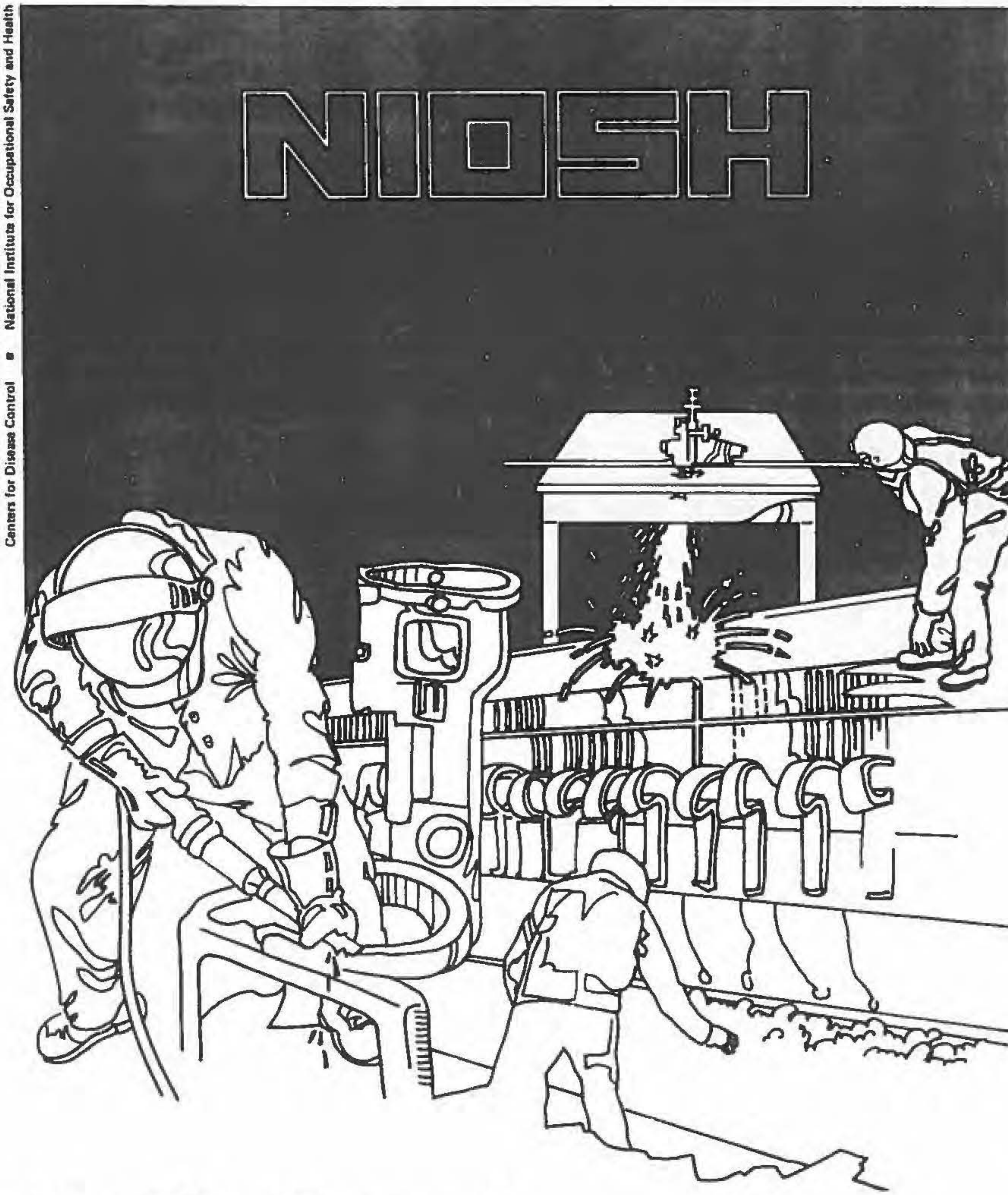
U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES ■ Public Health Service
Centers for Disease Control ■ National Institute for Occupational Safety and Health



Health Hazard Evaluation Report

HETA 85-064-1844
GTE/VALENITE CORPORATION
WESTMINSTER, SOUTH CAROLINA

PREFACE

The Hazard Evaluations and Technical Assistance Branch of NIOSH conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following 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 Hazard Evaluations and Technical Assistance Branch also provides, upon request, medical, nursing, and industrial hygiene technical and consultative assistance (TA) to Federal, state, and local agencies; labor; industry and other groups or individuals to control occupational health hazards and to prevent related trauma and disease.

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GTE/VALENITE CORPORATION
WESTMINSTER, SOUTH CAROLINA

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I. SUMMARY

In November 1984, the National Institute for Occupational Safety and Health (NIOSH) received a request for a Health Hazard Evaluation to evaluate exposure to hard metal dusts generated during the finish grinding of tungsten carbide cutting tool inserts at GTE/VALENITE, Westminster, South Carolina.

Personal and general area samples were collected for determination of airborne nitrosamines, cobalt, and tungsten. None of the seven nitrosamines evaluated (dimethyl, diethyl, dipropyl, dibutylamine, pyrrolidine, piperidine, morpholine) were found in detectable quantities. Since several nitrosamines are carcinogenic, any detectable levels would have been considered significant. Cobalt airborne concentrations ranged from non-detectable to 26.8 micrograms per cubic meter (ug/m^3). The American Conference of Governmental Industrial Hygienists (ACGIH) proposed Threshold Limit Value (TLV) for cobalt is 50 ug/m^3.

The Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) for cobalt is 100 ug/m^3. Both of these limits are time-weighted averages (TWA) based on an eight-hour exposure. There is no NIOSH Recommended Exposure Limit (REL) for cobalt.

Air samples for tungsten ranged from non-detectable to 0.41 milligrams per cubic meter (mg/m^3). The NIOSH REL for insoluble tungsten is 5 mg/m^3 (measured as tungsten). The ACGIH also recommends a TWA of 5 mg/m^3 for insoluble tungsten metal.

Of the employees with at least 24 months at the plant, the 9 current cigarette smokers and the 11 lifetime non-smokers had comparable prevalences of chest tightness (56% and 55%, respectively) and shortness of breath (44% and 46%), and somewhat less comparable prevalence of cough (60% and 46%) and wheezing (78% and 64%). Medical histories of the non-smokers did not reveal other causes for these symptoms.

This study did not find any overexposures to cobalt or tungsten and did not document any exposures to nitrosamines. Respiratory symptoms were not associated with current tungsten carbide exposure, but there was some indication that chronic or past exposures may be related to current symptoms.

KEYWORDS: SIC 3541 (Machine Tools, Metal Cutting Types); tungsten carbide, cobalt, tungsten, nitrosamines.

II. INTRODUCTION

On November 16, 1984, NIOSH received a confidential request for an evaluation of metal dust exposures at the Valenite No. 1 plant, Westminster, South Carolina. The metals of concern were tungsten carbide, cobalt, nickel, titanium, and other metals generated by the finish grinding of tungsten carbide cutting tool inserts.

NIOSH personnel conducted a walk-through inspection of the plant. on January 9-10, 1985, and environmental and medical surveys on June 18-19, 1985.

III. BACKGROUND

The Valenite #1 Plant is an approximately 13,000 ft^2 facility that was built in 1977 to perform finish grinding on tungsten carbide inserts for cutting tools. During the time of our survey, the plant employed 50 production workers, 30 on the day-shift and 20 on the night-shift.

The finishing process on the inserts is accomplished by grinding the periphery and sides of rough mold inserts according to customer specifications. Finishing is predominantly by wet grinding, although dry honing is also performed on some inserts to round-off edges. Most of the grinding machines use a recirculating water/coolant solution to control heat generation which has the added benefit of acting as a dust suppressor. The synthetic cutting fluid contains sodium nitrite and triethanolamine, which have the potential to form diethanolnitrosamine. After the finish grinding/honing, the inserts are inspected, marked (electrochemical etching), and boxed for shipment. The cobalt content of the inserts can range from 5.5 to 13.0 percent.

The production area ventilation system was designed to recirculate exhausted air during both the winter and summer months to maintain a temperature of 75° F in the plant. Nine heating and air conditioning units (Fedder and General Electric) filter and recirculate the plant's air. The system was not designed for high efficiency particulate removal. None of the grinding machines were equipped with local exhaust ventilation (LEV). One of the two honers was equipped with a LEV system, while the other was cleaned with an air hose.

In 1984, Valenite workers had medical evaluations by private consultants. Two workers were reported to have had chest x-ray findings and pulmonary function test results consistent with interstitial lung disease (which can result from excessive exposure to cobalt).

IV. METHODS AND MATERIALS

A. Environmental

Environmental sampling consisted of personal and area environmental air samples collected for nitrosamines and hard metals (tungsten, cobalt, nickel, titanium, etc.). Bulk samples of the water/coolant solution were also taken for nitrosamine and metals analysis.

Area samples for nitrosamines were collected utilizing Thermosorb/N tubes attached to battery-operated sampling pumps operating at a flowrate of 1.0 liters per minute (lpm). The tubes were desorbed with 2.0 ml of a solution of 75% methylene chloride and 25% methyl alcohol. The samples were then analyzed by gas chromatography with a thermal energy analyzer in the nitrosamine mode. The limits of detection for this method ranged from 10-100 nanograms per sample (depending upon the particular nitrosamine that was to be identified).

The bulk samples for nitrosamines were placed in separate vials. An extraction was performed three times with 10 ml of dichloromethane (DCM). The extracts were combined and dried over anhydrous sodium sulfate, filtered, and the sodium sulfate washed two times with 5 ml of fresh DCM. The combined extracts plus washings were concentrated on a Kuderna-Danish using isooctane as a Keeper to a volume of 1 ml. Aliquots of the final concentration were analyzed by gas chromatography with a thermal energy analyzer detector in the nitrosamine mode.

Personal and area samples for tungsten were collected by drawing air through an AA filter at a flowrate of 1.2 lpm using calibrated, battery-operated sampling pumps. Analysis was by atomic absorption spectroscopy according to NIOSH Method 7074. The analytical limit of detection for this method was 125 micrograms per sample.

Personal and area samples were also collected for metals (cobalt, nickel, titanium, etc.) that are constituents of cemented tungsten carbide. Total and respirable metal air samples were taken with a sampling train consisting of an AA filter, a 10 millimeter nylon cyclone size-selective sampler (respirable samples only), and a battery-operated sampling pump operating at 1.2 lpm (total metals) or 1.7 lpm (respirable metals). For analysis, the samples were ashed with concentrated nitric and perchloric acids. The residues were dissolved in a dilute solution of the same acids, and the resulting sample solutions analyzed for trace metals content by inductively coupled argon plasma, atomic emission spectroscopy (ICP-AES). The limit of detection for this sample set was 1.0 microgram per filter.

Bulk samples of the water/coolant solution were collected (to correlate coolant age with metals content) in glass vials and submitted for trace metals analysis. Each sample was shaken to suspend the particulates, and a 10 ml aliquot was withdrawn for analysis. The sample aliquots were digested with nitric and perchloric acids. The digestion residues were redissolved in a dilute solution of the same acids and analyzed by ICP-AES for trace metal content. The limit of detection for this sample set was 1 microgram/10 ml sample.

Colorimetric detector tubes (Draeger) were used for the measurement of hydrochloric and acetic acids during the electrolytic etching of the carbide inserts. The detection limit of the Draeger tubes was 1 part per million (ppm) for hydrochloric acid and 5 ppm for acetic acid.

B. Medical

On June 18-19, 1985, we asked first shift workers to complete a medical and occupational history questionnaire and to provide pre- and post-shift urine specimens for determination of cobalt concentration. The workers were requested to collect a morning urine sample at home (before they dressed for work, after a shower, and with their hair wrapped in a clean towel). When they arrived at work they placed surgical hats over their hair, removed their work shirt and washed their hands and arms before giving a urine sample. The workers repeated this procedure at the end of their shift. One worker also poured deionized water from a common, closed bottle into a urine collection container after providing a urine sample. This served as a field blank.

All urine samples were processed within 2-3 hours of collection; 0.1 ml concentrated, ultra pure nitric-acid was added to a 15-ml plastic tube which had been rinsed with 1% ultra-pure nitric acid to reduce metal contamination. Ten ml of urine was then added to the tube. Deionized water was poured into the 15-ml tube to serve as a laboratory blank. The samples were frozen immediately and shipped frozen to the laboratory. The urine samples were then analyzed at the Center for Environmental Health, Centers for Disease Control, by the modified Zeeman effect graphite furnace atomic absorption method.(1)

In order to standardize urinary cobalt to the degree of urine concentration, all urinary cobalt levels were expressed as amount of cobalt per gram (g) of creatinine (Cr). Urine creatine was measured by the Jaffe reaction method.(2)

V. 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 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 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 criteria documents and recommendations, 2) the ACGIH TLV's, and 3) the U.S. Department of Labor (OSHA) occupational health standards. Often, the NIOSH recommendations and ACGIH TLV's are lower than the corresponding OSHA standards. Both NIOSH recommendations and ACGIH TLV's usually are based on more recent information than are the OSHA standards. The OSHA standards also may be require to take into account the feasibility of controlling exposures in various industries where the agents are used; the NIOSH-recommended standards, 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 the report, it should be noted that industry is legally required 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 or ceiling values which are intended to supplement the TWA, where there are recognized toxic effects from high short-term exposures.

Tungsten Carbide

Cemented tungsten carbide is a unique metal commonly used in saw blades or cutting tools because its hardness approaches that of diamond. Tungsten and carbon powders are first blended and then heated to form tungsten carbide. Cobalt (Co) in various amounts (3% to 25%) is added to tungsten carbide powder as a binding agent. Depending on the desired properties of the final product, other metal powders such as titanium carbide, tantalum carbide, chromium carbide, and nickel may be added.[3] Exposures to cobalt and other metal constituents occur during grinding, milling, and cutting of new tools, or during the resharpening and repair of old tungsten carbide tools. NIOSH recommends that exposure to insoluble tungsten be controlled so that employees are not exposed at a concentration greater than 5 milligrams, measured as tungsten, per cubic meter of air (mg/m^3).[4] The ACGIH also recommemds a TWA of 5 mg/m^3 for insoluble tungsten metal.[5]

Cobalt

Cobalt occurs naturally and is an integral part of the cyanocobalanium molecule (vitamin B 12), which is essential to the human diet to prevent the development of pernicious anemia.[6] The average U.S. daily cobalt intake from food, water, and community air have been estimated to be 0.3 mg (milligrams), 0.006 mg, and 0.0001 mg respectively.[7] However, with higher exposure, cobalt can cause toxicity in humans.

Fibrotic lung changes have been observed in workers exposed to airborne cobalt concentrations of 0.1-0.2 mg/m^3.[3,8-13] A common pattern of illness is described in these reports. The worker may first develop a cough, followed by labored breathing on exertion. There may be a substantial weight loss, and the individual may go on to develop a progressive interstitial pulmonary fibrosis (scar tissue in the lung), which may be accompanied by cor pulmonale (heart failure due to hypertension in the lungs), leading ultimately to cardiorespiratory collapse and death.[6] The association between inhaled cobalt and the development of lung fibrosis is supported in studies conducted in swine.[14]

The reported latency period from exposure to disease varies from a few to 20 years.[6] It is unclear whether this variable latency is related to individual susceptibility or level of exposure.

A series of reports describe lung function test results among 155 Swedish cemented carbide workers and 74 controls matched for sex, age, and smoking history.[15-17] Persons exposed to an average of 0.06 mg/m^3 airborne cobalt showed obstructive changes on pulmonary function tests over the week that did not regress over the weekend. Smokers were more affected than non-smokers.

Several investigators have suggesteed evidence of bronchitis among hard metal workers.[9-23] Asthma has been reported,[9,10,24,25] as early as one month after initial exposure.[3] The development of asthma seems to be a true sensitization to cobalt. The occurrence of allergic lung sensitization has heightened plausibility in view of the occurence of documented cobalt allergic dermatitis that has been reported among workers using cobalt containing materials.[24,26] Sjogren et al have reported three non-smoking hard metal workers having symptoms and signs compatible with allergic alveolitis; the symptoms, signs and chest x-ray findings cleared with removal from work, and reexposure lead to reoccurrence of symptoms and chest x-ray findings.[27] Of concern is that these workers were located in the section of the plant with the lowest measured cobalt air levels. They utilized a cutting fluid when grinding tungsten carbide that caused a portion of the cobalt to dissolve and become ionized in the cutting fluid. Ionized cobalt reportedly reacts with proteins, and it is biologically plausible that it could form a hapten, and possibly induce an allergic response.[28] All three had contact eczema and were sensitive to cobalt on skin patch testing.

There are a number of other physiological effects associated with cobalt. Cardiomyopathy (enlargement and dilation of the heart) has been associated with heavy consumption of beer utilizing cobaltcus sulfate or cobaltous chloride as a foam stabilizer in the 1960's.[29-34] The signs and symptoms of the affected individuals (the majority who drank between 2 to more than 6 liters of beer per day) included abdominal pain, shortness of breath, lowered blood pressure, heart enlargement, pericardial effusion, tachycardia, and electrocardiographic (ECG) abnormalities. The amount of cobalt ingested daily by a 6-liter-per-day drinker was about 5-10 mg/day, much higher than that inhaled and absorbed by a worker breathing 10-15 m^3 at the current Federal OSHA limit of 0.1 mg/m^3.[6] Therapeutically administered cobalt has been used in treatment of anemias because it has been shown to increase hemoglobin and hematocrit levels in humans.[35-43] Hypothyroidism and goiter have been associated with oral daily cobalt chloride doses of 2-10 mg/kg administered over a 2-4 month period in a small percentage of people.[6] Additional effects reported in humans, but for which there is limited information available, include disturbed kidney function, hyperglycemia, mild to moderate changes in liver function tests and impaired sense of smell.[6]

The OSHA standard for cobalt is 0.1 mg/m^3.[44] The ACGIH has a proposed limit of 0.05 mg/m^3.[5] Although NIOSH does not have a recommended exposure limit specifically for cobalt, NIOSH does recommend an action level of 0.05 mg/m^3 for cemented carbide dust which contains more than two percent cobalt.[45]

Nitrosamines

Historically, nitrosamines have been regarded as one of the most potent families of animal carcinogens. Commercial cutting fluids have the potential for formation of nitrosamines by the reaction of secondary and tertiary amines with nitrites or other oxides of nitrogen (both substances are present in some cutting fluids). NIOSH recommends that exposure should be reduced to the lowest feasible level.(46)

VI. Results and Discussion

A. Environmental

Colorimetric detector tubes (Draeger) were used for the measurement of hydrochloric and acetic acids during the electrolytic etching of the carbide inserts. The odor of both acids was detectable, but measured concentrations in the breathing zone of all three workers were below the detection limit of the Draeger tubes (hydrochloric acid - 1 ppm, acetic acid - 5 ppm).

Table I (personal samples) and Table II (synthetic cutting fluid bulk samples) present the results of the sampling for nitrosamines. None of the seven nitrosamines evaluated were detected. The specific compounds evaluated included the nitrosamines of dimethyl, diethyl, dipropyl, and dibutylamine, plus those of pyrrolidine, piperidine and morpholine. The limit of detection for these compounds ranged from 10-100 nanograms/sample. Since several nitrosamines are carcinogenic, any detectable levels would have been considered significant.

Table III contains the data from the analysis of the bulk cutting fluid samples for cobalt, and the age (number of days since it was last changed) of the fluid. If the records on coolant change frequency are accurate, cutting fluid age may not contribute to cobalt concentration as much as other factors (centrifugal filter efficiency, cobalt content of the metal, coolant physical properties, etc.)

Tables IV and V present the results of the air samples for tungsten (N = 24, Non-Detectable = 17, Range = 0.23-0.41, Mean = 0.28) and cobalt (N = 24, Non-Detectable = 3, Range = 3.3-26.8, Mean = 13.5) all of which were below the evaluation criteria. The highest concentrations of tungsten were less than 6% of the exposure criterion (5 mg/m^3), while the highest cobalt sample was less than 54% of its evaluation criterion (50 ug/m^3). Several other trace metals (nickel, titanium, zinc, etc.) were found, but none in significant quantities. There is currently no evaluation criteria for respirable cobalt. The respirable samples taken during this survey were utilized to evaluate potential respirable metals sampling methods.

B. Medical

Thirty-five workers participated in the questionnaire survey. Table VI shows the prevalence of selected respiratory symptoms by length of employment and smoking status. Workers employed ≥24 months had comparable prevalences of respiratory symptoms regardless of smoking status, but the numbers in the various symptom/exposure categories were too small for meaningfull statistical comparisons. Since these groups are similar with respect to mean age and duration of employment, the non-smokers would be expected to have fewer symptoms. Medical histories of the non-smokers, however, did not reveal other causes for the symptoms. Workers employed less than 24 months had lower symptom prevalences than those of corresponding smoking status employed ≥ 24 months, but the workers employed less than 24 months were also substantially younger.

Job titles were divided into two groups based upon level (as judged by the NIOSH industrial hygienist) of tungsten carbide exposure:

Higher exposure: grinder, honer, set-up

Lower exposure: lapper, shipper, inspection, etching, janitor, office, others

Table VII shows the prevalences of selected respiratory symptoms in nonsmokers according to tungsten carbide category. Higher exposure category is not associated with higher symptom prevalences.

Ten workers had a personal air sample for cobalt during the shift for which they also had pre- and post-shift urine cobalt determination (Table VIII). All ten had a pre- to post-shift increase in urine cobalt concentration. Total airborne cobalt was not associated with urine cobalt concentration, but respirable cobalt was significantly associated with post-shift urine cobalt (Table IX). The correlation coefficients between respirable cobalt and pre-shift urine cobalt and the change (increase) in urine cobalt concentration were substantial but not significant at the 0.05 level.

VII. RECOMMENDATIONS

1. The air sampling program for cobalt and tungsten carbide should be continued. An ongoing program will be necessary to determine if exposure levels are increasing or decreasing.

2. General workplace housekeeping practices should be strictly enforced throughout the plant.

3. Workers should not eat, drink, or smoke on the job. Employees should wash their hands and faces before eating, drinking, or smoking.

4. Another cutting fluid, one that does not contain the ingredients (amines and nitrites) that can potentially form nitrosamines, should be used.

5. A medical surveillance program, including yearly spirometric tests and periodic chest x-rays, should be implemented.

6. Workers with persistent symptoms of cough, chest tightness, shortness of breath, wheezing or other symptoms of concern, should receive an appropriate medical evaluation including yearly chest x-rays.

VIII. REFERENCES

1. Slavin W, Carnick G, Manning D, and Truszkowska E: "Recent Experiences with the Stabilized Temperature Platform Furnace and Zeeman Background Correction", Atomic Spectroscopy 4 (3):69-86, 1983.

2. Annino JS, Clinical Chemistry Principals and Procedures, 3rd Ed., Little Brown and Company, Boston, 1964.

3. Coates OE and Watson J,: Diffuse Interstitial Disease in Tungsten Carbide Workers', Annals of Internal Medicine 75: 709-716, 1971.

4. National Institute for Occupational Safety and Health. Criteria for a recommended standard -- Tungsten and Cemented Tungsten Carbide. Cincinnati, Ohio: National Institute for Occupational Safety and Health, 1977. (DHEW publication no. (NIOSH) 77-127).

5. American Conference of Governmental Industrial Hygienists. Threshold limit values and Biological Exposure Indices for 1986-1987. Cincinnati, Ohio: ACGIH, 1986.

6. Criteria for Controlling Occupational Exposure to Cobalt. HEW Publication No. (NIOSH) 82-107. Cincinnati, USDHEW, PHS, CDC, NIOSH, 1982.

7. Schroeder HA, Nason AP, Tipton IH: "Essential Trace Metals in Man -- Cobalt," J Chronic Dis 20: 869-90, 1967.

8. Scherrer M, Parambadathumalail A, Burki H, Senn A, Zurcher R: [Three Cases of "Hard Metal" Pneumoconiosis.] J Suisse Med 100: 2251-55, 1970 (Ger).

9. Reber E, Burckhardt P: [Hard Metal Pneumoconiosis in Switzerland.] Respiration 27: 120-42, 1970 (Ger).

10. Bech AO: Hard Metal Disease and Tool Room Grinding. J Soc Occup Med 24: 11-16, 1974.

11. Husten K: [Hard-metal Fibrosis of the lungs.] Arch Gewerbepathol Gerwerbehyg 15: 721-92, 1959 (Ger).

12. Einbrodg HJ, Kuhne W: [Lung dust and morphological picture of a hard metal lung] in Reploh H, Klosterkotter W (eds.): Fortschritte der Staublungenforschung. Monograph on the Fourth International Dust-Lung Meeting of April 3-5, 1962, in Munster, Westfalen. Dinslaken, Niederrheinische Druckeri, 1963, 00 217-26 (Ger.).

13. Collet A, Liot F, Gallouedec C, Roussel G, Martin J, Reuet C, Brouet G: [Electron Microscopy Study of Various Cellular Aspects of Pulmonary Fibroadenomatoses with Diffusion Disorders--Discussion on the Etiological Role of Cobalt and Tungsten Carbide.] Rev Tuberc (Paris) 27:357-81, 1963 (Fre).

14. "Cobalt Metal Inhalation Studies on Miniature Swine:, Am Industrial Hyg Assoc J 36:17-25m 1975.

15. Alexandersson R: [Studies on Effects of Exposure to Cobalt. II. Reactions of the Respiratory Organs of Various Exposure Levels in the Hardmetal Industry.] Arbete Och Halsa 2:1-34, 1979 (SWE).

16. Alexandersson R: [Studies on Effects of Exposure to Cobalt. VI. Exposure, Uptake, and Pulmonary Effects on Cobalt in the Hardmetal Industry.] Arbete Och Halsa 10:1-24, 1979 (SWE).

17. Alexandersson R, and Hedenstierna G: [Studies on effects of Exposure to Cobalt: III. Ventilation Capacity, Distribution of inhaled Gas, and closing of Respiratory Passages During Ongoing Work and After Periods of Non-Exposure.] Arbete Och Halsa 7:1-25, 1979 (SWE).

18. Jobs H and Ballhausen C: [The Medical and Technical Viewpoints of Metal Ceramics as a Source of Dust.] Vertrauensorzt KranKenKasse 8:142-48, 1940 (Gre).

19. Rochemaure J, Ancla M, Trinquet G, Meyer A: [A case of pulmonary bifrosis--Possible role of tungsten dust.] J Fr Med Chir Thjorac 26:305-12, 1972 (Fre).

20. Joseph M: Hard metal pneumoconiosis. Australas Radiol 12:92-95, 1968.

21. Bartl F, Lichenstein ME: Tungsten carbide pulonary fibrosis -- A case report. Am Ind Hyg Assoc J 37:668-70, 1976.

22. Teyssier L, Guerin L, Frey N, Lesobre R: [Pulmonary fibrosis observed in the hard metal industry.] Arch Mal Prof 36:53-56, 1975 (Fre).

23. Siegesmund KA, Funahashi A, Pintar K: Identification of metals in lung from a patient with interstitial pneumonia. Arch Environ Health 28:345-49, 1974.

24. Bruckner HC, "Extrinsic Asthma in a Tungsten Carbide Worker", Ann Arbor Reports 9:518-9, 1967.

25. Pirila V, "Sensitization to Cobalt in Pottery Workers" Acta Derm Venereol 33:193-198, 1953.

26. Rystedt I and Fischer T, "Relationship Between Nickel and Cobalt Sensitization in Hard Metal Workers", Contact Dermatitis 9:195-200.

27. Sjorgren I, Hillerdal G, Anderson A and Zelterstrom O, "Hard Metals Lung Disease: Importance of Cobalt in Coolants", Thorax 35:653-659, 1980.

28. Hellsten E, Blomberg M, Henrikson - Enflo A, Sundbom M, and Vokal H, "Kobalt (Copbalt)" Stockholm: University of Stockholm, Institute of Physics, 1976, Report 76.

29. Alexander CS, Cobalt-beer cardiomyopathy -- A clinical and pathologic study of twenty-eight cases. Am J Med 53:395-417, 1972.

30. Morin YL, Foley AR, Martineau G, Roussel J: Quebec Beer-drinkers' cardiomyopathy -- Forty-eight cases. Can Med Assoc J 97:881-83, 1967.

31. The mystery of the Quebec beer drinkers' cardiomyopathy. Can Med Assoc J 97:930-31, 1967 (editorial).

32. Sullivan JF, Egan JD, George RP: A distinctive myocardiopathy occurring in Omaha, Nebraska--Clinical aspects. Ann NY Acad Sci 156:526-43, 1969.

33. Kesteloot H, Roelandt J, Willems J, Claes JH, Joossens JV: An inquiry into the role of cobalt in the heart disease of chronic beer drinkers. Circulation 37:854-64, 1968.

34. Kerr A Jr: Myocardiopathy, alcohol, and pericardial effusion. Arch Intern Med 119:617-19, 1967.

35. Berk L, Burchenal JH, Castle WB: Erythropoietic effect of cobalt in patients with or without anemia. N Engl J Med 240:754-61, 1949.

36. Kato K: Iron-cobalt treatment of physiolkogic and nutritional anemia in infants. J Pediat 11:385-96, 1937.

37. Coles BL: The use of cobalt in some common anaemias of childhood. Arch Dis Child 30:121-26, 1955.

38. Robinson JC, James GW III, Kark RM: The effect of oral therapy with cobaltous chloride on the blood of patients suffering with chronic suppurative infection. N Engl J Med 240:749-53, 1949.

39. Lindblad G, Wegelius R: Effect of cobaslt on the reticulocyte counts of young premature infants. Ann Paediat Fenn 3:103-08, 1957.

40. Rohn RJ, Bond WH: Observations on some hematological effects of cobalt-iron mixtures. J Lancet 73:317-24, 1953.

41. Wolf J, Levy IJ: Treatment of sickle-cell anemia with cobalt chloride. AMA Arch Intern Med 93:387:96, 1954.

42. Coles, BL, James U: Use of cobalt and iron in the treatment and prevention of anemia of prematurity. J Lancet 75:79082, 1955.

43. Duckham JM, Lee HA: The treatment of refractory anaemia of chronic renal failure with cobalt chloride. Q J Med 45:277-94, 1976.

44. Occupational Safety and Health Administration. OSHA Safety and Health Standards. 29 CFR 1910.1000. Occupational Safety and Health Administration, revised 1983.

45. National Institute for Occupational Safety and Health. Criteria for a Recommended Standard: Occupational Exposure to Tungsten and Cemented Tungsten Carbide. Cincinnati, Ohio: National Institute for Occupational Safety and Health, 1977. (DHEW publication no. (NIOSH) 77-227).

46. National Institute for Occupational Safety and Health. Current Intelligence Bulletin No. 15: Nitrosamines In Cutting Fluids. Cincinnati, Ohio: National Institute for Occupational Safety and Health, 1978. (DHEW publication no. (NIOSH) 78-127).

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X. DISTRIBUTION AND AVAILABILITY OF REPORT

Copies of this report are currently available upon request from NIOSH, Division of Standards Development and Technology Transfer, 4676 Columbia Parkway, Cincinnati, Ohio 45226. After 90 days, the report will be available through the National Technical Infromation Service (NTIS), 5285 Port Royal, 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:

1. Confidential Requestor
2. GTE/VALENITE Corporation
3. NIOSH Region IV
4. OSHA Region IV

For the purpose of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

Table I

Airborne Nitrosamines

Valenite #1 Plant
Westminster, South Carolina
HETA 85-064

June 18, 1985

Sample Location	Sample Type	Sampling Period	Nitrosamines*
Automatic grinder B-5 (top) 18" from wheel	Area	07:53-15:35	ND**
Automatic grinder E-1 (top) 18" from wheel	Area	07:55-15:35	ND
Automatic grinder F-5 (top) 18" from wheel	Area	07:30-14:50	ND
Automatic grinder D-5 (top) 18" from wheel	Area	07:30-14:50	ND
Rotary grinder 24" from wheel	Area	07:30-14:50	ND
Evaluation Criteria:			LFL***

* = NIOSH currently uses a seven-standard mixture to calibrate and identify specific nitrosamines. The mixture contains the nitrosamines of dimethyl, diethyl, dipropyl, and dibutylamine, plus those of pyrrolidine, piperidine and morpholine.

**ND = Non-detectable. Limits of detection range from 10-100 ng/sample (air adjusted concentrations would range from 0.02 - 0.2 ug/m^3).

*** = Exposure should be reduced to lowest feasible level (LFL).

Table II

Bulk Nitrosamines

Valenite #1 Plant
Westminster, South Carolina
HETA 85-064

June 18, 1985

Sample Location	Sample Type	Nitrosamine*
Automatic Grinders A-1-2	Bulk	ND**
Automatic Grinders A-3	Bulk	ND
Automatic Grinders B-1-2	Bulk	ND
Automatic Grinders C-3	Bulk	ND
Automatic Grinders D-1-2	Bulk	ND
Automatic Grinders E-1-2	Bulk	ND
Automatic Grinders F-1-2	Bulk	ND
Fresh Coolant Sample	Bulk	ND
Rotary Grinder	Bulk	ND
Rotary Grinder	Bulk	ND

* = NIOSH currently uses a seven-standard mixture to calibrate and identify specific nitrosamines. The mixture contains the nitrosamines of dimethyl, diethyl, dipropyl, and dibutylamine, plus those of pyrrolidine, piperidine and morpholine.

**ND = Non-detectable. Limits of detection ranged from 10-100 ng/sample.

Table III

Cobalt Bulk Samples

Valenite #1 Plant
Westminster, South Carolina
HETA 85-064

June 19, 1985

Sample Location	Cobalt Concentration ug/10 ml Bulk Sample Solution	Age of Coolant in Days
Automatic Grinders F-1-2	721*	6
Automatic Grinders D-1-2	436	13
Automatic Grinders G-3	316	15
Automatic Grinders C-4-5	249	24
Automatic Grinders C-1-2	98	25
Automatic Grinders A-1-2	37	30
Automatic Grinders E-1-2	537*	39
Automatic Grinders A-3	583	21
Automatic Grinders B-1-2	197	51
Automatic Grinders D-4-5	60	1
Rotary Grinder (47)	754	60
Rotary Grinder (1)	322	21
Top of Coke Machine in Lunchroom (before enclosure)	334	-
Top of Coke Machine in Plant	583	-

* = Filtration centrifuge broken.

Table IV

Tungsten and Cobalt

Valenite #1 Plant
Westminster, South Carolina
HETA 85-064

June 18, 1985

Sample Location/Job	Sample Type	Sampling Period	Tungsten (mg/m^3)	Total Cobalt (ug/m^3)	Respirable Cobalt (ug/m^3)
Set-Up	Personal	07:11-15:30	0.23	16.4	3.4
Set-Up	Personal	07:13-15:30	0.23	13.1	4.1
Automatic Grinder (C-Cluster)/Operator	Personal	07:17-15:30	ND*	14.9	5.4
Automatic Grinder (A-Cluster)/Operator	Personal	07:17-15:30	ND	19.8	4.0
Automatic Grinder (E-Cluster)/Operator	Personal	07:17-15:30	ND	15.6	5.0
Honer/Operator	Personal	07:25-15:10	ND	6.7	3.2
Rotary Grinder/Operator	Personal	07:28-15:30	0.24	20.0	5.7
Packaging and Marking	Area	07:30-15:30	ND	3.3	1.7
Lunchroom	Area	07:33-15:30	ND	ND	ND
Inspector	Personal	07:35-15:30	ND	5.1	2.0
Office	Area	07:37-15:30	ND	ND	ND
Control (Ambient Air)	Area	07:40-15:30	ND	ND	ND
Evaluation Criteria: NIOSH			5.0	50	-
OSHA			-	100	-

* = Non-detectable. Limits of detection are 125 ug/sample (tungsten) and 1 ug/sample (cobalt).
mg/m^3 = Milligrams of substance per cubic meter of air.
ug/m^3 = Micrograms of substance per cubic meter of air.

Table V

Tungsten and Cobalt

Valenite #1 Plant
Westminster, South Carolina
HETA 85-064

June 19, 1985

Sample Location/Job	Sample Type	Sampling Period	Tungsten (mg/m^3)	Total Cobalt (ug/m^3)	Respirable Cobalt (ug/m^3)
Automatic Grinder (C-Cluster)/Operator	Personal	06:55-15:00	0.31	17.9	5.5
Automatic Grinder (E-Cluster)/Operator	Personal	07:00-15:07	ND*	15.4	4.2
Set-Up.Electrical	Personal	07:00-15:13	ND	16.2	5.0
Set-Up	Personal	07:02-15:11	ND	12.3	4.5
Automatic Grinder (B-Cluster)/Operator	Personal	07:04-15:08	0.41	26.8	7.0
Honer/Operator	Personal	07:10-15:00	ND	9.0	3.8
Rotary Grinder/Operator	Personal	07:10-15:04	0.26	12.8	4.0
Automatic Grinder (G-Cluster)/Operator	Personal	07:10-15:11	0.31	26.0	8.4
Janitor	Personal	07:12-15:07	ND	10.2	4.0
Packaging and Marketing	Area	07:15-14:53	ND	5.0	2.2
Inspection	Area	07:15-14:53	ND	8.5	2.7
Honer/Operator	Personal	07:17-15:01	ND	8.0	3.7
Evaluation Criteria: NIOSH			5.0	50	-
OSHA			-	100	-

* = Non-detectable. Limits of detection are 125 ug/sample (tungsten) and 1 ug/sample (cobalt).
mg/m^3 = Milligrams of substance per cubic meter of air.
ug/m^3 = Micrograms of substance per cubic meter of air.

TABLE VI
Respiratory Symptoms by Length of Employment and Smoking Status

Valenite #1 Plant
Wesminster, South Carolina
HETA 85-064
June 18-19, 1985

	Number of Participants	Mean age (years)	Mean duration of employment (months)	Number and (%) of Workers with Symptom: Cough	Chest Tightness	Shortness of Breath	Wheezing	Number and (%) with ≥ 2 of the 4 Symptoms	Mean number of the selected symptoms
Non smoker (current & past)									
employed < 24 months	8	27	8	2 (25)	2 (25)	1 (13)	1 (13)	2 (25)	0.8
employed ≥ 24 months	11	38	67	5 (46)	6 (55)	5 (46)	5 (46)	7 (64)	1.9
Smokers (current and/or past)									
employed < 24 months	4	26	2	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	0.0
employed ≥ 24 months	12	36	70	8 (67)	6 (50)	4 (33)	5 (42)	8 (67)	1.9
Smokers (current only) employed ≥ 24 months	9	39	66	6 (60)	5 (56)	4 (44)	5 (56)	7 (78)	2.0

TABLE VII
Respiratory Symptoms Among Nonsmokers by Tungsten Carbide Exposure Category (See Text)

Valenite #1 Plant
Wesminster, South Carolina
HETA 85-064
June 18-19, 1985

	Number of Participants	Mean Age (years)	Mean duration of employment (months)	Number with Symptom: Cough	Chest Tightness	Shortness of Breath	Wheezing	Number with ≥ 2 of 4 symptoms
Higher Exposure Jobs	10	33	41	4	3	3	2	4
Lower Exposure Jobs	9	34	42	3	5	3	4	5

TABLE VIII
Air and Urine Cobalt Concentrations

Valenite #1 Plant
Wesminster, South Carolina
HETA 85-064
June 18-19, 1985

Participant	Air Cobalt Concentration (ug/m^3)		Urine Cobalt Concentration (ug/g creatinine)		
	Total	Respirable	Pre-Shift	Post-Shift	Change
1	8.0	3.7	4.7	11.4	+6.7
2	10.2	4.0	7.0	8.4	+1.4
3	12.8	4.0	9.1	16.6	+7.5
4	13.1	4.1	10.2	15.9	+5.7
5	14.9	5.4	10.7	13.4	+2.7
6	15.6	5.0	10.7	25.3	+14.6
7	16.4	3.4	15.9	17.6	+1.7
8	17.9	5.5	19.0	27.7	+8.7
9	19.8	4.0	11.5	26.6	+15.1
10	20.0	5.7	6.2	18.3	+12.1

TABLE IX
Correlations Between Air and Urine Cobalt Concentration

Valenite #1 Plant
Wesminster, South Carolina
HETA 85-064
June 18-19, 1985

Cobalt Exposure*	Urine Cobalt Concentration**	Spearman Rank Correlation Coefficient	p
Respirable	Pre-Shift	0.52	0.12
Respirable	Post-Shift	0.83	0.003
Respirable	Change	0.58	0.08
Total	Pre-Shift	0.07	0.84
Total	Post-Shift	0.39	0.27
Total	Change	0.39	0.27

 * = Respirable and total air cobalt concentrations (ug/m^3).
** = ug/g Creatinine.