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. 76-88-380

MINNESOTA MINING AND MANUFACTURING CO.
COPLEY, OHIO

APRIL 1977

I. TOXICITY DETERMINATION

An environmental study was conducted in the chromic oxide (Cr_2O_3) producing area of the Minnesota Mining and Manufacturing Company in Copley, Ohio, on November 29-30, 1976. In this study environmental assessment was conducted by obtaining time weighted average and ceiling measurements of employee exposure to chromium (VI) and chromium (III). Non-directed questionnaires were administered to employees during the initial survey on July 29-30, 1976. Certain employees who had experienced nosebleeds and other chromium (VI)-related problems in the past had not experienced such problems for at least the last 1 1/2-2 years of work. Local exhaust ventilation was installed over one year ago to control employee exposure to chromium (VI), which apparently caused the problems to cease.

The following determination has been made based on environmental samples collected during the survey, evaluation of ventilation systems, observations of employee work practices, and available toxicity information: employee exposures to non-carcinogenic chromium (VI) contained in sodium bichromate, as measured during the survey, did not constitute a health hazard. All atmospheric levels of chromium (VI) were below evaluation criteria. Presently, no standards exist for chromium (III). However, a recommendation is made to prevent the release of chromium (III) dust in the air through leaking seals, gaskets of the furnace, etc. Dry sweeping of floors should be discouraged in favor of vacuum or wet methods.

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) The Minnesota Mining and Manufacturing Co., Copley, Ohio
b) Authorized Representative of Employees - United Steelworkers of America - Local #12832
c) United Steelworkers of America
Safety & Health Department, Pittsburgh, Pennsylvania
d) U.S. Department of Labor - Region V
e) NIOSH - Region V

For the purpose of informing the approximately 20-30 "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 received such a request from an authorized representative of employees to evaluate the potential hazard associated with employee exposure to chromate pigments.

IV. HEALTH HAZARD EVALUATION

A. Description of Process

The Minnesota Mining and Manufacturing Company located in Copley, Ohio is involved in the production of chromic oxide by the reduction of sodium bichromate in high temperature furnaces.

Whereas sodium bichromate is a water-soluble orange hexavalent chromium material (Cr (VI)), chromic oxide is a water-insoluble green material containing chromium in the trivalent oxidation state (Cr III).

The starting materials - sodium bichromate, and reducing agents are fed into a ribbon mixer from bags by one or two "mixer operators" per shift. Since only one furnace (#1) was operating during the survey, only one mixer operator was needed. The materials are added to the ribbon mixer approximately 14 times per shift, or approximately every half hour with each addition taking about 5-10 minutes. The mix is conveyed to an adjacent furnace where water is added, and for a period of time chemical reduction takes place at temperatures of 1500-1800°F. From the furnace, the slurry containing insoluble chromic oxide and a soluble salt is conveyed along a "furnace cooler" (long horizontal cylindrical vessel), then to an outside holding tank and finally to the centrifuge washing units, which

separate the pigment from the soluble salt. The pigment is conveyed along a horizontal "screw drier" unit, which dries and grinds the material. All these operations are supervised by the "furnace" operator. From the screw drier, the pigment falls onto a "screw conveyer", then feeds onto a bucket elevator, and is stored in a holding tank. The pigment is gravity fed into a "micro-pulverizing" unit, and is again stored in a holding tank. The pigment is then bagged automatically. One employee performs the last two operations. Once bagged, the pigment is placed on pallets and transported on a forklift by a "shipping clerk." The bagging unit is fitted with a local exhaust ventilation system.

B. Study Progress and Design

1. Preliminary Survey

On July 29, 1976, an initial walk-through was conducted at the Minnesota Mining and Manufacturing Company facility by a NIOSH industrial hygienist. Following a tour of the work area, seven employees were interviewed using a non-directed questionnaire. The average employee age was 37 years (range 21-60). The average length of company employment was 13 years (range 1-30), and the average time employed in the pigment producing area was 9 years (range 1-30).

2. Follow-up Environmental Survey

Environmental sampling was planned to assess employee exposure to chromium (VI). Although chromium (VI) exposures were the prime concern, environmental levels of chromium (III) were also documented.

C. Evaluation Methods

Exposures to chromium (VI) from sodium bichromate can be compared to exposure criteria of either an 8-hour time-weighted average concentration (TWA) (1976 TLV and the NIOSH recommended standard) or an acceptable ceiling concentration (enforced by OSHA).

Atmospheric samples for chromium (VI) and (III) were collected on 37 millimeter Gelman VM-I polyvinyl chloride filters. The filters were encased in plastic three piece field monitor cassettes with face caps on and small plugs removed. Samples were taken in the employee's breathing zone using battery-powered Mine Safety Appliance* (MSA) gravimetric pumps operating at a flow rate of 2 liters per minute (lpm), a value recommended by the NIOSH publication on Chromium (VI). The pumps and samples were worn by the employees for approximately an 8-hour period to assess the TWA concentrations. Time weighted averages permit excursions above the standard provided they are compensated by equivalent excursions below the standard during the workday. Ceiling concentrations were determined by taking short term samples during periods when the highest employee exposures were expected (during bichromate addition). The ceiling limit places a definite boundry which concentrations should not be permitted to exceed.

*Mention of commercial names does not constitute endorsement by the National Institute for Occupational Safety and Health.

The samples were analyzed in the NIOSH laboratory in Cincinnati: Chromium (VI) was determined using the specific diphenylcarbizide method. Chromium (III) was determined by analyzing for total chromium using the atomic absorption spectrophotometry method and subtracting the chromium (VI) from it. The limit of detection was approximately two micrograms (ug) per filter for total chromium and 2.5 ug/filter for chromium (VI).

D. Evaluation Criteria

1. Toxic Effects

Chromium (VI) - Sodium bichromate is the specific chromate handled at the Minnesota Mining and Manufacturing Company facility. The chromium ion is in the hexavalent state or commonly termed "Chromium (VI)". Chromium (VI) compounds are known to cause ulceration and perforation of the nasal spectum and inflammation of the mucous membranes through inhalation. "Chrome holes", which are penetrating sores of the skin, result after contact of chromium (VI) compounds with the cutaneous layer of skin. Common sites include the backs of hands, forearms, skin folds over the knuckles, and the nail root areas. The NIOSH criteria for a recommended standard for chromium (VI) reports that exposure to chromium (VI) may cause kidney or liver damage, tooth erosion and discoloration, and perforated eardrums.[1]

Based on current evidence, NIOSH has defined "non-carcinogenic chromium (VI)" to be the chromium (VI) in monochromates and dichromates (bichromates) of hydrogen, lithium, sodium, potassium, rubidium, cesium, ammonium, and chromium (VI) oxide. Sodium bichromate, the substance handled at this facility, is a "non-carcinogenic chromium (VI)" material.

"Carcinogenic chromium (VI)" comprises any chromium (VI) material not included in the group above, such as lead, zinc, and calcium chromates.

Chromium (III) - Trivalent chromium compounds have not been proven to be of hygienic significance. A recent review of a foreign company's health insurance records showed no carcinogenic potential or skin sensitizations to exposed employees. Among reasons for retirement or job transfers, no health effects were involved.[2] No hygienic standards exist for chromium (III) other than the nuisance particulate standards.

2. Environmental Standards

Airborne exposure limits for the protection of the health of workers have been recommended or promulgated by several sources. These limits are established at levels designed to protect workers occupationally exposed to a substance on an 8-hour per day, 40-hour per week basis over a normal working lifetime. For this investigation the criteria used to assess the degree of health hazards to workers were selected from three sources:

a. NIOSH: Criteria for a Recommended Standard...Occupational Exposure to Chromium (VI), 1975.

b. Threshold limit Values (TLV): Guidelines for airborne exposures recommended by the American Conference of Governmental Industrial Hygienists (ACGIH) for 1976.

c. OSHA standard: The air contaminant standard for chromic acid and chromates enforced by the Occupational Safety and Health Administration of the U.S. Department of Labor and found in the Federal Register - CFR 1910.1000(b) (Table Z-2).

Source	Substance	8-Hour Time Weighted Average Concentration (TWA)	Acceptable Ceiling Concentration**
NIOSH Criteria Document	Non-carcinogenic Chromium (VI)	25 ug/M^3*	50 ug/M^3
1976 TLV	Chromates and Chromic Acid	100 ug/M^3	--
OSHA Standard	Chromates and Chromic Acid	--	100 ug/M^3

*Micrograms of Chromium (VI) per cubic meter of air.
**This value should never be exceeded during an 8-hour period.

E. Evaluation Results and Discussion

1. Environmental

The results of atmospheric sampling for Chromium (VI) and Chromium (III) are presented in Table I.

Several atmospheric samples were collected on the mixer operators to assess the highest expected exposure to chromium (VI) during the 7-10 minute sodium bichromate addition period. All samples were below the analytical detection limit. Although there is no evidence to show the recommended ceiling standard of 50 micrograms of chromium (VI) per cubic meter of air (ug/M^3) was exceeded, the limitations of the analytical method must be recognized; thus, atmospheric levels as high as 80 ug/M^3 in 15 minute or shorter samples may have been undetected.

Two mixer operators were exposed to atmospheric levels of chromium (VI) of 6.7 and 5.4 ug/M^3. An area sample taken near the ribbon mixer showed a level of 8.7 ug/M^3. This correlated well with the personal exposures of the mixer operators. The results are below the NIOSH recommended standard of 25 ug/M^3 for non-carcinogenic chromium (VI), as measured over an 8-hour workday.

Ventilation measurements were taken of the local exhaust system at the ribbon mixer. The average face velocity at the lateral side take-off was approximately 350 feet per minute (fpm). This value lies in the recommended design range of 200-500 fpm (capture velocity) for material loading.[3]

Chromium (III) - Although there is no hygienic standard for chromium (III), samples were analyzed for future reference.

The mixer operators were exposed to atmospheric levels of chromium (III) of 2.1 and 1.7 mg/M^3*. The short term samples during bichromate addition ranged from 1.2-3.8 mg/M^3 and 0.8-3.1 mg/M^3, respectively.

The furnace operators, baggerman, and shipping clerk were exposed to atmospheric levels of chromium (III) ranging from 0.08-1.3 mg/M^3. The baggerman's sample (29.5 mg/M^3) exceeded the hygenic standard for nuisance dust and can be explained as follows: The baggerman used a high pressure air hose to blow off settled chromium (III) from the automatic bagging unit. This practice creates much airborne dust, and is usually done once per week.

Canopy hoods were used over the screw driers and the end of the furnace cooler where chromium (III) dust may become airborne.

2. Medical

Some employees related past encounters with nosebleeds and nasal perforations which could have occurred from overexposure to chromium (VI). One employee with frequent bouts of nosebleeds, had not experienced any during the last 1 1/2-2 years of work.

Since employees had no health related complaints of the working conditions and no "carcinogenic" chromates were being used, medical records were not reviewed during the survey.

3. Conclusions

Due to the modification of the ribbon mixer ventilation system in the past year or so, employee exposure to sodium bichromate has been controlled to within acceptable levels. This is supported by the decrease of nosebleeds and other nasal problems over the past years to the present time. Based on ventilation measurements and the 8-hour sampling results, it is not believed that a health hazard to employees exists with regard to chromium (VI) exposure.

V. RECOMMENDATIONS

Although no health hazard exists from exposure to chromium (VI) or (III) based on current toxicity information and atmospheric samples, some recommendations can be made:

*Milligrams of chromium (III) per cubic meter of air.

A. Environmental

1) Reduce emissions of chromium (III) dust from Furnace #1 by preventing leaks through seals, gaskets, etc.
2) Improve housekeeping, clean up settled dust on floors, but avoid dry mopping.
3) Do not blow dust from objects using air pressure. Use wet methods or vacuum cleaning if possible.
4) Eye wash station near the ribbon mixer was not in proper working order. A maintenance program should be instituted for all first aid equipment.

B. Medical

Although the following surveillance methods may already exist, the following recommendations are given as minimum requirements:

1. Workers exposed to sodium bichromate dust should have periodic examinations to detect ulcerations in the nostrils and other parts of the body. Workers should also be examined for the presence of respiratory disease periodically.

2. Other examinations should include:

a) Medical history including conditions, such as dermalogic or respiratory, which may be aggravated by exposure to chromium (VI) materials.
b) Occupational work history.
c) Smoking history.
d) Urinalysis.
e) Chest x-ray.
f) An evaluation of a worker's ability to use respiratory protection.

VI. REFERENCES

1. Criteria for a Recommended Standard...Occupational Exposure to Chromium (VI), USDHEW, PHS, CDC, NIOSH, 1975.

2. U. Korallus, et.al.: Trivalent chromium compounds. Results of a study in occupational medicine. Part 2: Disease status analysis. Arbeitsmedizin - social-medizin - Praventivmedizin 9: No. 4, 1974.

3. American Conference of Governmental Industrial Hygienists: Industrial Ventilation, 13th ed., Lansing, Michigan, 1974.

VII. AUTHORSHIP AND ACKNOWLEDGMENTS

Report Prepared By:

William A. Evans
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

Analytical Laboratory Services:

Soo Wang Kim
Chemist
Measurement Services Section
Division of Physical Sciences
and Engineering
Cincinnati, Ohio

Table 1

Results of Air Sampling for Chromium (VI)
and Chromium (III)

3M Company
Copley, Ohio

November 29-30, 1976

Employee or Location	Date	Sample Number	Type Sample[1]	Sampling Period (hrs./min.)	Concentration[2] (ug/M^3)	
					Chromium VI	Chromium III
Mixer Operator	11/29/76	V 1981	P	7/50	6.7	2108
Mixer Operator	11/29/76	V 2376	P	0/ 8	ND	3750
Mixer Operator	11/29/76	V 2377	P	0/ 9	ND	1722
Mixer Operator	11/29/76	V 2380	P	0/ 8	ND	1188
Mixer Operator	11/29/76	V 2367	P	0/ 9	ND	3500
Mixer Operator	11/29/76	V 2846	P	0/10	ND	2200
Mixer Operator	11/30/76	V 1063	P	7/30	5.4	1727
Mixer Operator	11/30/76	V 2080	P	0/10	ND	750
Mixer Operator	11/30/76	V 1918	P	0/10	ND	3100
Mixer Operator	11/30/76	V 2368	P	0/ 7	ND	1438
Mixer Operator	11/30/76	V 2241	P	0/ 7	ND	3071
At Electrical Boxes near ribbon mixer	11/29/76	V 2274	A	7/37	8.7	6842
Furnace Operator	11/29/76	V 2399	P	7/ 5	ND	1139
Furnace Operator	11/30/76	V 2375	P	7/25	ND	78
Baggerman	11/30/76	V 2276	P	0/31	ND	29516
Baggerman	11/30/76	V 2265	P	6/07	ND	1282
Shipping Clerk	11/30/76	V 2153	P	6/40	ND	235

OP=Personal A=Area 2 ug/m^3=Micrograms of substance per cubic meter of air (1ug=0.001 milligrams)
ND=Non detectable