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U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE  
CENTER FOR DISEASE CONTROL  
NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH  
CINCINNATI, OHIO 45226  
HEALTH HAZARD EVALUATION DETERMINATION  
REPORT NO. 76-38-326

RYCRAFT, INC.  
CORVALLIS, OREGON

SEPTEMBER 1976

I. TOXICITY DETERMINATION

It is determined that the employees' exposure in the kiln room to sulfur dioxide, formaldehyde, phenols, and heavy metals (cobalt, lead, manganese, tin, and vanadium) are not toxic as used or found on April 15, 16 and May 3 and 4, 1976. This conclusion is based on 1) the sample results which showed the phenols and metals were not detectable and the sulfur dioxide and formaldehyde average concentrations were well below the most restrictive of the evaluation criteria (formaldehyde concentrations were 8% or less of the American Conference of Governmental Industrial Hygienists recommended levels of 2 ppm and sulfur dioxide concentrations were 20% or less than the NIOSH recommended levels of 2 ppm); and, 2) slight nose and throat irritation experienced by the employees exposed to sulfur dioxide and formaldehyde are expected responses at the concentrations found and are not considered detrimental. In addition the employees do not usually work in the kiln room on a regular basis during the firing of the kiln.

II. DISTRIBUTION AND AVAILABILITY

Copies of this Determination Report are available upon request from the Information Resources and Dissemination Section, Division of Technical Services, NIOSH, Robert A. Taft Laboratories, 4676 Columbia Parkway, Cincinnati, Ohio 45226. Copies have been sent to:

- (1) RyCraft, Inc., Corvallis, Oregon
- (2) Accident Prevention Division, State of Oregon
- (3) Occupational Safety and Health Administration, Seattle, Washington

For the purpose of informing the approximately eleven affected employees, the employer will promptly "post" the Determination Report, for a period of thirty (30) calendar days, at or near the work place(s) of the affected employees.

### III. INTRODUCTION

Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6), authorizes the Secretary of Health, Education, and Welfare, following receipt of 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 National Institute for Occupational Safety and Health (NIOSH) received such a request from the owners of RyCraft, Inc., Corvallis, Oregon to determine if gases being emitted from the kilns during the firing of greenware and glazes have toxic effects in concentrations found.

### IV. HEALTH HAZARD EVALUATION

#### A. Description of Process

RyCraft manufactures small ceramic cookie stamps. Production of the stamps includes rolling of the clay, cutting the blanks, pressing in the design, installation of a handle, firing the greenware, dipping the bisque in a glaze and firing of the glaze. This evaluation covers only the firing of the greenware and glaze in the kiln room.

The kiln room is approximately 11 feet by 12 feet and contains six (6) kilns. There is a small ceiling fan in a corner of the room that exhausts approximately 1000 cubic feet of air per minute. When the fan is on, the window is cracked to provide for make-up air. Smoke tube tests indicated a poor air flow pattern.

The unfired stamps are placed in kilns and are heated to 1940° F. After the bisque is cooled, they are removed and the glaze applied. They are then inserted in the kiln and fired to 1915° F. During the firings, the materials that are volatile at temperatures less than 1940° F are emitted from the kiln. Once in the general atmosphere of the kiln room, they are exhausted through a ceiling fan.

#### B. Study Progress and Design

The initial survey was conducted on April 15 and 16, 1976 and a follow-up on May 3 and 4, 1976.

The request involved the kiln room where, during the firing of the greenware and glaze, irritating vapors are given off. The paper (e.g., small boxes, written material, etc.) in the room is deteriorating with time which indicates some sulfur dioxide (SO<sub>2</sub>) has been present.

On April 15, samples were collected during the glaze firing for SO<sub>2</sub> and metals present in the glazes. Detector tube measurements taken right at the kilns, indicated SO<sub>2</sub> was not present but an irritating substance was coming off the kiln. On April 16, samples were collected for SO<sub>2</sub> during the greenware firing. Detector tubes indicated SO<sub>2</sub> to be present in low concentrations.

RyCraft had a letter from the glaze manufacturer that listed the chemical composition of the glazes; however, none of the materials listed when heated, would produce an irritation to the exposed employee similar to the type they were experiencing. Subsequent correspondence with the glaze manufacturer revealed trace quantities of o-phenylphenol and formaldehyde were added but were not listed on the original correspondence. On May 3 and 4 samples were collected for phenols and formaldehyde during the glaze firing.

A total of thirteen (13) general air samples were collected, seven (7) of which were in the kiln room and six (6) in adjacent rooms. Of the thirteen (13) samples, six (6) were for sulfur dioxide, two (2) for phenols, two (2) for formaldehyde and three (3) for metals.

#### C. Evaluation Methods

##### 1. Environmental

Employees' potential exposures to the substances present were determined by the collection of general area samples near the kiln. General area samples were collected in lieu of personal samples in order to evaluate maximum exposures since employees do not work in the kiln room on a regular basis during the firing of the kilns.

Sulfur Dioxide - The sampling method consisted of collection of the gas in midget impingers using 0.3 N hydrogen peroxide as the absorbing solution with subsequent titration with barium perchlorate<sup>(1)</sup>. A MSA Model G pump was used to draw the air through the impingers at a flow rate of 1.5 lpm.

Phenols - The sampling method consisted of collection of the vapor in midget impingers using sodium hydroxide as the absorbing reagent with subsequent analysis using gas chromatography<sup>(1)</sup>. A MSA pump was used to draw the air through the impingers at a flow rate of 1.0 lpm.

Formaldehyde - The sampling method consisted of collection of the vapor in midget impinger using 1% sodium bisulfite as the absorbing reagent with subsequent colorimetric analysis<sup>(1)</sup>. MSA Model G pumps were used to draw the air through the impingers at a flow rate of 1.0 lpm.

Metals (lead, tin, manganese, cobalt, vanadium) - The sampling method consisted of collection of the metals on Millipore, type AA 37 mm filters with subsequent analysis using atomic absorption techniques<sup>(1)</sup>. MSA Model G pumps were used to draw the air through the filters at a flow rate of 1.5 lpm.

## 2. Medical

Employees were asked non directed questions to elicit past and current complaints of symptoms which the individual attributed to his work.

The adverse effects which can be caused by exposures to the substances measured in detectable concentrations during this evaluation are listed below.

Formaldehyde - "The major effect of exposure to formaldehyde in air is local irritation of the eyes, nose and throat. Some persons, if not acclimatized, will experience unpleasant eye, nose and throat irritation at concentrations below 5 ppm. Exposure to 10 - 20 ppm of the nose and throat may be associated with sneezing, difficulty in taking a deep breath, and coughing. Recovery is prompt from these transient effects."<sup>(2)</sup>

Sulfur Dioxide - "Sulfur dioxide gas is an irritant gas: 6 to 12 ppm causes immediate irritation to nose and throat. Three-tenths to 1 ppm is the least amount irritating to the eyes. Although sulfur dioxide dissolves readily and its inhalation affects chiefly the upper respiratory tract and bronchi, it may cause edema of the lungs or glottis and can produce respiratory paralysis."<sup>(3)</sup>

## D. EVALUATION CRITERIA

The evaluation criteria applicable to this evaluation is as follows: the Occupational Health Standards as promulgated by the U.S. Department of Labor, Code of Federal Regulations, Dated July, 1975, Part 1910, Title 29, Chapter XVII, Subpart Z, Table Z-1 and Z-2; American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Values (TLV) for Chemical Substances and Physical Agents in the Workroom Environment for 1975; and NIOSH Criteria Documents for Recommended Standards of Occupational Exposure to Sulfur Dioxide <sup>(4)</sup>, and Occupational Exposure to Lead<sup>(5)</sup>.

SUBSTANCE	8-HOUR TIME WEIGHTED AVERAGE		
	U.S. Dept of Labor Standards	ACGIH TLVs	NIOSH Recommended Levels
Cobalt	0.1 mg/m <sup>3</sup> **	0.1 mg/m <sup>3</sup>	-
C* Formaldehyde	3 ppm ***	2 ppm	-
Lead	0.2 mg/m <sup>3</sup>	0.15 mg/m <sup>3</sup>	0.15 mg/m <sup>3</sup>
C Manganese	5 mg/m <sup>3</sup>	5 mg/m <sup>3</sup>	-
o-Phenylphenol	-	-	-
Sulfur Dioxide	5 ppm	5 ppm	2 ppm
Tin	2 mg/m <sup>3</sup>	2 mg/m <sup>3</sup>	-
C Vanadium Oxide Fumes	0.1 mg/m <sup>3</sup>	0.1 mg/m <sup>3</sup>	-

\* C - Ceiling concentration not to be exceeded

\*\* mg/m<sup>3</sup> - Milligrams of substance per cubic meter of air

\*\*\* ppm - Parts of vapor or gas per million parts of air

#### E. EVALUATION RESULTS AND DISCUSSION

The environmental sample results are shown in Table I. Sulfur dioxide was not detectable in the kiln room on April 15 during the firing of the glaze. The reason sulfur dioxide is not detectable during the firing of the glaze is that all sulfur dioxide is probably driven off during the firing of the greenware.

On April 16 the kilns containing the greenware were away from the ceiling fan and out of the air flow patterns from the window to the ceiling fan. The average sulfur dioxide concentration during this firing was 0.4 ppm. Sulfur dioxide was not detectable in the adjacent rooms during the firing.

The metals present in glazes were not detectable either in the kiln room or in the adjacent rooms.

Phenols were not detectable in the kiln room on May 3 and 4 during the firing of the glaze. During the same period, the average formaldehyde concentrations were 0.16 ppm and 0.07 ppm. The concentrations measured were average concentrations and hence the peak concentrations are not known. The peaks can be assumed to be higher since the sample periods started when the kilns were turned on and until the temperatures in the kilns were elevated to a point when the formaldehyde would be vaporized, very little would be collected, thus giving a lower average concentrations.

Two of the employees, who entered and did some work in the rooms on the day the samples were collected, stated they had irritation of the nose and throat. This investigator, upon entering the room to check the sampling equipment, also felt an immediate irritation of the nose and throat; but it went away upon leaving the room.

#### F. CONCLUSIONS

It is determined that the employees' exposures in the kiln room to sulfur dioxide, formaldehyde, phenols and heavy metals (cobalt, lead, manganese, tin, and vanadium) are not toxic as used or found on April 15, 16 and May 3 and 4, 1976. This conclusion is based on 1) the sample results which showed the phenols and metals were not detectable and the sulfur dioxide and formaldehydes average concentrations were well below the most restrictive of the evaluation criteria (formaldehyde concentrations were 8% or less of the American Conference of Governmental Industrial Hygienists recommended levels of 2 ppm and sulfur dioxide concentrations were 20% or less of the NIOSH recommended levels of 2 ppm); and, 2) slight nose and throat irritation experienced by the employees exposed to the sulfur dioxide and formaldehyde are expected responses at the concentrations found and are not considered detrimental. In addition the employees do not usually work in the kiln room on a regular basis during the firing of the kilns.

#### G. RECOMMENDATIONS

A local exhaust ventilation system directly over the kilns to capture the gases as they are emitted was recommended. Suggested drawings from the ACGIH Industrial Ventilation Manual were sent to RyCraft, Inc. At the time of the completion of this report, a new local exhaust ventilation system has been installed. The owner reports a tremendous improvement and the odor and irritation produced previously by the gases are no longer present.

V. REFERENCE

1. NIOSH Manual of Analytical Methods, HEW Publication NO. 75-121
2. Formaldehyde - Hygienic Guide Series of the American Industrial Hygiene Association
3. Patty, F.A., "Industrial Hygiene and Toxicology", Vol II, 2nd Edition, Page 894, John Wiley and Love, Inc., New York, 1963
4. NIOSH Criteria Document for Occupational Exposure to Sulfur Dioxide, 1974
5. NIOSH Criteria Document for Occupational Exposure to Inorganic Lead, 1972

VI. AUTHORSHIP AND ENVIRONMENTAL EVALUATION

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TABLE II  
RYCRAFT INC., CORVALLIS, OREGON  
RESULTS OF GENERAL AREA SAMPLES

LOCATION	DATE	MATERIAL BEING FIRED	SAMPLE NUMBER	SAMPLE TIME MIN.	VOL. AIR SAMPLED LITERS	SUBSTANCE
						SULFUR DIOXIDE ppm *
Packing Room	4-15-76	Glaze	1	420	630	ND **
Main Assembly Room	4-15-76	Glaze	2	270	405	ND
Kiln Room	4-15-76	Glaze	3	420	630	ND
Packing Room	4-16-76	Greenware	4	690	1035	ND
Main Assembly Room	4-16-76	Greenware	5	690	1035	ND
Kiln Room	4-16-76	Greenware	6	945	1417	0.4
						PHENOLS ppm
Kiln Room	5-3-76	Glaze	8	90	90	ND
Kiln Room	5-4-76	Glaze	10	90	90	ND
						FORMALDEHYDE ppm
Kiln Room	5-3-76	Glaze	7	90	90	0.16
Kiln Room	5-4-76	Glaze	9	90	90	0.07
						METALS
Packing Room	4-15-76	Glaze	AA 1	420	630	All Less than Detectable Amounts of Cobalt, Lead, Manganese, Tin, Vanadium
Main Assembly Room	4-15-76	Glaze	AA 2	270	405	
Kiln Room	4-15-76	Glaze	AA 3	420	630	

\* ppm - Parts of vapor or gas per million parts of air

\*\* ND - Non detectable (Lower limits of detection, SO<sub>2</sub> - 0.01 mg/ml; Phenols - 0.01 mg/ml  
Cobalt - 0.001 mg; Lead - 0.002 mg; Manganese - 0.001 mg; Tin - 0.003 mg;  
Vanadium - 0.005 mg)