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. 76-108-365

ROCKY MOUNTAIN MANUFACTURING AND WIRE COMPANY
CLEANING DEPARTMENT
PUEBLO, COLORADO

MARCH 1977

I. TOXICITY DETERMINATION

An environmental investigation was conducted at the Rocky Mountain Manufacturing and Wire Company, Pueblo, Colorado in September 1976 and January 1977. The purpose of the investigation was to evaluate the exposures of wire cleaners to materials used in the Cleaning Department. On the basis of environmental data collected during the survey, administration of medical questionnaires, observation of work practices, and a review of the available literature relevant to the toxicity of the substances used in the work area, it has been determined that worker exposures to potassium permanganate and copper sulfate were not toxic under the conditions which existed during this evaluation. While air sampling results indicate that worker exposures to airborne sulfuric acid were within acceptable levels, workers have experienced upper respiratory tract irritation in the past. This irritation appeared to have been caused by sulfuric acid mist. Recommendations are provided for reducing worker exposures to these substances.

II. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this Determination Report are currently available upon request from NIOSH, Division of Technical Services, Information and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 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:

a) Rocky Mountain Manufacturing and Wire Company, Pueblo, Colorado
b) U.S. Department of Labor - Region VIII
c) NIOSH - Region VIII

For the purpose of informing the approximately eight "affected employees" the employer shall promptly "post" for a period of 30 calendar days the Determination Report in a prominent place(s) near where exposed employees work.

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 a written request by an 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 Plant Supervisor of the Rocky Mountain Manufacturing and Wire Company to evaluate the exposures to the employees to the various materials used in the Cleaning Department. The wire cleaners who work in this Department are exposed to sulfuric acid, potassium permanganate and copper sulfate. The requester expressed a desire to become knowledgeable about the appropriate safe handling and use of these materials. The employees had experienced symptoms such as "headaches, skin burns, rhinitis, dermatitis, coughing and sneezing."

IV. HEALTH HAZARD EVALUATION

A. Plant Process

The cleaning department occupies approximately 2,800 square feet on the west end of Rocky Mountain Manufacturing and Wire Company, the total building area being 45,000 square feet. A 12 foot by 10 foot area on the west wall of the cleaning room consists of metal slots open to the outside environment. The prevailing winds of the area are from the west, thus, the wind current brings air into the Cleaning Department from the outside. A large fan manufactured by the Penn Ventilation Company, #FX50B is located in the ceiling approximately six feet east of the north end of the wall slots. This fan vibrates on its mounts when in operation and was found to exhaust approximately 40,500 cfm. This provides about 45 room air changes per hour.

Six open surface, 1800 gallon (8,182 liters) capacity tanks are arranged in "L" formation at the west end of the room. An "L" shaped cat-walk elevated to a height of four feet runs the length of the tanks so that the persons performing the wire cleaning may be nearer to the tank tops for easier handling of the crane.

To the south side of the room is an electric furnace in a pit approximately 10 feet lower than the surrounding floor, enclosed by a metal rail. The wire cleaning process begins at the electric furnace. A catch weight of mild steel wire (200 pounds) is put on an annealer base, then the bell is placed over the retort all in the pit on the south end of the cleaning room. The retort houses an electric unit that heats the wire to 200°F (94°C) to "soften" it. After treatment, the wire is lifted off with a crane and allowed to cool to room temperature.

When the wire is at room temperature various procedures are initiated to prepare it for copper coating. The first is a dip into a 200°F (94°C) sulfuric acid (10% by volume) bath lasting 30 seconds to one minute. The wire is then rinsed over a water tank with water emitted from a hose at 90 pounds pressure. Vast amounts of "steam" are generated when the water contacts the wire.

A potassium permanganate ($KMNO_4$) 200°F (94°C) bath for four minutes constitutes the next process. This is followed by a second water bath and a second sulfuric acid bath for another 30 seconds. The wire is now sufficiently prepared for the copper coat and is dipped by crane into a 120°F (56°C) copper sulfate (Cu_2SO_4) bath for six minutes. A coating of 2% borax is then applied via a dip in the last tank. The borax acts as a lubricant allowing for an easier draw through the diameter reducing machines. The final product is a copper-coated mild steel wire of the correct diameter for use in welding guns.

Ten thousand pounds per day of welding wire is produced by Rocky Mountain Manufacturing and Wire Company. The cleaning operation employs eight workers on two 8-hour shifts. The men are exposed to the mist created by the heated tanks upon entrance to the cleaning department but probably receive the highest exposure moving the catch from tank to tank with the crane while on the cat-walk. The mists are heavier than air and are not drawn to the ceiling fan at an effective rate for removal from the area. The slots to the west of the tanks increase potential exposure by allowing outside air to blow the mist toward the workers in the room.

The wire cleaners had been equipped with respirators manufactured by Welsh Manufacturing Company but they had not been instructed in respirator maintenance. The cartridges in the respirators provided over protection in that they were protective against organic vapors, sulfur dioxide, radionuclides plus dust and mist under NIOSH approval number TC-21B-11F. However, the cartridges had not been replaced since their installation three months prior to the survey. The inhalation and exhalation valves on the respirators were observed to be damaged or missing and an accumulation of dirt indicated little to no cleaning of the face piece.

B. Evaluation Design

An initial industrial hygiene survey was conducted by NIOSH industrial hygienists on September 27 and 28, 1976. Air sampling was conducted and medical questionnaires were administered at this time. The results of laboratory analysis of these air samples were judged to not be accurate and air sampling was again conducted on January 4 and 5, 1977.

C. Evaluation Methods

Personal air sampling was performed by attaching two MSA Model G Sampling pumps to the belts on each worker in the wire

cleaning area. These pumps drew air at 1.5 liters per minute through a 37 mm/0.8 um mixed cellulose ester membrane filter. One filter was analyzed for sulfuric acid by conversion to the sulfate ion and titration to an end point. The second filter, attached to the second pump, was analyzed for copper and manganese representing exposure to copper sulfate and potassium permanganate. Analysis for copper and manganese involved filter digestion with nitric acid, solubilization in hydrochloric acid and analysis by the atomic absorption spectrophotometry method (analysis was performed under contract for NIOSH by the Utah Biomedical Test Laboratory).

The flow rates were adjusted for temperature and pressure by the following equation:

$$Q \text{ actual} = Q \text{ indicated} \left(\frac{P \text{ calculated}}{P \text{ actual}} \times \frac{T \text{ actual}}{T \text{ calculated}} \right)^{1/2}$$

Q = flow rate in lpm
P = press. in mm Hg
T = temperature in degrees Kelvin

The correction factor was deemed necessary because the pumps had been calibrated in Cincinnati, Ohio, elevation 490 feet above sea level, and the sampling performed in Pueblo, Colorado elevation 4,668 feet above sea level.

The actual barometric pressures at the time of sampling in Pueblo were obtained from the Department of Commerce, Division of National Oceanic and Atmospheric Administration, Pueblo, Colorado. The actual flow rate of the pumps was calculated to be 1.62 lpm instead of 1.5 lpm for both the 27th and 28th of September.

2. Medical Investigation

Health Hazard Evaluation Initial Survey form number 68-R1236, a non-directed medical questionnaire, was administered to six of the eight wire cleaners. This questionnaire is designed to elicit health complaints attributable to work exposures.

D. Evaluation Criteria

1. Environmental Standard

The set of standards promulgated by the U.S. Department of Labor, designed to protect the health and safety of workers exposed to any of approximately 400 chemicals for an 8-hour work day, 40-hour work week, over a working lifetime, list sulfuric acid at 1.0 mg/M^3, copper dust or mist at 1.0 mg/M^3 and a ceiling value of 5.0 mg/M^3 for manganese.[1] The Threshold Limit Values (TLV's) recommended by the American Conference of Governmental Industrial Hygienists have the same values for these compounds as the Department of Labor[2]. The TLV's represent airborne concentrations of substances to which "nearly all" workers may be exposed

without adverse effect. NIOSH recommends 1.0 mg/M^3 [3] as a safe occupational standard for sulfuric acid but has not made recommendations for copper mist or manganese.

2. Toxicological Effects

a) Sulfuric Acid

Sulfuric acid has a great affinity for water and reacts with water producing a strong exothermic reaction. For this reason, it will remove water from any organic material in which it comes into contact, especially skin, thus causing burns and charring of the skin. Sulfuric acid contact with the cornea of the eye causes irreparable corneal damage resulting in blindness. Inhalation of sulfuric acid mist can result in respiratory tract irritation cough, alterations in respiration, pulmonary edema and chronic pulmonary fibrosis.[3]

Rocky Mountain Manufacturing and Wire Company uses a 10% by volume solution of sulfuric acid heated to 200°F in their cleaning process.

b) Copper

The wire is coated with copper by dipping it into a tank containing copper sulfate heated to 200°F. The compound is purchased from Amchem Corporation under the brand name of Cuprodine 9®. Copper is absorbed in the intestinal tract and bound initially to serum albumin and ultimately to alpha cerulo plasmin. Excess copper is stored in the bones. Excessive exposure does not generally result in chronic disease, however there is increased speculation that increased serum copper levels may lead to atherosclerosis.[5]

Acute poisoning resulting from the ingestion of copper sulfate may cause death. The more common symptoms are vomiting, hypotension, melena, coma and jaundice.[5] Both copper and manganese have the capability to produce vomiting.

c) Manganese

Manganese is used in the Cleaning Department as potassium permanganate ($KMNO_4$) at 200°F. The compound is also purchased from the Amchem Corporation under the trade name of Redolene 7000®.

Potassium is bound to permanganate by an ionic bound that would dissociate in solution

$$KMNO_4 \longrightarrow K^+ + MnO_4^-$$

The standard reduction potential of the following reaction:

$$MnO_4^- \longrightarrow MnO_2$$

is + 1.679[6] meaning this reaction has a great tendency[7] to occur especially considering that the open surface tank in which it is used is heated to 200°F. The complete balanced equation is as follows:

$$MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O.$$ [6]

In summary, potassium permanganate may be the compound added to the open surface tank, but manganese dioxide would be the compound to which the wire cleaners would have potential exposure.

The human body regulates the tissue level of manganese with a homeostatic system involving its excretion from the gastrointestinal tract via the bile. The regulating mechanism accounts for the lack of systemic toxicity from over exposure to manganese. However, the inhalation of manganese dioxide may cause two industrial diseases. The less serious is manganese pneumonitis that is a result of acute exposure. Men working in plants with high concentrations of manganese show 30 times higher than normal incidence of respiratory disease.[5]

The more serious disease results from chronic inhalation of manganese dioxide and involves the central nervous system. Those who suffer from the disease exhibit psychiatric disorders such as irritability, difficulty in walking, speech difficulties and various other symptoms. These symptoms would occur after two years of chronic exposure to manganese dioxide. Rocky Mountain Manufacturing and Wire Company has operated their cleaning department for a period of six months, thus one would not expect the more serious manganese dioxide disease symtomatology to be exhibited in the wire cleaners.[5]

E. Evaluation Results

1. Air Sampling Results

The results of personal air sampling in the Wire Cleaning Department for sulfuric acid, copper, and manganese are summarized in Table I.

Air concentrations of sulfuric acid ranged from below the limit of detection to 0.64 mg/M^3. The sulfuric acid analysis results for September 27 and 28, 1976 are questionable because of unexpectedly high concentrations of sulfuric acid on blank filter samples (blank filters are those which are handled identically to filter samples except that no air is drawn through them).

Air concentrations of copper ranged from 0.002 to 0.050 mg/M^3. Air concentrations of manganese ranged from below the limit of detection to 0.097 mg/M^3. These levels are all below the OSHA standards of 1.0 mg/M^3 (for copper) and 5.0 mg/M^3 (for manganese).

2. Medical Questionnaire Results

Medical questionnaires administered to the six employees (all male with a mean age of 23 years, and a mean period of five months working in the Cleaning Department) elicited health complaints of the following type and frequency.

Reported Symptom(s)	Number of Workers Reporting These Types of Symptoms
Skin irritation/itching/rash	5
Increased nasal or sinus secretions/sneezing	3
Irritation/watering of eyes	3
Increased time required for minor cuts to heal	2
Loss of hair	1
Fatigue	1
Blood discharge when blowing nose	1
Upset stomach	1

Most of these reported symptoms were apparently of a non-serious nature and had not required medical treatment.

F. Conclusions

Air sampling conducted during these survey dates failed to detect either sulfuric acid, copper, or manganese levels exceeding exposure limits. These air sampling results are supportive of the fact that acute/immediate effects were not reported by workers during these visits. However, worker complaints (in the past) of eye and nasal irritation suggest that excessive exposure to sulfuric acid mist has occurred at times. The reported skin irritation and burns were probably a result of direct skin contact with sulfuric acid or because of skin contact with contaminated clothing. While vomiting is one of the symptoms of excessive manganese or copper exposure(s), there were no other reported symptoms suggesting that over exposure(s) to manganese or copper had occurred.

The reported health complaints are not unexpected since the wire cleaning operation was conducted in such a manner that the potential for worker exposures existed: the sulfuric acid, copper sulfate, and potassium permanganate tanks had inadequate control of mist generation; the respirator program was inadequate (e.g. - poorly fitting face pieces, and poor maintenance and cleaning) for preventing inhalation exposures; and poor personal hygiene (soiled work clothing, and cigarette smoking in the work area) increased the potential for ingestion and inhalation exposure.

V. RECOMMENDATIONS

1. The mist generated from the cleaning tanks should be controlled. This could be accomplished in the following ways:

a) Keep the tanks covered when not in use.

b) Apply a surface tension liquid to each tank to retard the generation of mist. Plastic balls could also be used.

Mist generation control at these operations would reduce maintenance and material costs:

1) there was evidence of corrosion of the I-beams,

2) there was evidence of corrosion of the fan and roofing material around the fan,

3) the company would lose less of its chemicals,

4) less heat would escape the tanks and therefore less fuel would be needed to keep the tanks at the proper temperature.

2. Personal Protection and Personal Hygiene:

A respirator program meeting the requirements of 29 CFR 1910.134 should be established. The respirators in current use should be used as an interim measure until engineering controls can be implemented at this operation. Workers should not be assigned to tasks requiring use of respirators unless it has been medically determined that they are physically able to perform the work and use the equipment. Respirators must be properly fitted (faces differ greatly in shape and a given respirator does not fit everyone) and maintained to provide the intended protection.

A respirator should be assigned to an individual and not shared by several workers. The respirator cartridges should be changed on a regular basis, probably once a week (heavy use may require that they be changed more frequently). Respirators should be cleaned and inspected after use each day: time should be made available for an individual to dismantle the respirator (removing the straps, cartridges, and exhalation and inhalation valves), inspect for damaged parts, wash the respirator (soap and water or products specifically for respirator cleaning and sanitizing are appropriate), and assemble the respirator, replacing any damaged parts. The respirator manufacturer should be contacted for more details on the proper use and maintenance. NIOSH has recently published a guide to respiratory protection.[8]

The workers also should be instructed about necessary personal hygiene practices when working with acid solutions. These are as follows:

a) Wear protective gloves when working around the tanks.

b) Wear freshly laundered clothes daily.

c) Wash exposed areas of the skin before eating.

d) Shower daily to rid the skin of any acid residue.

e) Do not smoke, eat or drink in the cleaning department.

In conclusion, it is possible to reduce the discomforts and health hazards associated with working in the cleaning department by a team effort on the part of both the employer and the employees by following the suggestions outlined above.

VI. REFERENCES

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5. Casarett, LJ., Doull, J., Toxicology The Basic Science of Poisons, MacMillan Publishing Company, Inc., New York, pg. 472-474, 1975.

6. CRC Handbook of Chemistry and Physics, 54th Edition, CRC Press, Cleveland, Ohio, pg. D 121, 1973-1974.

7. Sienko, MJ., Plane, RA., Chemistry: Principles and Properties, McGraw Hill Company, New York, N.Y., pg. 301-303, 1966.

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VII. AUTHORSHIP AND ACKNOWLEDGMENTS

Report Prepared By:

Brenda H. Haas
Industrial Hygienist

Jack O. Geissert
Industrial Hygienist
Industrial Hygiene Section
Hazard Evaluation and
Technical Assistance Branch
Cincinnati, Ohio

Originating Office:

Jerome P. Flesch, Acting Chief
Hazard Evaluation and
Technical Assistance Branch
Cincinnati, Ohio

Acknowledgments

Environmental Investigation:

Bobby J. Gunter, Ph.D.
Industrial Hygienist
Region VIII
Denver, Colorado

TABLE I

Summary of Personal Air Sampling Results for Sulfuric Acid, Copper, and Manganese in the Wire Cleaning Department of Rocky Mountain Manufacturing and Wire Company, Pueblo, Colorado

September 27 & 28, 1976
January 4 & 5, 1977

Sample Period	Sulfuric Acid (mg/M3)	Concentration of Copper (mg/M^3)	Manganese (mg/M^3)
9/27/76			
1830 - 2129	N.D.	0.008	0.097
1830 - 2130	0.24	0.005	0.010
1841 - 2130	N.D.	0.002	0.018
1842 - 2130	N.D.	0.002	0.007
9/28/76			
0816 - 1050	N.D.	(Not Analyzed)	(Not Analyzed)
0816 - 1250	(Not Analyzed)	0.006	0.010
0820 - 1055	0.20	(Not Analyzed)	(Not Analyzed)
0820 - 1255	(Not Analyzed)	0.004	0.011
0822 - 1125	N.D.	(Not Analyzed)	(Not Analyzed)
0822 - 1300	(Not Analyzed)	0.005	0.005
0827 - 1303	N.D.	0.002	N.D.
1050 - 1250	0.26	(Not Analyzed)	(Not Analyzed)
1055 - 1255	0.26	(Not Analyzed)	(Not Analyzed)
1200 - 1300	N.D.	(Not Analyzed)	(Not Analyzed)
1/4/77			
1400 - 2200	0.64	0.010	0.007
1400 - 2200	0.60	0.005	0.004
1400 - 2200	0.35	0.050	0.006
1/5/77			
0600 - 0930	0.30	0.006	0.003
0600 - 0930	0.14	0.003	N.D.
0600 - 0930	0.16	0.003	N.D.
0825 - 1100	(Not Analyzed)	0.003	N.D.
0930 - 1310	0.42	0.009	0.006
0930 - 1310	0.36	0.012	0.006
0930 - 1310	0.48	0.012	0.015
OSHA Standard	1.0	1.0	5.0
NIOSH Limit of Detection (Per Sample)	0.010	0.001	0.001

mg/M^3 = Approximate milligrams per cubic meter of air

N.D. = None detected (refer to Limit of Detection)