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HETA 86-251-1842 OCTOBER 1987 AMERICAN CYANAMID MICHIGAN CITY, INDIANA

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I. <u>SUMMARY</u>

On March 12, 1986, the National Institute for Occupational Safety and Health (NIOSH) received a request from an authorized representative of the International Chemical Workers Union, to evaluate employee exposures to nickel in the Specialties Department at the American Cyanamid, Michigan City, Indiana plant.

On April 17, 1986, NIOSH investigators conducted an initial survey of the facility to obtain background information about the workforce, industrial processes, and medical, safety, and industrial hygiene programs. Additionally, a walk-through evaluation of the muller area was conducted. On November 12-14, 1986, an industrial hygiene survey was conducted to characterize employee exposures to metals and dusts. Personal and general area air sampling was conducted in the impregnation area, the muller area, and the product load-out area.

Airborne samples collected for metals were analyzed for 28 specific elements of toxicological importance. Analytical results showed the presence of aluminum, molybdenum, and nickel on all 11 air samples analyzed. Additionally, six other metals including calcium, cobalt, copper, iron, magnesium, and zinc were detected on some samples. Molybdenum concentrations ranged from 0.01 to 0.12 milligrams per cubic meter of air (mg/M³); none of the samples exceeded the Occupational Safety and Health Administrations (OSHA) Permissible Exposure Limit (PEL) of 5 mg/M³. Nickel concentrations ranged from 0.004 to 0.29 mg/M³; 6 of the 11 samples exceeded the NIOSH Recommended Exposure Limit (REL) of 0.015 mg/M³, but none exceeded the OSHA PEL of 1.0 mg/M³ for nickel. Aluminum concentrations ranged from 0.07 to 0.09 mg/M³; none of the samples exceeded the ACGIH TLV of 10 mg/M³. All other metals detected did not exceed any of the applicable environmental criteria.

The results of personal and general area air sampling for total dust ranged from 0.61 to 5.69 mg/ M^3 on the six samples analyzed. These results are all below the ACGIH TLV of 10 mg/ M^3 for nuisance particulates, however, because of the presence of nickel these dusts cannot be considered nuisance particulates.

On the basis of the data obtained during this investigation it has been determined that employees working at the American Cyanamid, Michigan City, Indiana facility in the impregation area, the muller room, and the product load-out area were exposed to airborne concentrations of nickel in excess of the NIOSH REL. Recommendations for reducing employee exposures are presented in Section VIII of this report.

KEYWORDS: SIC 2819 (Industrial Inorganic Chemicals, Not Elsewhere Classified), nickel, total dust, petroleum catalysts.

II. INTRODUCTION

On March 12, 1986, the National Institute for Occupational Safety and Health (NIOSH) received a request from an authorized representative of the International Chemical Workers Union (ICWU), to evaluate employee exposures to nickel in the Specialties Department at the American Cyanamid, Michigan City, Indiana plant.

On April 17, 1986, NIOSH investigators conducted an initial survey of the facility which included an opening conference during which background information about the workforce, industrial processes, and medical, safety, and industrial hygiene programs at the plant were discussed. Following the opening conference a walk-through evaluation of the muller was conducted. The information obtained during the initial survey was used to develop an air sampling protocol for a follow-up environmental survey. Due to infrequent use of nickel during the production of catalysts, an environmental survey was not possible until the fall of 1986.

On November 12-14, 1986, a NIOSH industrial hygienist conducted an industrial hygiene survey at the American Cyanamid plant in Michigan City, Indiana, to evaluate employee exposures to metals and dusts during the production of nickel catalysts for the petroleum industry. On May 5, 1987, an interim letter presenting the environmental findings of the November, 1986 survey, along with preliminary recommendations, was transmitted to all interested parties.

III. <u>BACKGROUND</u>

A. Plant Production and Workforce

The American Cyanamid Company's Michigan City, Indiana, facility manufactures catalysts for the petroleum industry. The company manufactures several different products which consist of a metal impregnated on an alumina-silica base. The finished catalyst is produced in the Specialties Department. The Michigan City, Indiana facility was built in 1951 and the muller department was added in 1974. The facility provides employment for about 96 workers, 33 administrative personnel, and 63 production workers.

B. Process Description

The Specialties Department is divided into three areas, the impregnation area, the muller area, and the product load-out area. In the impregnation area one employee prepares the solutions for each product. The individual ingredients are added to the mixers both manually and automatically. Acid solutions are automatically piped into mixers which are local exhaust ventilated. Molybdenum and nickel powders are added to the acid solutions manually. Bags of molybdenum oxide powder are manually dumped into the mixers. Nickel oxide powder is manually scooped out of 55 gallon drums with hand held metal scoops into smaller 5 gallon containers, weighed, and then dumped into the mixers containing the acid solutions. The solutions are mixed, piped to storage tanks, and then piped to the muller when needed. The muller operator automatically charges the solutions and alumina powders into the muller mixer via control panel. The products are blended in the muller and dumped into a hopper one floor below. The material which has a semi-solid consistency is forced through an extruder which further dries the product at high temperatures. The product proceeds via conveyor to the product load-out area where it is packaged and sent to the warehouse for storage and shipment to the customer.

C. Engineering and Personal Protective Controls

The mixers in the impregnation area and the muller mixers are local exhaust ventilated to the outside. The impregnator operator is required to wear 3M 9900 disposable masks when weighing nickel oxide powder and when dumping molybdenum powder into the mixer. The muller operator, and the muller helper are provided with 3M 8710 disposable dust masks.

IV. EVALUATION DESIGN AND METHOD

On November 13 and 14, 1986, workers were monitored for exposure to metals and total dust. General area air samples were collected in the muller room and at the bagging operation. General area air samples were placed in areas where the employees were likely to be present. Personal samples were collected near the breathing zone of workers in the impregnation area, the muller room, and the product load-out area.

Air samples for total dust were collected on pre-weighed polyvinyl chloride (PVC) filters and samples for metals were collected on mixed cellulose ester membrane (AA) filters. The filter media were connected via tygon tubing to battery operated pumps operating at an air flow rate of 2.0 liters per minute (LPM) for total dust and at an air flow rate of 1.5 LPM for metals.

The pre-weighed PVC filters were analyzed gravimetrically for total dust.¹ All AA filters were analyzed via inductively coupled Argon plasma-atomic emission spectroscopy (ICP-AES) according to NIOSH Method No. 7300; a technique which provides for the simultaneous analysis of 28 metals of toxicological importance.¹ A list of these elements and their corresponding analytical limits of detection are presented in Table I.

V. EVALUATION CRITERIA

A. Environmental Evaluation Criteria

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects if their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy).

In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the evaluation criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: 1) NIOSH Recommended Exposure Limits (RELs)², 2) the American Conference of Governmental Industrial Hygienists' (ACGIH)

Threshold Limit Values (TLVs)³, and 3) the U.S. Department of Labor/Occupational Safety and Health Administration (OSHA) occupational health standards⁴. Often, the NIOSH RELs and ACGIH TLVs are lower than the corresponding OSHA standards. Both NIOSH RELs and ACGIH TLVs usually are based on more recent information than are the OSHA standards. The OSHA standards also may be required to take into account the feasibility of controlling exposures in various industries where the agents are used; the NIOSH RELs, by contrast, are based primarily on concerns relating to the prevention of occupational disease. In evaluating the exposure levels and the recommendations for reducing these levels found in this report, it should be noted that industry is required by the Occupational Safety and Health Act of 1970 (29 USC 651, et seq.) to meet those levels specified by an OSHA standard.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8 to 10-hour workday. Some substances have recommended short-term exposure limits (STEL) or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from high, short-term exposures.

A list of the sampled substances included in these evaluations and their applicable environmental criteria are provided in Table 2. For nickel which was found in excess of the NIOSH REL the following discussion is presented.

B. Health Effects of Nickel ^{5,6,7,8}

Metallic nickel and certain soluble nickel compounds such as dust or fume can cause sensitization dermatitis and may produce cancer of the paranasal sinuses and the lung; nickel fume in high concentrations is a respiratory irritant. Severe but transient pneumonitis in two workers resulted from exposure to nickel fume; in one cause, exposure was for six hours, and post-incident sampling suggested a nickel concentration of 0.26 mg/M³. "Nickel itch" is a dermatitis resulting from sensitization to nickel; the first symptom is usually itching, which occurs up to seven days before skin eruption appears. The primary skin eruption is erythematous, or follicular, it may be followed by superficial discrete ulcers, which discharge and become crusted, or by eczema; in the chronic stages, pigmented or depigmented plaques may be formed. Nickel sensitivity, once acquired, is apparently not lost; recovery from the dematitis usually occurs within seven days of cessation of exposure, but may take several weeks. A worker who had developed cutaneous sensitization also developed apparent asthma from inhalation of nickel sulfate; immunologic studies showed circulating antibodies to the salt, and controlled exposure to a solution of nickel sulfate resulted in decreased pulmonary function and progressive dyspnea; the possibility of developing hypersensitivity pneumonitis could not be excluded. In animals, finely divided metallic nickel was carcinogenic when introduced into the pleural cavity, muscle tissue, and subcutaneous tissues; rats and guinea pigs exposed to a concentration of 15 mg/M³ of powdered metallic nickel developed malignant neoplasms. Several epidemiologic studies have shown an increased incidence of cancer of the paranasal sinuses and lungs among workers in nickel refineries and factories; suspicion of carcinogencity has been focused primarily on respirable particles of nickel, nickel subsulfide, nickel oxide, and on nickel carbonyl vapor.

VI. RESULTS AND DISCUSSION

Qualitative and quantitative analytical results for metals by ICP-AES are presented in Table II. These results show the presence of aluminum, molybdenum, and nickel on all 11 air samples that were analyzed; a 12th sample was not analyzed due to evidence of tampering during the sampling period. In addition, to these three metals, six other metals including calcium, cobalt, copper, iron, magnesium, and zinc were detected on some samples.

The results of personal and general area air sampling for the metals, molybdenum and nickel, are presented in Table III. Molybdenum concentrations ranged from 0.01 to 0.12 milligrams per cubic meter of air (mg/M³); none of the samples exceeded the American Conference of Governmental Industrial Hygienists (ACGIH) Threshold Limit Value (TLV) of 5 mg/M³. Nickel concentrations ranged from 0.004 to 0.29 mg/M³; 6 of the 11 samples exceeded the NIOSH Recommended Exposure Limit (REL) of 0.015 mg/M³; none exceeded the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) of 1.0 mg/M³. In addition to molybdenum and nickel, aluminum was detected on all 11 samples and was found in concentrations ranging from 0.07 to 0.09 mg/M³; none of the samples exceeded the ACGIH TLV of 10 mg/M³ for aluminum. All other metals which were detected did not exceed any of the environmental criteria.

The results of personal and general area air sampling for total dust are presented in Table IV. The sample values ranged from 0.61 to 5.69 mg/M³ on the six samples which were analyzed, a seventh sample was not analyzed due to evidence of tampering during the sampling period, and an eighth sample was lost during the sampling period. These results are all below the ACGIH TLV of 10 mg/M³ for nuisance particulates, however, because of the presence of nickel and other metals which have more stringent environmental criteria, these dusts should not be considered nuisance particulates.

Disposable half-mask (3M 9900) respirators were available to employees working in the muller area and the impregnation area. These masks were not worn by the employees working in the muller, but was worn by the impregnator operator during the weighing of nickel and while dumping nickel and molybdenum into the mixers. However, this type respirator is not recommended by NIOSH for use with potential carcinogens. Nickel compounds are considered by NIOSH to be suspect carcinogens. In the absence of evidence to the contrary, nickel metal and all inorganic nickel compounds, when airborne, should be considered carcinogens. The product being manufactured during the November 1986, survey contained nickel metal and analyses of samples collected show the presence of nickel above the NIOSH REL.

VII. CONCLUSIONS

Based on the data collected it can be concluded that employees working in the impregnation area, the muller room, and the product load-out area were exposed to excessive airborne concentrations of nickel in comparison to the NIOSH REL. Since this product is only one of several which are manufactured in this area of the facility, the toxicity of the individual components of the products being manufactured should always be taken into consideration when determining what protective measures should be taken.

VIII. <u>RECOMMENDATIONS</u>

In view of the environmental findings the following recommendations (provided to the company and union in the interim reports) were made to ameliorate existing or potential hazards, and to provide a better work environment for employees. These recommendations should be implemented if they have not already been completed.

- 1. During the environmental survey of November 1986, a leak of powders was noted on the west muller. Gaskets and seals on the mullers should be replaced where necessary and a preventive maintenance program should be implemented to prevent future leaks of materials from the mullers. Reducing dust emissions from the mullers should significantly reduce the housekeeping requirements in the muller area.
- 2. Engineering controls should be installed in the impregnation area to control the generation of nickel dusts and other materials and to minimize employee exposures. Personal samples collected from the impregnator operator indicated that airborne concentrations of nickel were nearly 20 times the NIOSH REL.
- 3. All accumulated dust in the muller area and other areas of the facility should be cleaned up and a regular housekeeping schedule should be implemented to prevent future accumulation of dusts.
- 4. The removal of accumulated dusts should be accomplished by the use of a vacuum system. Dry sweeping techniques should not be used. Ideally, a central vacuum system equipped with a high efficiency particulate air (HEPA) filter should be installed in the muller area to accomplish housekeeping activities. A portable vacuum system equipped with a HEPA filter could be used as an alternative to the installation of a central vacuum system.
- 5. Until effective engineering controls are installed, the use of an appropriate respirator should be required and enforced in the impregnation area, the muller room, and the product load-out area. During our environmental survey of November 1986, there was some confusion regarding the required use of respirators in the muller area.
- 6. When the installation of engineering controls are completed, the areas should be monitored for airborne concentrations of nickel to determine the effectiveness of these controls.
- 7. The present respirator program should be thoroughly reviewed and updated to prevent any further confusion regarding the mandatory use of appropriate respirators. The respirator program should comply with all requirements of 29 CFR 1910.134.
- 8. NIOSH recommends that supplied air respirators be used when exposed to airborne concentrations of carcinogens in excess of the NIOSH REL. Airborne concentrations of nickel were detected (in excess of the NIOSH REL) in the impregnation area, the muller area, and the product load out area.

IX. <u>REFERENCES</u>

- 1. National Institute for Occupational Safety and Health. NIOSH manual of analytical methods, 3rd Edition. Cincinnati, Ohio 1984. (DHHS (NIOSH) publication no. 84-100).
- 2. NIOSH Recommendations for Occupational Safety and Health Standard. Morbidity and Mortality Weekly Report Supplement. Vol. 35/No. 1S. September 26, 1985.
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- 4. Occupational Safety and Health Administration. OSHA safety and health standards, 29 CFR 1910. Occupational Safety and Health Administration, revised 1983.
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XI. DISTRIBUTION AND AVAILABILITY OF DETERMINATION REPORT

Copies of this Determination Report are currently available upon request from NIOSH, Division of Standards Development and Technology Transfer, Resources and Dissemination Section, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days the report will be available through the National Technical Information Services (NTIS), Port Royal Road, Springfield, Virginia 22161. 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 the following:

- 1. American Cyanamid, Michigan City, Indiana
- 2. American Cyanamid Corporate Office, Wayne, New Jersey
- 3. International Chemical Workers Union, Akron, Ohio
- 4. International Chemical Workers Union, Local #493
- 5. U.S. Department of Labor, OSHA Region V

For the purposes of informing the affected employees, copies of the report should be posted in a prominent place accessible to the employees, for a period of 30 calendar days.

Table I Elements Analyzed by ICP-AES and Their Corresponding Analytical Limits of Detection American Cyanamid Michigan City, Indiana HETA 86-251

	Analytical Limit of Detection
Element	(micrograms per sample)
Aluminum	10
Antimony	10
Arsenic	5.0
Boron	10
Barium	1.0
Beryllium	1.0
Calcium	5.0
Cadmium	1.0
Cobalt	1.0
Chromium	1.0
Copper	1.0
Iron	1.0
Lanthanum	5.0
Magnesium	1.0
Molybdenum	1.0
Nickel	1.0
Lead	2.5
Selenium	10
Silver	2.5
Tin	10
Tellurium	10
Thallium	10
Titanium	10
Vanadium	10
Yttrium	1.0
Zinc	1.0
Zirconium	10

Note: 1000 micrograms = 1 milligram

Table II Metals detected on personal and general area air samples American Cyanamid Michigan City, Indiana HETA 86-251

November 13, 14, 1986

Substance (Metal)	Range (mg/M ³)	Number of samples detected on	NIOSH REL	ACGIH TLV	OSHA PEL
Aluminum	0.07 - 0.09	11		10	
Calcium	0.010 - 0.030	2		10*	
Cobalt	0.002 - 0.007	5	0.1	0.1	0.1
Copper	0.01 - 0.02	3		1	1
Iron salts (soluble)	0.002 - 0.009	8		1	
Magnesium	0.007	1		1	
Molybdenum (soluble)	0.01 -0.12	11		5	5
Nickel (soluble)	0.004 - 0.29	11	0.015	0.1	1
Znc	0.002 - 0.006	5		10*	

* - As nuisance particulate

Table III Personal and general area air samples for Metals American Cyanamid Michigan City, Indiana HETA 86-251 November 13, 14, 1986

Date	Job/Location	Sample Time	Sample Volume	TWA Exposures (mg/M ³	
		(minutes)	(liters)	Molybdenum	Nickel
11/13/86	Muller oper/Muller room	381	572	0.12	0.06*
11/13/80		462	693	0.02	0.00
11/14/00		402	0)3	0.02	0.005
11/13/86	Die changer/Muller room	379	568	0.08	0.02*
11/14/86		438	657	0.02	0.03 *
11/13/86	Impreg. oper./Impreg. area	366	549	0.03	0.29 *
11/14/86		401	602	0.01	0.01
11/12/06	Des d las d seet man #1 Calainan	200	540	0.01	0.004
11/13/86	Prod. load-out man/#1 Calciner	360	540	0.01	0.004
11/14/86		429	644	0.03	0.04 *
11/13/86	Spec. helper/#2 Calciner	359	538	0.02	0.007
11/14/86	spoornopoine cuonici	424	636	0.03	0.01
11,1,1,00				0.02	0101
11/13/86	Area sample/Prod. load-out desk	x 362	543	NA	NA
11/13/86	Area sample/Muller room	352	528	0.10	0.04 *
	(between mullers)				
ENVIRONM	ENTAL CRITERIA:		NIOSH REL		0.015
			ACGIHTLV	5.0	0.013 1.0
			OSHA PEL	5.0	1.0

* - Exceeded the most stringent environmental criteria (NIOSH REL).

Table IVPersonal and general area air samples for Total Dust

American Cyanamid Michigan City, Indiana HETA 86-251

November 13, 14, 1986

Date	Job/Location	Sample Time (minutes)	Sample Volume (liters)	Total dust (mg/M ³)
11/13/86	Muller oper./Muller room	381	762	2.31
11/14/86		462	924	1.26
11/13/86	Die changer/Muller room	379	758	5.69
11/14/86				Filter lost during sample period
11/13/86	Prod. load-out man/#1 Calciner	360	720	2.46
11/14/86		429	858	0.61
		10.1	0.40	0.01
11/14/86	Spec. helper/#2 Calciner	424	848	0.81
ENVIRONMENTAL CRITERIA			NIOSH REL	
			ACGIHTLV	10.0
			OSHA PEL	15.0