spray furfural into the mixers.

4. A larger percentage of fresh outside air could be added to the room heating and ventilation system.

VI. REFERENCES


VII. AUTHORSHIP AND ACKNOWLEDGMENT

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Olympia, Washington

Billy McArthur
Washington Industrial Safety & Health Agency
Olympia, Washington

Originating Office: Jerome P. Flesch
Chief, Hazard Evaluation Services Branch
Cincinnati, Ohio
<table>
<thead>
<tr>
<th>Date and Time</th>
<th>Total Sample Time in Min.</th>
<th>ppm Furfural (average)</th>
<th>ppm Furfural 10 Minute Averages (Range)</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>August 21, 1973</td>
<td>9:00 a.m. - 9:50 a.m.</td>
<td>50</td>
<td>13.5</td>
<td>10-17</td>
</tr>
<tr>
<td></td>
<td>11:00 a.m. - 3:00 p.m.</td>
<td>240</td>
<td>6.0</td>
<td>4.1-8.1</td>
</tr>
<tr>
<td>December 5, 1973</td>
<td>4:50 p.m. - 8:20 p.m.</td>
<td>210</td>
<td>10.0</td>
<td>8.5-13.5</td>
</tr>
<tr>
<td></td>
<td>8:20 p.m. - 11:30 p.m.</td>
<td>190</td>
<td>8.7</td>
<td>7.3-12.3</td>
</tr>
<tr>
<td>December 6, 1973</td>
<td>7:40 a.m. - 9:40 a.m.</td>
<td>120</td>
<td>16.3</td>
<td>11.5-18.5</td>
</tr>
<tr>
<td></td>
<td>1:00 p.m. - 4:10 p.m.</td>
<td>190</td>
<td>7.4</td>
<td>5.0-9.5</td>
</tr>
<tr>
<td></td>
<td>4:10 p.m. - 8:10 p.m.</td>
<td>240</td>
<td>5.9</td>
<td>5.0-7.8</td>
</tr>
<tr>
<td></td>
<td>8:10 p.m. - 10:40 p.m.</td>
<td>150</td>
<td>5.1</td>
<td>3.5-7.5</td>
</tr>
</tbody>
</table>

1390 Minutes =
23 hours 10 minutes

* ppm - parts of vapor or gas per million parts of air by volume at 25°C and 760 mm Hg pressure
### TABLE II
AIR SAMPLE RESULTS OF LEAD AND FLUORIDE
AUGUST 21-23, 1973

**LEAD AND FLUORIDE**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Sample #</th>
<th>Location</th>
<th>Air Concentration mg/m³</th>
<th>Sample Time minutes</th>
<th>Evaluation Criteria mg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lead</td>
<td>1</td>
<td>Resinoid Mixer BZ</td>
<td>0.0075</td>
<td>515</td>
<td>0.15</td>
</tr>
<tr>
<td>Fluoride</td>
<td>1</td>
<td>Resinoid Mixer BZ</td>
<td>0.02</td>
<td>515</td>
<td>2.5</td>
</tr>
<tr>
<td>Fluoride</td>
<td>2</td>
<td>Resinoid Mixer GA</td>
<td>0.006</td>
<td>497</td>
<td>2.5</td>
</tr>
<tr>
<td>Fluoride</td>
<td>3</td>
<td>Resinoid Mixer BZ</td>
<td>0.004</td>
<td>392</td>
<td>2.5</td>
</tr>
<tr>
<td>Fluoride</td>
<td>4</td>
<td>Resinoid Mixer BZ</td>
<td>0.003</td>
<td>516</td>
<td>2.5</td>
</tr>
</tbody>
</table>

* mg/m³ Milligrams of substance per cubic meter of air
** BZ Breathing zone of the worker
*** GA General area the worker performs his job
### TABLE III

**AIR SAMPLE RESULTS OF TOTAL DUST AND FREE SILICA**

**AUGUST 21-23, 1973, MARCH 19, 1974**

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Location</th>
<th>Sample Time</th>
<th>Total Dust mg/m³</th>
<th>Inert Dust mg/m³</th>
<th>% Free SiO₂ In Sample</th>
<th>Evaluation Criteria mg/m³ for Silica Bearing Dust</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>vitrified mixer GA</td>
<td>490</td>
<td>0.56</td>
<td>10</td>
<td>10</td>
<td>2.3</td>
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<tr>
<td>2</td>
<td>vitrified mixer BZ</td>
<td>510</td>
<td>1.5</td>
<td>10</td>
<td>10</td>
<td>2.3</td>
</tr>
<tr>
<td>3</td>
<td>resinoid mixer BZ</td>
<td>460</td>
<td>3.4</td>
<td>10</td>
<td>10</td>
<td>7.5</td>
</tr>
<tr>
<td>4</td>
<td>resinoid mixer BZ</td>
<td>300</td>
<td>4.4</td>
<td>10</td>
<td>10</td>
<td>7.5</td>
</tr>
<tr>
<td>5</td>
<td>resinoid mixer BZ</td>
<td>320</td>
<td>2.7</td>
<td>10</td>
<td>1.8</td>
<td>6.3</td>
</tr>
</tbody>
</table>

* mg/m³ Milligrams of substance per cubic meter of air

** BZ Breathing zone of the worker

** GA General area the worker performs his job

** Evaluation criteria = \( \frac{30}{\% \text{ free SiO}_2 + 3} \) in sample
TABLE IV
URINE SAMPLES FOR LEAD AND FLUORIDE
AUGUST 21-23, 1973

<table>
<thead>
<tr>
<th>Mixer Number</th>
<th>Pre or Post-Shift Sample</th>
<th>Fluoride mg/liter of Urine</th>
<th>Lead mg/liter of Urine</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pre</td>
<td>0.43</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>Post</td>
<td>0.37</td>
<td>0.01</td>
</tr>
<tr>
<td>2</td>
<td>Pre</td>
<td>0.41</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Post</td>
<td>0.46</td>
<td>0.02</td>
</tr>
<tr>
<td>3</td>
<td>Pre</td>
<td>0.69</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>Post</td>
<td>0.48</td>
<td>0.01</td>
</tr>
<tr>
<td>4</td>
<td>Pre</td>
<td>0.41</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Post</td>
<td>0.48</td>
<td>0.02</td>
</tr>
<tr>
<td>5</td>
<td>Pre</td>
<td>0.35</td>
<td>0.01</td>
</tr>
<tr>
<td>6</td>
<td>Pre</td>
<td>1.17</td>
<td>Insufficient sample</td>
</tr>
<tr>
<td>7</td>
<td>Pre</td>
<td>0.33</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Biological evaluation criteria

Fluoride in urine 5 mg/liter of urine
Lead in urine 0.20 mg/liter of urine