

Health Hazard

Evaluation UNITED CATALYSTS, INC. - WEST PLANT LOUISVILLE, KENTUCKY

Report

#### 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.

HETA 83-075-1559
FEBRUARY 1985
UNITED CATALYSTS, INC. - WEST PLANT
LOUISVILLE, KENTUCKY

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### I. SUMMARY

In August and Novem'er 1982, the National Institute for Occupational Safety and Health (NIOSH) was requested by the Kentucky Department of Labor top conduct a Health Hazard Evaluation (HHE) at two United Catalysts, Inc. plants (South and West Plant) located in Louisville, Kentucky. The requestor expressed concern as to the incidence of cancer in the workplace.

In November 1982, NIOSH conducted an initial site visit to the West Plant. Subsequently follow-up medical and/or environmental field surveys were conducted in March and June of 1983.

Environmental sampling was conducted to evaluate employee exposures to nickel, chromium, chromium VI, copper, cobalt (and other metals), particulates, crystalline silica, ammonia, oxides of nitrogen, and inorganic acids. The company's exposure control programs were also evaluated.

NIOSH distributed a medical questionnaire to 98 South Plant employees and 135 West Plant employees, reviewed company pulmonary function test results and testing methods, and reviewed company retirement and insurance death records for a possible cancer excess.

Airborne concentrations on personal samples for the various chemicals were 8 to 1780  $ug/m^3$  for nickel, below the laboratory limit of detection to 327  $ug/m^3$  for total chromium, 25.3 to 7900  $ug/m^3$  for copper, 1 to 34  $ug/m^3$  for lead, below the laboratory limit of detection to 7  $ug/m^3$  for cobalt, 1 to > 10700  $ug/m^3$  for zinc, 0.39 to 3.63  $mg/m^3$  for respirable particulate, 0.53 to 24.2  $mg/m^3$  for total particulate, 2.55 to 13.5  $mg/m^3$  for ammonia, 0.18 to 0.39  $mg/m^3$  for nitric oxide, 0.96 to 1.04  $mg/m^3$  for nitrogen dioxide, and below the laboratory limit of detection to 0.84  $mg/m^3$  for phosphoric acid. Twenty-two of 38 nickel samples exceeded the NIOSH recommended standard of 15  $ug/m^3$ , and 12 of 38 copper samples were in excess of the OSHA permissible exposure limit of 1000  $ug/m^3$ . For the other materials, no more than one sample exceeded any criterion.

Deficiencies were noted in the company's respiratory protection program, employees training and education, engineering controls, and housekeeping.

Questionnaire data showed that 70% of the 98 South Plant employees and 72% of the 235 West Plant employees reported having one or more symptom. Cough was the symptom reported most often at both plants (49% of South Plant workers and 45% of West Plant workers). Nasal sores were reported more often by South Plant workers (35%) than by West Plant workers (20%), and skin rashes were reported more at the West Plant (39%) than at the South Plant (27%). Smoking status did not appear to affect the prevalence of respiratory symptoms. Symptom prevalences in high and medium exposure groups were greater than those in the low exposure groups. Almost half of the pulmonary function tests were interpreted in company records as being slightly to severely abnormal. The number and distribution of cancer cases identified did not appear to be unusual.

Based on the results of this investigation, NIOSH investigators have determined that a health hazard existed for employees from exposure to nickel and copper. Employees were also found to have a high prevalence of work-related symptoms. Improvements are needed in several exposure control programs including engineering controls, respiratory protection, employee training and education, and house keeping. Recommendations to improve employee working conditions are made in section VIII.

KEYWORDS: SIC 2819 (Industrial inorganic chemicals, chemical catalysts), catalyst-manufacturing, nickel, copper, chromium, chromium VI, ammonia, phosphoric acid, skin rash, cough, nasal sores.

# II. INTRODUCTION

In the fall of 1982, the National Institute for Occupational Safety and Health (NIOSH) received a request from the Kentucky Department of Labor to evaluate environmental exposures and employee health at two United Catalysts Incorporated plants (called the South and West Plants) in Louisville, Kentucky. The request indicated a potential high incidence of cancer among the workforce.

NIOSH made an initial visit to each facility on November 2-5, 1982. A follow-up environmental/medical survey was conducted at the West Plant on February 28 through March 4, 1983. A second environmental survey was conducted on June 27-29, 1983.

Interim report No. 1 was distributed in May 1983. This report presented preliminary environmental findings and recommendations for improving working conditions at the West Plant. Interim report No. 2, presenting medical findings and recommendations, was distributed in January 1984. Interim report No. 3, presenting environmental findings and additional recommendations from the second follow-up survey, was distributed in March 1984.

### III. BACKGROUND

# History

United Catalysts, Inc. was formed in 1977 by a merger of Catalysts and Chemicals, Inc. and Girdler Chemical, Inc. Girdler Chemical, Inc. (now called the South Plant), began production in the early 1940's as the Girdler Catalyst Division of the Girdler Corporation. Catalysts and Chemicals, Inc. (now known as the West Plant), began operation at its present location in 1957.

### Workforce

The West Plant has approximately 260 employees, of which 240 are involved in maintenance and production. Job classifications include operators, screening employees, maintenance, and janitors. Operators are divided into chief operators who are responsible for catalyst production, and operator helpers who assist the chief operators. Screening employees are responsible for screening various catalysts to insure uniformity in the size and shape of the finished products. Maintenance employees are responsible for routine equipment maintenance and emergency repairs. Janitors are responsible for general plant housekeeping.

# Catalyst Production

The catalysts manufactured cover a broad range of uses including hydrogen and synthesis gas manufacturing (e.g carbon monoxide conversion and methanation), gas.purification (e.g., conversion of organic sulfur to hydrogen sulfide), hydrogenation (e.g. hydrogenation of fats and oils), dehydrogenation (e.g. styrene manufacturing), oxidation (e.g. production of sulfuric acid), synthesis and dissociation (e.g. methanol synthesis), and acid catalysts (e.g. alkylation). Custom catalysts made to the specification of the client are also produced.

A finished catalyst typically consists of the reactive component such as nickel, chromic oxide, phosphoric acid, or a combination such as iron oxide/potassium carbonate, on a carrier such as aluminum oxide and silicon dioxide. Some catalysts, however, have no carrier, consisting only of the reactive or functional component. The percentage of the chemicals that constitute the reactive component cover a broad range. Nickel, for example, varies from less than 1% in some mixed metal catalysts to more than 60% in catalysts in which it is the single reactive component.

Specific catalyst carriers are formulated to provide various chemical and physical properties. Depending on raw materials used, surface areas can range from less than 0.1 m<sup>2</sup> per gram to more than 200 m<sup>2</sup> per gram. The carriers are available in various shapes, including spheres, cylinders, rings, tablets, gears, irregular shaped granules, and fluid-bed spherical particles.

Catalyst manufacturing is based primarily on batch production which involves mixing together the raw materials and then forming the mix into spheres, powder, rings, etc. Subsequently, the material is calcined to cure it and then screened to insure uniform size and shape for the finished product. The actual catalyst production can be relatively simple or quite complex, depending on the specific catalyst involved and whether it is produced using a dry (generally less complex) or a wet system.

One of the simpler catalyst production processes involves mixing the raw materials (phosphoric acid and diatomaceous earth) while simultaneously forming the mix into spheres. Subsequently, the material is sent through a calciner to be dried and cured. After screening the material is ready for shipment. Conversely, a more complex process involves initially dissolving nickel metal into a solution of ammonium hydroxide and carbon dioxide to form nickel amine carbonate. Subsequently, a carrier (SiO<sub>2</sub>) is added and the nickel amine carbonate is precipitated onto the carrier. The material is then

filtered to reduce the moisture content, and the resulting slurry is processed through a spray dryer to remove more of the moisture and separate out improper sized particles. Next, the material is calcined, which converts it to nickel oxide by removing ammonia and carbon dioxide. Then, the material is milled, sent to a reduction furnace where it is converted to nickel metal, stabilized using soya oil, and subsequently formed into flakes. The material is then ready for shipment. The time required to produce a catalyst normally varies from two to 24 hours. For those which require repeated processing steps such as washing or dipping, additional time is required.

The wide range in catalyst function, and the modifications which can be made to a particular catalyst series result in a large number of catalysts that can, and have been produced at each plant. There are however, a much smaller number of catalysts that constitute most of the day to day production. Some catalysts are run almost every day, while others will be produced sporadically.

The West Plant has four processing areas called Building 1 (formerly called 1 and 2), 3, 4, and 12, that were evaluated for this study and others (the Clays Division) that were not. The West Plant is non-unionized and operates 12-hour shifts. It has no reduction/-stabilization equipment and subsequently produces none of the catalysts used in the hydrogenation of fats and oils. The plant has a centralized screening room where 95% of the finished catalysts are processed.

Less than 50% of the catalysts produced at the West Plant contain nickel, as compared to approximately 60% at the South Plant. Most of the other routinely produced catalysts have copper, cobalt, zinc, iron, molybdenum, or phosphoric acid in the reactive component.

# Raw Materials

The list of raw materials used at united Catalyst includes metals (nickel, copper, aluminum, zinc, chromium, platinum, palladium, iron, molybdenum, cobalt, vanadium, bismuth) in the form of a metal wire or brick, metal powder, metal oxide, or metal nitrate; acids (phosphoric, nitric and sulfuric); and other materials including diatomaceous earth, attapulgite clay, aluminum oxide, silicon dioxide, sodium hydroxide, sodium bichromate, ammounium zirconiuim carbonate, potassium carbonate, cerium carbonate, aqua ammonia, hydrogen, carbon dioxide, soya oil, air, and water.

## Processing Equipment

The major types of processing equipment used at United Catalysts include:

- 1. Dryers to reduce the moisture content of a material.
- Calciners to reduce moisture content, attain the appropriate particle size, and/or to change the chemical nature of a material (e.g. remove nitrates from a metal nitrate solution to form a metal oxide).
- High temperature furnaces used to heat treat and subsequently strengthen certain types of formed catalyst carriers (e.g. aluminum oxide rings).
- Spray dryers used to produce a high moisture solid out of a liquid slurry and subsequently separate out improperly sized particles.
- 5. Filters used to remove the solid component of a solution.
- Filter presses used to separate components and to remove impurities from a solution during washing operations.
- 7. Reduction furnaces used to reduce nickel oxide using hydrogen.
- Stabilization units used to stabilize elemental nickel using either an oil process (soya oil) or dry stabilization with a mixture of oxygen and carbon dioxide.
- Strip tanks in which steam heat is used to remove ammonia and carbon dioxide from a metal amine carbonate solution forming a metal oxide.
- Precipitation tanks in which the reactive component of a catalyst is precipitated onto a carrier.
- Decant tanks in which heavier materials in a mixture are allowed to settle, after which, the liquid upper portion is removed.
- 12. Grinding mills used to reduce the particle size.
- 13. Mixers used to combine materials.
- 14. Drum elevators used to raise and empty drums of material.

- 15. Forming machines (which include tablet machines, ring machines, extruders, and ball wheels) used to produce various sizes and shapes of the finished catalyst material.
- 16. Reactors in which metal raw materials are dissolved into solution.

### IV. METHODS AND MATERIALS

### A. Environmental

The environmental investigation consisted of an evaluation of the West Plant's exposure control programs and airborne monitoring of various agents.

Environmental data collected by management was reviewed to assess the type and magnitude of exposure in different work areas. The data indicated where highest personal exposures had been measured previously, but was limited in usefullness because exposures had been determined for total and/or respirable particulates only, not for specific chemicals (e.g. nickel).

During the first follow-up survey airborne monitoring was conducted to evaluate employee exposures to airborne concentrations of particulates, metals, hexavalent chromium (chromium VI), crystalline silica, ammonia, phosphoric acid, and oxides of nitrogen (nitric oxide and nitrogen dioxide). In addition, a bulk insulation sample was collected for asbestos analysis. Area samples were also collected as a screening technique for inorganic acids, amines, and general organic materials. Additionally, direct-reading instruments were used to collect grab samples for vapors and/or gases and to measure total ionizing radiation. Settled dust samples were collected to evaluate inorganic metals and crystalline silica content.

### Total and Respirable Particulates

Total and respirable dust samples were collected on polyvinyl chloride (PVC) filters, contained in two piece plastic casettes, attached via flexible tubing to a battery-operated pump calibrated at 1.5 liters per minute (lpm) for total dust samples and 1.7 lpm for respirable dust samples. For respirable samples the PVC filters were loaded into 10mm nylon cyclones. The samples were analyzed by weighing the sample plus the filter on an electrobalance and subtracting the previously determined tare weight of the filter.

High volume area airborne respirable particulate samples were collected on PVC filters loaded into a 1/2-inch stainless steel cyclone attached via flexible tubing to an electric vacuum pump. A critical orifice located in the tubing controlled the flow rate at approximately 9 lpm. These samples were analyzed for percent crystalline silica using X-ray diffraction according to NIOSH Method No. P&CAM 259 (modified).1

#### Metals

Metals samples were collected on mixed cellulose ester membrane filters attached via flexible tubing to battery-operated pumps calibrated at 1.5 lpm. Some of these samples were analyzed for four specific metals (chromium, nickel, copper, and cobalt) using atomic absorption according to NIOSH Method No. P&CAM 173.1 Other metals samples were analyzed for twenty-eight separate metals, using inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

#### Hexavalent Chromium

Hexavalent chromium samples were collected on PVC filters attached via flexible tubing to battery-operated pumps calibrated at 2 lpm. These samples were analyzed by colorimetric spectrophotometry according to NIOSH Method No. P&CAM 319.<sup>2</sup>

#### Amines

Samples for airborne amines were collected on citric acid-coated silica gel tubes attached via flexible tubing to battery-operated pumps calibrated at 0.1 lpm. The samples were then screened qualitatively for aliphatic and/or aromatic amines since only one type (aliphatic or aromatic) could be evaluated on individual samples. Aliphatic amines were evaluated according to NIOSH Method No. P&CAM 276.3 Aromatic amines were analyzed according to NIOSH Method No. P&CAM 168.1

### Inorganic Acids

Inorganic acid samples (samples for phosphoric acid and screening samples) were collected on sulfuric acid treated silica gel tubes attached via flexible tubing to battery-operated pumps calibrated at 0.1 lpm. The samples were analyzed by ion chromatography according to NIOSH Method No. P&CAM 339.4

### Oxides of Nitrogen

Long-term nitric oxide and nitrogen dioxide samples were collected on three-section molecular sieve sorbent tubes attached via flexible tubing to a battery-operated pump calibrated at 0.02 lpm. These samples were analyzed using a colorimetric procedure according to NIOSH Method No. P&CAM S321.3 Grab samples for oxides of nitrogen were collected using direct-reading gas detector tubes and a detector tube pump. These samples were visually analyzed immediately after collection.

#### Ammonia

Long-term ammonia samples were collected on a sulfuric acid-treated silica gel tube preceded by a mixed cellulose ester membrane filter. These samples were attached via flexible tubing to a battery-operated pumps calibrated at 0.05 lpm. Ammonia samples were analyzed using a colorimetric automated phenate method. Grab samples for ammonia were collected using direct-reading gas detector tubes and a detector tube pump. These samples were visually analyzed immediately after collection.

### Organic Materials

Area samples for general organic compounds were collected on charcoal tubes attached via flexible tubing to battery-operated pumps calibrated at 0.5 lpm. The samples were analyzed qualitatively by splitting each sample in half and analyzing one portion with a gas chromatograph equipped with a flame ionization detector. The second portion was analyzed by gas chromatography/mass spectroscopy.

### Bulk Samples

The bulk insulation sample was collected in a glass vial and analyzed for the percent and type of asbestos present, utilizing polarized light microscopy and dispersion staining techniques.

Material bulk samples were collected in glass vials and analyzed for percent crystalline silica utilizing X-ray diffraction. Two milligram portions of each material bulk sample were weighed onto PVC filters in duplicate. The samples were then analyzed according to NIOSH Method No. P&CAM 259 (modified).1

Settled dust samples were collected in glass vials and subsequently analyzed for the percent (by weight) metals and/or the percent crystalline silica. For metals analysis, replicate aliquots of each sample were weighed and digested in acids. The resulting solutions were analyzed by ICP-AES. For analysis of crystalline silica, two milligram portions of each sample were weighed onto a PVC filter and subsequently analyzed according to NIOSH Method No. P&CAM 259 (modified). 1

### Ionizing Radiation

Area radiation measurements were obtained using a Mini Con-Rad portable survey meter (Model 3032). Reading were obtained for the total exposure rate from alpha, beta, and gamma radiation.

During the second follow-up survey, the NIOSH industrial hygiene team evaluated the respiratory protection program, the condition of engineering controls throughout the plant, general housekeeping, and also conducted personal sampling for airborne metals of selected job classifications, per a request by management.

Sampling and analytical techniques for all materials evaluated are summarized in Table I.

### B. Medical Evaluation

### 1. Questionnares

A questionnaire seeking information on demographic characteristics; smoking, work, and medical histories; and current health problems was distributed to 98 employees at the South Plant and 235 at the West Plant. The purpose was to determine if employees at United Catalyst exhibited symptoms associated with potential exposures at the plant. Questionnaires were administered to employees in groups ranging in size from 15 to 25. (This procedure allowed the NIOSH investigator to explain the purpose of the survey and to answer specific questions about the survey and the questionnaire.) For analysis of the questionnaire data, employees were divided into high, medium, and low exposure groups using the environmental total airborne metals concentrations collected during the first follow-up survey, and for those jobs not monitored, the NIOSH industrial hygienist's estimates of relative exposure.

#### 2. Record Review

To evaluate the possibility of an excess cancer rate at United Catalyst, a union-supplied list of 43 occurrences of illnesses and/or deaths among employees was reviewed. This list was prepared by several senior plant employees. In addition, the company's retirement benefit plan and death records dating back to 1977 were reviewed. Finally, company insurance carriers were contacted concerning their death records on nasal and lung cancer, cancer types which are associated with exposure to nickel and hexavalent chromium.

The company's pulmonary function test (PFT) results, the testing methods, and criteria for interpretation were reviewed. These records contain one set of PFT's for each employee. The company began the testing in 1982, and reportedly plans to continue the program, along with additional medical surveillance, on an annual basis.

### V. EVALUATION CRITERIA

## A. Environmental evaluation

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 Criteria Documents and recommendations, the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLV's), and 3) the U.S. Department of Labor (OSHA) occupational health standards. 5-8 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 required 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 this report, it should be noted that industry is legally required to meet only 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. Since employees worked 12-hour shifts at the West Plant, the appropriate 8- or 10-hour criteria may not be suitable. Extended works shifts involve not only increased exposure to occupational chemicals but also a reduced recovery time away from the exposures. 9 For this report, the criteria have been adjusted by a corresponding factor of one-third for an 8-hour or one-fifth for a 10-hour criteria. The technique is similar to that presented in the OSHA standard for lead. $^{10}$  While there is some question as to the best technique for evaluating the personal exposures found at this facility. The NIOSH investigators believe it is prudent to use the conservative approach and thus have chosen the adjusted criteria for assessing employee exposures at the West Plant. Standard (8- to 10-hour) environmental criteria and associated health effects for the materials evaluated are listed in Table II. On each subsequent table, standard and adjusted environmental criteria are presented.

#### B. Chromium

Chromium compounds may exist in the bivalent (+2), trivalent (+3) or hexavalent (+6) states. Exposure to chromium compounds has been associated with dermatitis and the development of pulmonary sensitization. In general, bivalent and trivalent compounds are considered to be of a low order of toxicity. 7,11

Hexavalent chromium compounds have been implicated in a number of health problems including skin ulceration, ulcerated nasal mucosal, perforated nasal septum, rhinitis, nosebleed, perforated eardrums, kidney damage, pulmonary congestion and edema, epigastric pain, erosion and discoloration of the teeth, and dermatitis. In addition, some hexavalent chromium compounds have been associated with an increased rate of lung cancer. 12

Noncarcinogen chromium (+6) compounds include the monochromates and bichromates of hydrogen, lithium, sodium, potassim, rubidium, cesium, and ammonium, and chromium (+6) oxide (chromic acid anhydride). All other chromium (+6) compounds are considered carcinogenic. 12

The OSHA Permissible Exposure Limit (PEL) for chromium compounds is 0.5 mg/m³ for soluble chromic and chromous salts as Cr, and 1.0 mg/m³ for chromium metal and insoluble salts, with a ceiling value of 0.1 mg/m³ for chromic acid and chromates. The ACGIH TLV is 0.50 mg/m³ for chromium metal, and chromium +2 and +3 compounds. The TLV for +6 chromium compounds is 0.05 mg/m³, with certain water insoluble compounds being considered as human carcinogens. The NIOSH recommended standard is 0.025 mg/m³ for noncarcinogenic, and 0.001 mg/m³ for carcinogenic chromium (+6) compounds.  $^{12}$ 

# C. Nickel

Nickel is a malleable and ductile, ferromagnetic metallic element which is resistant to corrosion in many acids, salts and alkalis, water, and gases. In addition to catalysts, nickel is used in alloys such as stainless steel. It is also used in electroplating, production of magnetic tapes, coins, batteries and paints. 13

Exposure to nickel and its compounds has been associated with many health effects including allergic reactions, irritation of the skin and mucous membranes, and an increased incidence of various types of cancer.  $^{13,14}$  Nickel and its compounds are among the most common causes of allergic dermatitis. Nickel is also associated with irritation of the conjunctiva of the eye and mucous membranes of the upper respiratory system. Perforation of the nasal septum is another reported symptom.  $^{11,13}$ 

Workers in the nickel refinery industry were found to have an increased incidence of lung and nasal cancer. 13,14 The exact nickel compounds responsible for the increased cancer risk were not definitely proven, but nickel subsulfide, nickel oxide, nickel chloride, and nickel sulfate were among the suspected materials. 14

The OSHA PEL for nickel metal and soluble compounds (as Ni) is  $1 \text{ mg/m}^3$ . In establishing its criterion for exposure to nickel, ACGIH distinguished between nickel metal and insoluble nickel compounds, and soluble nickel compounds. Additionally, nickel sulfide roasting dusts and fume were designated as being associated with an increased risks of respiratory cancer. 7

NIOSH, however, defines "nickel" as elemental nickel and includes all nickel compounds except organonickel compounds. In the criteria document for occupational exposure to inorganic nickel, NIOSH states: "There is overwhelming evidence that nickel refinery workers have had an excess of deaths from cancer of the respiratory organs. Evaluation of this evidence has led NIOSH to conclude that many of these cancers were nickel-induced, and that inorganic nickel should be regarded as a carcinogen." The NIOSH recommended standard for nickel is 15 ug/m³.14

# D. Copper

Copper dusts or mists can affect the body through inhalation, ingestion, or direct contact.<sup>5</sup>

Short-term exposures to powdered copper or dust and mists of copper salts are associated with cold-like symptoms including sensations of chills and head stuffiness. If copper particulates enter the eyes they may cause irritation, discoloration, and damage.  $^5$ 

Inhalation of dusts and mists of copper and copper salts may cause mucous mambrane irritation and may also cause ulceration with perforation of the nasal septum.  $^{5,15}$  Other symptoms reported to be associated with metallic copper exposure are keratinization of the hands and soles of the feet, metallic taste, nausea, metal fume fever and discoloration of skin and hair. The OSHA PEL and ACGIH TLV for copper dust are  $1000~\text{ug/m}^3$ . NIOSH currently has no recommended standard for copper.

### VI. RESULTS

### A. Environmental

# 1. Environmental Monitoring, First Follow-Up Survey

# Me tals

Table III presents the results of sampling for six metals (nickel, copper, chromium, lead, zinc, cobalt) most likely to cause health effects. Airborne concentrations of nickel ranged from 8 to 1780 ug/m³ for 29 personal samples. Twenty-three of the 29 samples exceeded the adjusted NIOSH recommended standard of 12.5 ug/m³ and one of the 29 samples exceeded the adjusted OSHA PEL and ACGIH TLV of 667 ug/m³. Seven of the nickel samples exceeding the NIOSH criterion were collected in the Screening Area in Building 1; this includes three of the four samples which exceeded 100 ug/m³.

Airborne concentrations of copper ranged from 28.6 to 7060  $ug/m^3$  for 29 personal samples. Seven of the 29 samples exceeded the adjusted OSHA PEL and ACGIH TLV of 667  $ug/m^3$ . The highest copper air concentrations were measured in Building 1 (3270  $ug/m^3$ ) and Building 3 (4620 and 7060  $ug/m^3$ ). These values were obtained on the C79 Dry End operator; and the C18 Tab Bay and C61 operators, respectively.

Airborne concentrations of chromium ranged from below the laboratory limit of detection to 232 ug/m<sup>3</sup> for 29 personal samples. All values were below the current criteria for total chromium. The highest value is approximately 70% of the adjusted ACGIH TLV of 333 ug/m<sup>3</sup>, which is the lowest current criterion. This sample was collected on the C12 operator in Building 1. Airborne concentrations of lead ranged from 1 to 34 ug/m<sup>3</sup> for 19 personal samples. One of the 19 samples exceeded the adjusted lowest criterion of 33 ug/m3 (OSHA PEL). This sample was obtained on a screening employee in Building 1. Airborne concentrations of zinc ranged from 1 to greater than 10700 ug/m<sup>3</sup> for 19 personal samples. One of the values exceeded the adjusted lowest current criterion of 4170 ug/m<sup>3</sup> (NIOSH). This sample was collected on the C61 operator in Building 3. Airborne concentrations of cobalt ranged from below the laboratory limit of detection (1 ug/sample) to 7 ug/m<sup>3</sup> for 29 personal samples. All values are less than 12% of the adjusted environmental criteria of 66.7 ug/m3 (OSHA and ACGIH).

### Particulates

Table IV presents the results of sampling for total and respirable particulates for 14 personal samples. Concentrations of respirable particulate ranged from 0.39 to 3.63 milligrams per cubic meter (mg/m³) for 12 samples. One of the 12 values exceeded the adjusted criteria of 3.3 mg/m³ (OSHA and ACGIH). The two total particulate samples had concentrations of 0.53 and 24.2 mg/m³. One value exceeded the lowest criterion (6.7 mg/m³ ACGIH) by a factor of 4. Most of the high values were obtained in Buildings 1 and 3. The Screening Area in Building 1 had the highest value of both respirable and total particulate.

#### Chromium VI

Table V presents the results of area sampling for chromium VI. Airborne concentrations on two samples in the C12 Tab Bay were 73.4 and 66  $\mbox{ug/m}^3$ . Two samples collected in the Screening Area had concentrations of 6.4 and 3.2  $\mbox{ug/m}^3$ . All four samples were above the adjusted NIOSH recommendation for carcinogenic chromium VI of 0.8  $\mbox{ug/m}^3$ . Two of the samples were also above the adjusted NIOSH recommendation for noncarcinogen chromium VI of 20.8  $\mbox{ug/m}^3$ . The NIOSH recommended standards are the lowest of the current criteria.

### Crystalline Silica

Table VI presents the results of analysis of crystalline silica in three area high-volume respirable dust samples. Neither polymorph of crystalline silica (quartz and cristobalite) was detected in the three samples. Additionally, no crystalline silica was detected on two settled dust samples. However, one bulk material sample of a raw material used for C84 catalysts contained 5.3% quartz. The material container listed a warning that it contained varying amounts of crystalline silica.

#### Ammonia

Table VII presents the results of sampling for airborne ammonia. Concentrations ranged from 2.55 to 13.5 mg/m $^3$  for seven personal samples. One of the seven values exceeded the adjusted ACGIH TLV of 12 mg/m $^3$ . The two highest values (11.8 and 13.5 mg/m $^3$ ) were measured in Building 4.

### Oxides of Nitrogen

Table VIII presents the results of sampling for airborne oxides of nitrogen ( $NO_X$ ). Concentrations on three personal and two area samples ranged from 0.29 to 3.03 mg/m $^3$  for nitric oxide (NO) and from 0.96 to 2.73 mg/m $^3$  for nitrogen dioxide ( $NO_2$ ). All concentrations for personal samples were below all adjusted criteria.

# Inorganic Acids

Table IX presents the results of sampling for inorganic acids. Nitric acid was the only inorganic acid found on two area screening samples collected in Building 1. Airborne concentrations were 0.54 and 3.72 mg/m $^3$ . The sample collected in the Nitrate Alley was above the adjusted criteria for OSHA and ACGIH (3.33 mg/m $^3$ ). Eight personal samples were collected for phosphoric acid in Building 12. Concentrations ranged from below the laboratory lower limit of detection (8 ug/sample) to 0.84 mg/m $^3$ . One value was above the adjusted criteria of 0.67 mg/m $^3$  (OSHA and ACGIH).

## Bulk Dust

Table X presents the results of the analysis of percent metals in settled dust samples. Results are listed for six metals thought to present the most significant health concern. Percentages for these six metals ranged from less than 0.05 to 11.5 (copper) in one sample. Copper, chromium, nickel, and

zinc were found in excess of 1% in at least one sample. Zinc and copper were both detected in excess of 3.8% on two of the three samples. These results indicate that general dust build up in the plant could contribute to airborne concentrations of the various metals via employee or vehicular traffic and/or work practices (e.g. sweeping).

### Detector Tube Sampling

Results of grab samples for ammonia and  $NO_X$  using direct reading detector tubes, are presented in Table XI. Airborne concentrations of ammonia ranged from nondetected to greater than 50 parts per million (ppm). There are no criteria directly comparable to the detector tube results. The NIOSH ceiling criterion of 50 ppm for a 5-minute period is probably the best comparison. Four of the readings were above the NIOSH criterion. Airborne concentrations for NO2 ranged from a trace (the amount detected was not sufficient for quantification) to 25 ppm. Airborne concentrations for  $NO_X$  ranged from nondetected to greater than 25 ppm. The  $NO_X$  detector tubes collect both NO and  $NO_2$ . It is not possible to distinguish either material individually.

However, in many instances, samples for both NO<sub>2</sub> and NO<sub>x</sub> were collected in the same general area. In some instances, the NO<sub>2</sub> concentration was very close to the NO<sub>x</sub> value, indicating that NO<sub>2</sub> was the principle component. There are also no criteria that are directly comparable to these grab sample results. NIOSH has a recommended 15-minute criteria for NO<sub>2</sub> of 1 ppm. Many of the detector tube results greatly exceeded this value.

NIOSH previously administered a certification program for gas detector tube units. Certified direct-reading gas detector tubes were certified to an accuracy of  $\pm 35\%$  at one-half the test gas concentration and  $\pm 25\%$  at 1, 2, and 5 times the test gas concentration. The test gas concentration usually corresponded to the OSHA PEL.8, $\pm 16$ -17 As of September 1983, the certification program was terminated.

### Ionizing Radiation

Table XII presents the results of total ionization radiation monitoring using a direct-reading survey meter. These readings were obtained primarily as a comparison to similar measurements collected at the South Plant. All readings were less than 1 millirem per hour. The Nuclear Regulatory Commission's criteria for unrestricted areas is 2.0 millirem in any one hour.

1.

## Insulation Sample

The bulk insulation sample collected from process pipes for the Midrex System in the Low Bay Area of Building 1, contained no asbestos material.

### Amines and General Organics

The analysis of screening samples for aromatic and aliphatic amines and general organics did not reveal any specific compounds. The aliphatic samples contained no peaks other than for the solvent. One peak was found in the aromatic amine samples, was thought to be caused by ammonia due to detector tube sampling results and subsequent laboratory tests of ammonia retention time. Small peaks were detected on the charcoal tubes for organics but they could not be qualitatively identified.

# 2. Environmental Monitoring, Second Follow-up Survey

Table XIII presents the results of airborne sampling for metals. Three metals (nickle, copper, chromium) were detected on at least one of the nine personal samples collected. Airborne concentrations of nickel ranged from 12.2 to 262 ug/m³. Eight of the nine samples exceeded the adjusted NIOSH criterion of 12.5 ug/m³. All samples were below the adjusted OSHA and ACGIH criteria. Airborne concentrations for copper ranged from 25.3 to 7900 ug/m³. Five of nine personal samples exceeded the adjusted ACGIH TLV and the OSHA PEL of 667 ug/m³. Airborne concentrations for chrominum ranged from below the laboratory limit of detection to 327 ug/m³. All samples were below current criteria for total chromium but one sample was 98% of the adjusted ACGIH TLV of 333 ug/m³.

Comparing these values to those listed in Table III for the same jobs, reveal that the concentrations were similar for both the first and second follow-up surveys. For example, the C18 Tab Bay operator had an airborne copper concentration of 4620 ug/m³ in March and values of 3190 and 7900 ug/m³ during the second follow-up survey. Similarly consistent results were obtained for the fork lift operator. One difference between the metals results is that no airborne lead was detected during the second follow-up survey. Management reported that lead is a poison to catalyst products and expressed concern about its presence. It is difficult to determine the exact source of the lead but one possibility is gasoline powered fork lifts, which the company used. A second possibility is that lead

particulate was present in small amounts in the settled dust and became airborne due to employee's use of compressed air. This possibility is supported by the fact that one bulk dust sample (Table X) contained 0.05% lead, and that the lead in most air samples (Table III) represented less than one percent of the total material.

### 3. General Observations

Deficiencies were noted in the companies exposure control programs (respiratory protection, engineering controls, and housekeeping).

### Respiratory Protection

The respiratory protection program was deficient in many aspects, including lack of a centralized storage area, poor maintenance and cleaning, no fit testing of respirators, and insufficient employee training. Specific problems observed included employees altering respirators by removing one of the head straps, thus reducing the effectiveness of the respirator. A second problem concerned facial hair on some employees who were wearing respirators. Facial hair (beards and oversized moustaches) that extends into the sealing surface, compromises the seal between the respirator and the employee's skin. These problems emphasize the lack of an effective training program. A third problem observed during the survey concerned a self-contained breathing apparatus (SCBA) that was only half charged. Poor maintenance of SCBA's could result in injury to an employee who attempted to use these items in a hazardous atmosphere.

# Engineering Controls

Airborne materials (aerosols/gases) were visibly high in many locations in the West Plant. This is not surprising considering the number of emission points noted at various locations at this facility.

The plant engineering control program was not effective in controlling employee exposures. Existing controls, for the most part, were not properly maintained. Some controls were in need of modification and additional controls were needed in many locations.

During a walk-through survey on February 28, 1983, powdered material was observed pouring out of a hole in the bottom of a conveyor at the C12 Tab Bay. Subsequently, the hole was covered with cardboard which did control some of the emissions.

Others emission sources included an oven located near the C12 Tab Bay and tab machines located in several processing areas. When operating, the oven emitted fumes from its badly corroded top. Results of spot sampling using detector tubes (Table XI) suggest that the emissions included oxides of nitrogen.

Specific problems noted for existing engineering controls included a ring machine located in Building 3, that had a flexible exhaust pipe sticking into a larger metal pipe. Paper towels had been stuffed into the connection in an attempt to close the gap between the flexible pipe and the metal pipe. Problems were noted for tab machines at C12, C18, Special Tab, and C79 Tab Bays. Holes were found in flexible exhaust pipes on two tab machines (2 and 4) at C79 Tab Bay. Most of the tab machines were equipped with local exhaust ventilation at the tablet exhaust. However, some of the ventilation was ineffective as evidenced by flexible exhaust pipes that were filled with dust, on tab machines at the C12 Tab Bay. A blender located next to the C79 Tab Bay had a defective gasket which leaked as the mixer revolved, if drums were not attached perfectly. Problems were noted at the drum filling station under the C18 bag house in the High Bay of Building 1. The drum cover had no gasket and the operation was not exhausted. A lot of material spilled onto the floor while this operation ran.

Problems were also noted at the CS 303 Drum Filling Station. Oversized material dropped a the screener, through a cloth pipe into an open drum. Airborne dust was emitted from the drum during the filling operation.

The C18 Drum Filling Station for the rotary calciner (RC) had a cover and local exhaust ventilation. Although this drum filling station worked better than most, it still periodically emitted dust from under the cover and at the flexible exhaust pipe connection. These periodic emissions indicate that the operation was not working properly.

Areas and machines in need of engineering controls included tab machines at the C18 Tab Bay. These machines had a flexible exhaust pipe positioned within two inches of a screen that tabs passed over before dropping into small buckets. These tab exhausts, however, were not equipped with enclosures under the screens, as were some of the other tab machines. Such enclosures collect dust more effeciently.

The loading end of RC No. 8 was badly corroded. While C78 material was being processed, the NIOSH investigators observed a tremendous amount of smoke being emitted at the loading end. The room air was relatively clean before processing began. After 10 minutes, the room filled with smoke. Subsequently, smoke was observed escaping through upper windows into the outside atmosphere.

Most drums used to transport materials around the plant were not equipped with covers. This provided another source of dust emissions as many of the raw materials and intermediate materials were in powder form.

Problems were noted in the confined space entry procedure.
NIOSH industrial hygiene personnel observed an employee enter a process vessel in the High Bay area in Building 1, with a second confined space entry team member nearby. The second employee had to leave for supplies. The individual inside the confined space was, thus by himself in an untested atmosphere. The process vessel had a door and/or window at both the top and bottom. Both were open, which conceivably provided some ventilation. However, there should always be a second employee outside the confined space in case of an emergency.

### Work Practices

Techniques used to load most tab machines add to airborne materials. For example, at Tab Bay C18, employees use small scoops to transfer powdered material form a barrel to the tab machine hopper. Airborne dust is created when employees dip into the barrel, as the scoop is carried to the tab machine hopper, and as the scoops are emptied into the hopper.

Other poor work practices included using compressed air to clean up work areas, particularly in screening. Dry sweeping was also observed and while it is better than using air hoses, it also adds to airborne dust. Vacuuming is the best clean up technique.

Problems noted for other work practices included employees using shovels to transfer powdered material on the Mezzanine Level of Building 4. A lot of the material fell from the shovel through a grid floor down to the first floor. Another problem was observed during the loading operation at the C78 Mixer. If powdered material was added before the liquid component, a lot of particulate was emitted from the loading port as the mixer revolved.

Some operations were not monitored closely. The drum filling station at RC No. 9 filled up and material ran onto the floor. This added to both floor contamination and airborne materials.

### Other

NIOSH industrial hygiene personnel experienced irritation of the eyes and respiratory tract in certain plant locations when not wearing respirators. The locations included the Dipping Area (when dipping was ongoing) in Building 4, leaking storage tanks near Building 1, and the Ball Mill Area in Building 12. Air monitoring results indicate that the irritation at Dipping and near the leaking tanks was probably due to ammonia exposure (Table XI), while irritation experienced in the Ball Mill Area was probably due to phosphoric acid (Table IX).

Most of the eye wash stations and emergency showers were not maintained in a sanitary condition. These items were not routinely inspected as evidenced by the fact that some eye wash stations had nozzle covers off and when tested, some nozzles emitted rust colored water (Building 12). Some locations are in need of eye wash stations such as the Dipping Operation in Building 4. A water hose, located in the area, is not suitable for use as an emergency eye wash.

Employees were observed smoking and consuming food/drink in various work area. These activities could contribute to on increased uptake of hazardous chemicals through ingestion.

Problems were noted for the overall plant housekeeping. The poor house keeping is probably one reason that bathrooms at the facility were not clean.

Management reported that employees were given the opportunity to shower at the end of the shift. In addition, the company provided work clothes so employees did not have to wear their work clothes home. These practices were intended to prevent the spread of hazardous materials to the home environment.

### Effective Controls/Improvements

Although there were many problems, as noted, for the exposure control programs (respiratory protection, engineering controls, etc.) at the West Plant, some effective techniques and/or work practices were observed.

The company provides work clothes and shoes so that employees do not have to wear their work clothes home. In conjunction with the shower rooms, these practices help insure that

employees do not transfer hazardous chemicals (nickel, chromium, copper) from the worksite to their home. There is a question over whether employees were allowed to shower before the end of their shift. While management indicated that employees were allowed time to shower, several employees stated that they had to wait until the shift was complete. One employee, in fact, said he waited to shower until he got home.

Vacuum cleaners instead of air hoses, were used to clean up some work stations, as noted at C79 Tab Bay. Vacuuming is a better clean-up technique than sweeping or compressed air. Additionally, the more cleaning done at individual work stations the less material will be spread throughout the plant.

An effective safety control was noted for the blender located near the C79 Tab Bay in Building 1. Drums of raw material were emptied into the blender and the last drum remained on the blender as it rotated. There was a danger of serious injury if an individual accidentally got hit by the rotating machinery. This operation has been fenced off and the controls placed outside. In addition, a gate allowing access to the blender, had to be closed for the controls to operate.

Management had instituted some improvements subsequent to the initial follow-up survey. The cafeteria had been cleaned and stainless steel tops put on all tables. The improvements, if maintained, should help keep the lunchroom cleaner.

As mentioned earlier, a new tab machine loading technique had been developed for the C79 Tab Bay. Instead of using a scoop and manually filling the tab machine hoppers, barrels of powdered material were suspended above the tab machines so that the hoppers were gravity fed. The tab bay operator stated that the new technique provided more time for cleaning. The C79 Tab Bay appeared cleaner than those tab bays using the old loading technique.

The C84-1 Ball Wheel Operation had been modified by the addition of on exhaust hood. Visually, the air in the room was much cleaner and dust arising as the powdered phosphoric acid dropped onto the ball wheel, appeared to be effectively captured by the exhaust hood.

#### B. Medical

# 1. Questionnaire Analysis

The 98 South Plant employees were similar to the 235 West Plant employees in age, proportion of males and females, and current smoking status (Table XIV).

The proportion of employees having one or more symptoms at the South Plant (70%) was similar to that at the West Plant (72%) (Table XV). The symptom reported most often at both plants was cough. Nasal sores were reported more often at the South Plant (35%) than at the West Plant (20%), and skin rashes were reported more often at the West Plant (39%) than at the South Plant (27%). Other symptoms were reported by comparable proportions of employees at the two plants.

The rank order of areas of the body affected by skin rash was the same at both plants (Table XVI). The area most often reported was the hands. The area least often reported was the feet. At the South Plant, affected employees reported a higher prevalence of rash at each area than West Plant employees. The differences for hands, face and neck, and arms were statistically significant. This could happen because an employee could list more than one location. Therefore, it appears that South Plant employees had skin rashes affecting more parts of their bodies than those of West Plant employees.

The skin rash type most often reported at the South Plant was red, itchy skin, and at the West Plant, dry cracked skin (Table XVII), but the differences in prevalences between the two plants for these types of rash were not statistically significant. Rash characterized by red skin and blisters was reported more than twice as often at the South Plant than at the West Plant (43% vs 18%,  $X^2 = 6.26$ , p < 0.025). Differences in prevalence between the two plants for other types of rash were not statistically significant.

Smokers at the West Plant reported slightly more respiratory symptoms than did non-smokers for all symptoms; at the South Plant this was also true except for cough (Table XVIII). Except for cough, former smokers had symptom prevalences greater than non-smokers. At the South Plant, former smokers tended to have symptom prevalences intermediate between those of smokers and non-smokers, whereas at the West Plant, their prevalences tended to be greater than those of smokers, with the exception of cough. None of those differences was statistically significant, except for the differences at the West Plant for shortness of breath between former members and non-smokers, and for cough between current and former smokers.

The exposure ranges, means, and medians were calculated for each group using total airborne metal concentrations including Co, Cu, Cr, Ni, Pb, and Zn from personal samples collected during the NIOSH survey. The high exposure group included operators, helpers, and laborers from the West Plant. Their range, mean, and median exposures were 58 ug/m<sup>3</sup> to 17, 799 ug/m<sup>3</sup>; 2,810 ug/m<sup>3</sup>; and 402 ug/m<sup>3</sup>, respectively. The

medium exposure group included operators, helpers, and laborers from the South Plant, and maintenance workers from the West Plant. Their range, mean, and median exposures to the total airborne metals were 94 ug/m³ to 919 ug/m³; 325 ug/m³; 179 ug/m³, respectively. The low exposure group was composed of warehousemen, forklift operators, and electricians from both plants. These workers were estimated by the NIOSH industrial hygienist to have the lowest exposure.

The high and medium exposure groups had similar symptom prevalences. Both groups reported each individual symptom significantly more often than the low exposure group (Table XIX). This suggests that once a "medium" exposure is reached, further increases in exposure do not increase symptom prevalences.

#### 2. Record Review

Among the 43 occurrences of illnesses and/or deaths, there were two lung cancers and one case each of skin, blood and salivary gland cancer. The company's retirement benefit death records revealed six additional cancer cases: one each of skin, colon, non-Hodgkins lymphoma, stomach, and one unknown type. Company health insurance carriers did not have any additional cancer cases in their records. The number and distribution of cancer cases identified do not appear to be remarkable.

Almost half of the pulmonary function tests (PFT's) were interpreted in company records as slightly to severely abnormal. Test methods and criteria for interpretation did not conform to American Thorasic Society recommendations. A test did not necessarily have three acceptable trials; the test was ended as soon as two trials agreed within 10%. Company officials indicated that each employee was notified personally of his or her PFT results.

### VII. DISCUSSION AND CONCLUSION

#### A. Environmental

Based on the results of this investigation, NIOSH has determined that a health hazard existed at the West Plant due to employee exposure to nickel and copper.

In addition, a potential health hazard existed for chromium VI, lead, zinc, ammonia, and phosphoric acid. Table XX presents a summary of the personal sampling results. Fifty-eight percent of the nickel and 32% of the copper samples were in excess of the lowest evaluation criterion. Six other chemicals were found in excess of a criterion on one sample each.

The results of area sampling for chromium VI indicated that part of the total chromium on personal samples is chromium VI. The criteria for exposure to chromium VI is dependent on the solubility, with water insoluble compounds being considered potential human carcinogens.

ACGIH and OSHA criteria distinguish between copper fume and dust. For zinc oxide, OSHA and ACGIH have a specific criteria for zinc oxide fume and treat zinc oxide dust as a nuisance material. NIOSH has the same criteria for both zinc oxide fume and dust. The NIOSH investigators believe that generally, exposures at the West Plant were to dust rather than fume, although some jobs may involve exposure to the fume. Work activities involving heating zinc oxide or copper above their melting points could result in fume exposure (i.e. welding).

Many process areas had high levels of visible airborne dust. Many unnecessary emission sources were observed and many have been discussed in this report. Many of the noted sources could be greatly adjusted by applying varying degrees of engineering control. While certain process machinery may require elaborate engineering controls (i.e. forming wheels on tab machines), others could be improved by very simple modification such as the addition of a metal plate over the hole in the base of the C12 Tab Bay conveyor.

In addition to engineering controls, other plant reduction control programs need to be improved including general housekeeping, respiratory protection, and employee training and education.

Some improvements were noted during the second follow-up survey. These represent a beginning in improving general working conditions, but much remains to be accomplished.

The NIOSH investigators were unable to find any other published articles discussing environmental/medical surveys in nickel/copper/chromium type catalyst facilities. These have been evaluations in facilities producing other catalysts, including at least one previous health hazard evaluation. Additionally, there are publications discussing hazards in catalyst manufacturing in general, as well as, specific catalyst materials. 15,20-21

#### B. Medical

Since symptoms reported at both plants have previously been reported among individuals having similar exposures, and since in general, exposures measured at the West Plant were higher than those measured at the South Plant, one would expect symptom prevalences at the West Plant to be higher than those at the South Plant. The questionnaire survey, however, failed to show West

Plant prevalences to be higher than those at the South Plant. In fact, the only symptom reported significantly more often at the West Plant was skin rash. The lower prevalence of nasal sores and similar prevalences of the other symptoms at the West Plant is unexpected, given the higher over all exposures.

The skin rash characteristics and locations reported most often at the South Plant (see Tables XVI and XVII), which include red, itchy, dry skin with red blisters, thickened patches, and color changes on the hands, arms, and face, are compatible with (but not specific for) nickel dermatitis in its various stages.<sup>22</sup> However, nickel dermatitis involves immunologic (allergic) hypersensitization and would thus not be expected at the prevalences of rash found in this survey (27% and 39% at the South Plant and West Plant, respectively).

Furthermore, if nickel exposure is arguably higher at the South Plant, the higher prevalence of rash at the West Plant is not consistent with the rashes, in general, being nickel dermatitis. Therefore, while there may possibly be cases of nickel dermatitis at these plants, this survey provides no documentation of this and suggests that, in general, the reported rashes have some other etiology.

Cracked fingernails, reported more often at the West Plant where higher chromium levels were measured, can be caused by chromium exposure 12, and several West Plant employees indicated that their dry cracked fingernails were stained yellow, which is characteristic of those associated with chromium exposure in the past.

On the basis of the relationship between estimated exposure level and symptoms, and because the reported symptoms are consistent with the exposures occurring at United Catalyst, NIOSH concludes that symptoms reported among United Catalyst employees are, at least in part, work related. Considering the documentation of acute symptoms and overexposure to various contaminants, including one carcinogen (nickel) and a potential overexposure to a second (chromium VI), implementation of corrective measures should begin immediately.12,14

# VIII. RECOMMENDATIONS

 A program to educate the employees of the hazards associated with the materials that they work with should be implemented. They will be better able to follow safe work practices if they understand why they are asked to perform tasks using specific precautions.

- 2. In conjunction with recommendation number 1, an identification system should be developed to insure that all employees are aware of the potential hazards associated with the various materials they work with. The system should coordinate specific hazards listed on material containers with additional information (i.e. material safety data sheets) available at the plant. The requirements of the OSHA Hazardous Communication Standard must be met.<sup>23</sup> Guidelines for developing an identification system are presented in NIOSH's "An Identification System for Occupationally Hazardous Materials" criteria document.<sup>24</sup>
- 3. The engineering controls program is critical to reducing exposures at this facility. Initial efforts should be directed at correcting those items (not already corrected) discussed in the results section of this report. Subsequently, a systematic approach to monitoring the program should be implemented. The following items should be incorporated into the ongoing program.
  - a. A through inspection of all engineering controls should be conducted at least once every three months. At a minimum, this should include visually checking for damage to equipment (i.e. holes, dents) and face velocity measurements of all exhaust hoods.
  - b. All drums should be inspected for bent tops and repaired as needed. To reduce unnecessary emissions drums should be covered at all times.
  - c. Drum filling operations should be equipped with gasketed covers and local exhaust ventilation. Guidelines for exhausting drum filling and similar operations are presented in the ACGIH Industrial Ventilation Manual.<sup>25</sup>
  - d. A training program should be developed to emphasize the need for local exhaust ventilation equipment. Concurrently, employees input should be encouraged when process/engineering control changes are anticipated. This will help insure that the changes are practical and that employees will accept them.
- 4. The respiratory protection program needs improvements in many areas. One individual should be responsible for the entire program at the West Plant. This individual could be under the direction of the plant's industrial hygiene/safety department. In order to have an effective program, the individual would need to devote most of their work time to it. The requirements of an acceptable program are discussed in the NIOSH guide to Industrial Respiratory Protection. <sup>26</sup> The program must meet the requirement of the OSHA standard (CFR 1910.134). <sup>27</sup> The principal improvements needed are as follows:

- A centralized storage area incorporating separate storage compartments for non-disposable respirators.
- b. Maintenance and cleaning of all non-disposable respirators.
- c. Fit testing of each employee who wears a respirator (including disposable respirators).
- d. An employee training program emphasising the reason why respirators are needed and proper techniques in wearing respirators.
- 5. The company's airborne monitoring program should be modified so that employee's exposures are evaluated for specific hazardous materials (i.e. nickel, chromium, chromium VI, copper, etc.) rather than only respirable or total particulate. Sampling and analytical methods for the various materials evaluated at this facility are available in the new NIOSH Manual of Analytical Methods. 28,29 Data presented in this report can serve as a reference for comparison with future sampling results. The monitoring program should be used to assess the effectiveness of engineering controls in each processing area.
- Housekeeping should be improved to eliminate the spread of hazardous materials around the plant.
- 7. Work practices should be evaluated and modified when possible to help reduce the amount of material becoming airborne or falling on the floor during processing. Some examples are:
  - a. Restrict the use of compressed air to clean equipment and/or process areas. Use vacuum cleaning whenever possible.
  - b. Reduce the distance between containers of raw materials and the corresponding loading postitions, such as carrying scoops of powdered material from drums to tab machine hoppers.
  - Enclosed continuous feeding operations are generally much less dusty than open manual feeding operations.
  - d. Whenever possible powdered and liquid components should be mixed or the liquid component added first.
- 8. All emergency eye wash/showers should be tested monthly. An additional eye wash is needed in the Dipping area in Building 4. All eye washes should be of the type that leave an employee's hands free to hold his/her eyes open.
- 9. Food and beverages should not be consumed at employee work stations.

- The Confined Space Entry Program should meet the guidelines presented in the NIOSH Criteria Document for entering confined spaces. 30
- 11. A medical surveillance program should be provided to all occupationally exposed employees. It should include:
  - medical and work histories, paying particular attention to skin conditions or allergies, respiratory illnesses, and smoking histories;
  - preplacement and periodic physical examinations of the upper respiratory tract for evidence of irritation, bleeding, ulcerations, or perforations; of the lungs for evidence of respiratory impairment; and of the skin for dermatitis;
  - an evaluation of the employee's ability to use positive or negative pressure respirators; and
  - d. Baseline pulmonary function tests. Additional pulmonary function tests are not needed for the exposures identified by NIOSH, but they should be utilized as needed to further evaluate problems detected by the routine medical surveillance.

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Laboratory Analysis:

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- 1. Kentucky Department of Labor
- 2. United Catalyst, Inc.
- 3. West Plant employees
- 4. NIOSH, Region IV
- 5. 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
Sampling and Analytical Methods

United Catalysts Inc.
West Plant
Louisville, Kentucky
HETA 83-075

Contaminant	Flow Rate (LPM)	Sampling Method	Analytical Method
Nitric Oxide	0.02	3-Section Triethanol Amine Sorbent Tube	P&CAM No. S321
Nitrogen Dioxide	0.02	3-Section Triethanol Amine Sorbent Tube	P&CAM No. S321
Inorganic Acids (Screening) And Phosphoric Acid Specifically	0.05	Silica Gel Tube	P&CAM No. 339
Ammonia	0.05	Sulfuric Acid Treated Silica Gel Tube, Preceded By a Mixed Cellulose Ester Membrane Filter	Colorimetric Automated Phenate Method
Organic Materials	0.5	Charcoal Tube	Gas Chromatograph/Flame Ionization Detection and Gas Chromatography/Mass Spectroscopy
Amines	0.1	Citric Acid Coated Silica Gel Tube	Aliphatic - P&CAM No. 276 Aromatic - P&CAM No. 168
Crystalline Silica (Quartz and Cristobalite)	9.0 for High-Volume	Polyvinyl Chloride Filter	P&CAM No. 259
Respirable and Total Particulate	1.7 (Respirable) 1.5 (Total)	Polyvinyl Chloride Filter	Gravimetric

(continued)

TABLE I (continued)

Contaminant	Flow Rate	Sampling Method	Analytical Method		
Ionizing Radiation	-	Mini Con-Rad Portable Survey Meter (Model 3032)	Visual		
Spot Checks for Various - gases/vapors -		Direct-Reading Indicator Tubes	Vi sua 1		
Hexavalent Chromium 2.0 (Cr <sup>+6</sup> )		Polyvinyl Chloride Filter	Colorimetric Via NIOSH No. 319		
Copper, chromium, cobalt, nickel, lead, zinc	1.5	Mixed Cellulose Ester Membrane Filter	Atomic Absorption Via NIOSH Method No. 173 or Inductively Coupled Plasma Atomic Emission Spectroscopy		

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TABLE II

Environmental Criteria and Associated Health Effects

	Environ (mg/m <sup>3</sup> unlo			
Contaminant	OSHA	NIOSH	ACGIH	Associated Health Effects
Ni ckel	1	0.015	1	Lung and nasal cancer, dermatitis, pneumonitis (inflammation of the lungs), and allergic asthma
Chromium +6 (carcinogenic, water insoluble)		0.001	0.05	Lung cancer
Chromium +6 (noncarcinogenic, water soluble)	0.05	0.025	0.05	Respiratory tract irritation, kidney and liver damage
Chromium Metal, 2+ and 3+ compounds	0.5 (sol. chronic and chromous salts) (Metal and insoluble salts)		0.5	Dermatitis
Crystalline Silica	10 mg/m <sup>3</sup>	0.05	10 mg/m <sup>3</sup>	Silicosis
(respirable)	% Si0 <sub>2</sub> + 2		% SiO2 + 2	
Cobalt (metal, fume, and dust)	0.1	N.A.	0.1	Allergic dermatitis, possible chronic interstitial pneumonitis (lung damage)

TABLE II (continued)

Env	/iro	nmen	ta	1 (	Cr.	i ter	ia
$(mg/m^3)$	un 1	ess	otl	her	·W.	i se	noted)

89	(1119	/III- dilitess otherwise i	io cc a /	
Contaminant	OSHA	NIOSH	ACGIH	Associated Health Effects
Ammonia	35	34.8 (for 5-min period)	18	Eye damage, irritation to eyes and respiratory tract
Nitric Acid (HNO <sub>3</sub> )	5	5	5	Chronic bronchitis, chemical pneumonitis
Sulfuric Acid	1	1	1	Pulmonary edema (fluid in the lungs), dental erosion, mucous membrane (eye, nose, and throat) irritation
Nitric Oxide	30	30	30	Drowsiness; eyes, nose, and throat irritation
Nitrogen Dioxide	9	1.8 (15-min ceiling value)	6	Pulmonary edema, increased heart rate, dyspnea, cough, eye irritation, chest pain
Phosphoric Acid	1	-	1	Dermatitis, mucous membrane irritation, skin burns, respiratory problems
Copper (dusts and mists)	1	-	1	Mucous membrane irritation, nasal septum perforation, eye irritation, dermatitis

TABLE II (continued)

	En <b>vi</b> (mg/m <sup>3</sup> u			
Contaminant	AHZO	NIOSH	ACGIH	Associated Health Effects
Lead	0.05	0.05	0.15	Abdominal cramps, fatigue, muscle weakness, muscle pains, anemia, kidney damage
Zînc (as zinc oxide)	5 (fume)	5	5 (fume) 10 (dust)	Dry throat, cough, chills, fever, nausea, vomiting, blurred vision

TABLE III

## Airborne Concentrations of Metals Personal Samples

United Catalysts Inc. West Plant Louisville, Kentucky HETA 83-075

March 1-3, 1983

		C7		V - 1		(	Concenti	ration (u	$g/m^3$ )	W- 10
	Location/Job	Sample Time	Date	Volume (Liters)	Со	Cu	Cr	Ni	Pb	Zn
Bldg. 1,	C12, Dryer Oper. 2	0606-1710	3-2	996	LLD	29	20	9	-	-
B1dg. 1,	C12, Oper. 2	0602-17	3-1	987	LLD	85	31	16	-	-
B1dg. 1,	C12, Tab Bay	0553-1708	3-2	1013	LLD	29	178	18		-
B1dg. 1,	C61	0555-1701	3-1	999	LLD	66	8	8	% <b>1</b>	114
B1dg. 1,	Nickel Carb Oper.	0555-1707	3-1	1008	LLD	09	5	55	3	260
B1dg. 1,	C79, Dry End, Oper. 2	0651-1703	3-2	918	LLD	3270	8	16	_	k <b>—</b> ):
Bldg. 3, Oper. 4	C18, Tab Bay,	0558-1702	3-1	1000	LLD	4620	LLD	36	-	-
B1dg. 3,	C61, Oper. 4	0601-1658	3-1	986	LLD	7060	15	67	10	>10700
B1dg. 4,	C8-6, Chief Oper.	0557-1704	3-1	1001	5	390	4	8	-	-
B1dg. 4,	C29-2, Oper. 4	0559-1705	3-1	999	3	125	1	10	2	53
B1dg. 1,	Screening	0557-1714	3-1	1016	2	215	155	20	-	=
B1dg. 1,	Screening	0605-1714	3-1	1004	1	729	70	551		-
B1dg. 1,	Screening	0605-1711	3-1	999	LLD	54	3	11	34	1

TABLE III (continued)

					Concentration (ug/m <sup>3</sup> )					
Location/Job	Sample Time	Date	Volume (Liters)	Со	Cu	Cr	Ni	Pb	Zn	
Bldg. 1, Screening	0610-1708	3-1	. 987	LLD	82	6	12	2	83	
Bldg. 1, Screening	0608-1711	3-1	995	LLD	120	6	24	2	48	
Bldg. 1, Screening, Fork Lift Oper.	0611-1717	3-2	999	LLD	40	3	16	2	41	
Bidg. 1, Screening, Screen No. 2	0558-1714	3-2	1014	3	487	75	1780	4	443	
Bldg 1, Screening, Screen No. 5	0617-1719	3-2	999	LLD	38	3	90	2	43	
Bldg. 1, Screening, Screen No. 3	0605-1719	3-2	1011	1	59	4	124	2	46	
Bldg. 1, C12, Oper. 3	0602-1705	3-1	995	LLD	79	32	37	3	230	
Bldg. 1, C12, Oper. 3	0604-1704	3-1	990	LLD	79	232	20	_	-	
Maintenance, Bldg. 1, Welding at RC Discharge	0610-1707	3-1	986	1	519	14	59	3	323	
Maintenance, Bldg. 3, Adjusting C18 Tab Machines	0610-1703	3-1	980	LLD	912	1	15	1	1040	
Maintenance, Bldg. 1	0604-1717	3-2	1010	LLD	145	6	18	2	157	
Maintenance, Bldg. 1	0608-1710	3-2	993	LLD	56	4	10	2	29	
aintenance, Bldg. 3	0606-1710	3-2	996	LLD	180	8	13	3	957	
Maintenance, Bldg. 3	0609-1701	3-3	978	LLD	828	6	15	-	2	

TABLE III (continued)

					Concentration (ug/m <sup>3</sup> )					
Location/Job	Sample Time	Date	Volume (Liters)	Co	Cu	Cr	Ni	РЬ	Zn	
Maintenance	0615-1717	3-3	993	1	110	16	16	2	86	
Maintenance	0623-1717	3-3	981	7	1980	40	173	17	>2040	
Environmental Criteria for		OSHA		100	1000	1000	1000	50	15000	
Normal Shift, 8 Hours for OSHA and ACGIH, Up to 10 Hours for		NIOSH		N	N	N	15	50	5000	
HZOIN		ACGIH		100	1000	500	1000	150	10000	
Environmental Criteria for		OSHA		66.7	667	667	667	33.3	10000	
Long Workshift (12 Hours at This Plant). The adjusted		NIOSH		N	N	N*	12.5	41.7	4170	
criteria equals the normal criteria multiplied by the hours the normal criteria is based on divided by the hours worked in the extended shift		ACGIH		66.7	667	333	667	100	6670	

Co = Cobalt, Cu = Copper, Cr = Chromium, Ni = Nickel, Pb = Lead, Zn = Zinc

LLD = Below the laboratory limit of detection which = 1 to 3 ug/filter depending on the specific metal

<sup>- =</sup> Not evaluated for on this sample

N = NIOSH currently has no specific criteria for this material

<sup>\*</sup> NIOSH has criteria for chromium VI compounds. These are not used in this instance because the chromium reported includes all valence states of chromium (bivalent, trivalent, hexavalent).

TABLE IV

Airborne Concentrations for Respirable and Total Particulates Personal Samples

March 2-3, 1983

Location/Job	Sample Time	Date	Volume (Liters)	Type Of Sample	Concentration (mg/m <sup>3</sup> )
Bldg. 1, C61, Wet End Oper.	0603-1710	3-2	1133.9	Respirable	0.49
Bldg. 1, C12, Tab Bay Oper.	0614-1700	3-3	1098.2	Respirable	2.31
Bldg. 1, C12, Dryer Oper.	0603-1702	3-3	1120.3	Respirable	0.80
Bldg. 1, Screening	0633-1706	3-3	1076.1	Respirable	2.68
Bldg. 1, Screening	0637-1708	3-3	1072.7	Respirable	1.77
Bldg. 3, C61, Tab Bay Oper.	0558-1355	3-3	810.9	Respirable	3.03
Bldg. 3, Cl8, Tab Bay	0608-1555	3-3	880.5	Tota1	24.20
Bldg. 3, C61, Oper. 4	0601-1708	3-2	1133.9	Respirable	1.34
Bldg. 3, C18, Tab Bay Oper.	0611-1707	3-2	1115.2	Respirable	3.63
Bldg. 3, Cl8, Tab Bay Oper.	0557-1705	3-2	1135.6	Respirable	1.53
Bldg. 12, C84-1, Oper.	0604-1653	3-3	1103.3	Respirable	1.19
Bldg. 12, C84-3, Oper.	0608-1655	3-3	1110.1	Respirable	0.95
31dg. 12, Cobalt Reactor Oper.	0619-1700	3-3	961.5	Total	0.53
Bldg. 4, C8-6, Oper.	0604-1716	3-3	1142.4	Respirable	0.39
Analytical Sensitivity of Electro	balance = 0.01 m	9			
Fandananatal Caltura	OCUA -	T-A-7		8-Hour Shift	12-Hour Shift
Environmental Criteria:	OSHA =	Total = Respirabl	e =	15 5	10 3.3
	ACGIH =	Total =		10	6.7

TABLE V

Area Airborne Concentration of Chromium VI

March 1-2, 1983

Location	Sample Time	Date	Volume (Liters)	Concentration ug/m <sup>3</sup>	
Оп Conveyor Support, C-12 Tab Bay	0831-1529	3-1	627	73.4	
On Conveyor Support, C-12 Tab Bay	0640-1706	3-2	939	66	
On Drum Elevator, Screener No. 2	0725-1522	3-1	716	6.4	
On Drum Elevator, Screener No. 2	0649-1722	3-2	950	3.2	

Sampling and analytical technique does not distinguish between soluble and insoluble forms of  ${\rm Cr}^{+6}$ 

Environmental	criteria	$(ug/m^3)$ :	Carcinogenic	Non-carcinogenic
			1 NIOSH 10-hr 0.8 NIOSH 12-hr	25 NIOSH 10-hr 20.8 NIOSH 12-hr

TABLE VI

Airborne Concentrations for Crystalline Silica
Area High-Volume Respirable Samples

March 3, 1983

					Concentration (mg/m <sup>3</sup> )			
			Volume (Liters)	Weight of Dust on Filter (mg)		Crystalline Silica		
	Location	Sample Time			Respirable Dust	Quartz	Cristobalite	
Bldg.	1, Screening, Screen No. 2	0805-1002	1053	19.65	18.7	LLD	LLD	
Bldg.	3, C61, Tab Bay	0754-1457	3989	12.94	3,24	LLD	LLD	
Bldg.	12, C84-3, Ball Wheel Room	1352-1530	882	13.78	15.6	LLD	LLD	

LLD = Below Laboratory Limit of Detection = 0.03 mg/sample.

Environmental Criteria: 10-Hour Shift 12-Hour Shift NIOSH =  $50 \text{ ug/m}^3$  41.7

TABLE VII

Airborne Concentrations of Ammonia
Personal Samples

March 2-3, 1983

Location/Job	Sample Time	Date	Volume (Liters)	Concentration mg/m <sup>3</sup>
Bldg. 4, C8-6, Oper.	0604-1716	3-3	36.5	2.55
Bldg. 4, C29, Dipping Oper.	0620-1420	3-3	25.4	11.8
Bldg. 12, No. 12 Rotary Oper.	0607-1708	3-3	36.9	7.05
Bldg. 12, C18, Oxide Calciner Oper.	0607-1707	3-2	35.7	8.41
Bldg. 12, C84-1, Ball Wheel Oper. 3	0555-1705	3-2	31.2	4.97
Bldg. 4, C8-6, Chief Oper.	0559-1720	3-2	35.8	8.1
Bldg. 4, C8-6, Oper. 4	0554-1720	3-2	36.3	13.5
Laboratory Limit of Detection = 4 ug,	'sample			
Environmental Criteria (mg/m³)	OSHA =	8-Hour 3		12-Hour Shift 23.3
	ACGIH =	18	}	12

100

TABLE VIII
Airborne Concentrations of Nitric Oxide and Nitrogen Dioxide

March 2-3, 1983

						ntration g/m <sup>3</sup>
Location/Job	Sample Time	Date	Volume (Liters)	Type Of Sample	NO	NO2
Bldg. 1, Cl2, Tab Bay	0706-1358	3-3	17.7	A	1.08	1.42
Bldg. 1, Control Aisle	0720-1355	3-3	16.9	Α	3.03	2.73
Bldg. 1, C12, Press Oper. 3	0602-1709	3-2	27.8	P	0.18	1.04
Bldg. 1, C12, Dryer Oper. 2	0607-1710	3-2	27.6	P	0.29	0.98
Bldg. 1, C12, Tab Bay Oper. 3	0554-1708	3-2	28.1	Р	0.39	0.96

Laboratory Limit of Detection = 2 ug/sample for NO and 3 ug/sample for NO2

P = Personal sample

A = Area sample

			10-Hour Shift for NIOSH	
			8-Hour Shift (OSHA, ACGIH)	12-Hour Shift
Environmental Criteria mg/m <sup>3</sup> :	OSHA	NO	30	20
		NO <sub>2</sub>	9	6
	NIOSH	NO	30	25
		NO <sub>2</sub>	No long-term cri	terion
	ACGIH	NO	30	20
		NO2	6	4

TABLE IX Airborne Concentrations for Inorganic Acids

March 1-3, 1983

					Concer	ntration m	g/m <sup>3</sup>
Job/Location	Sample Time	Date	Volume (Liters)	Type Of Sample	11 <sub>3</sub> P0 <sub>4</sub>	117504	нноз
ldg. 1, Low Bay	0945-1640	3-3	20.5	Area - Screening	LLD	LLD	0.54
1dg, 1. Witrate Alley	0055-1643	3-3	19.6	Area - Screening	LLD	110	3.72
ldg. 12, C84-1 Oper. 3	0628-1716	3-1	33.2	Personal - For Phosphoric Acid	0.84	-	-
1dg. 12, C84-1 Ball Wheel Oper. 3	0555-1705	3-2	32	Personal - For Phosphoric Acid	LLD	-	-
ldg. 12, C84-1 1	0604-1653	3-3	29.6	Personal - For Phosphoric Acid	0.30	-	-
ldg. 12, C84-1 Oper. 4	0556-1716	3-1	37.2	Personal - For Phosphoric Acid	0.24	-	-
1dg. 12, C84-3 Oper. 2	0603-1722	3-1	33.6	Personal - For Phosphoric Acid	LLD	-	38
1dg. 12, C84-3 Oper. 4	0557-1714	3-1	32.8	Personal - For Phosphoric Acid	LLD	-	-
ldg. 12, C84-3 Oper. 4	0550-1707	3-2	32.8	Personal - For Phosphoric Acid	LLD	4	-
1dg. 12, C84-3	0608-1655	3-3	29.1	Personal - For Phosphoric Acid	LLD	-	-

 $H_3PO_4$  = Phosphoric Acid,  $H_2SO_4$  = Sulfuric Acid,  $HNO_3$  = Nitric Acid - = not analyzed for on this sample  $H_1D$  = Below the lower laboratory limit of detection (8 ug/sample for all 3 acids)

Invironmental Criteria for Those Natorials Detected (mg/m<sup>3</sup>):

	8- or 10-Hour Shift		12-llour Shi	
	H3P04	нио3	113P04	111103
OSHA	1	5	0.66	3.33
1110511	llone	5	Hone	4.2
ACGIH	1	5	0.66	3.33

TABLE X

Analysis of Bulk Settled Dust Samples Percentage of Various Metals (By Wt.)

March 3, 1983

	Percentage of Metal (By Weight)						
Location	Со	Cu	Cr	Ni	Pb	Zn	
Bldg. 1, Sample Collected From Top of Control Panel in C12 Tab Bay	<0.05	0.21	3.98	<0.05	<0.05	0.17	
Bldg. 1, Low Bay, Sample Taken Off Floor Behind Guard, 14" From Aisle, 12' From C12 Tab Bay	0.08	5.03	1.91	1.23	0.05	3.84	
Bldg. 1, Screening Sample Collected on Top of Elec. Equipment (Painted Orange)	0.01	11.5	1.83	2.16	<0.05	10.8	

TABLE XI

Airborne Concentrations of Gases and/or Vapors
Samples Collected With Direct-Reading Detector Tubes

March 1-3, 1983

Location	Date	Time	Contaminant	Concentration (ppm)
Bldg. 1, At Corner of Box Oven Across From C-12 Tab Bay	3-1	1343	NOX	ND
Bldg. 1, At Corner of Box Oven Across From C-12 Tab Bay	3-1	1352	NO <sub>2</sub>	trace
Bldg. 1, Behind Dryer Near C12 Tab Bay, Dryer Used to Burn Off Nitrates From UZ1101	3-1 3-1	1400 1400	NO <sub>2</sub>	5-7 25
Bldg. 1, Next to Dryer Near C12 Tab Bay, Dryer Used to Burn Off Nitrates From UZ1101	3-1 3-1	1410 1410	NO <sub>2</sub>	>25 25
Bldg. 1, In Aisle Next to Dryer Near C12 Tab Bay, Dryer Used to Burn Off Nitrates From UZ1101	3-1 3-1	1415 1415	NO <sub>2</sub>	15 15
Bldg. 4, Back of Bldg. In Same Room As Old Stack and Mixer. This is designed as ambient sample for Bldg. 4	3-1	1030	инз	10-15
Bldg. 12, C-18 Oxide Process Measurement Taken At Midpoint Of Calciner	3-1	1545	NH3	25
Bldg. 12, C-18 Oxide Process Measurement Taken At Drum Loading From Calciner	3-1	1550	инз	20
Bldg. 4, Cobalt/Amine Being Dumped into Tank on Mezzanine Level	3-1	1600	инз	>50*

TABLE XI (continued)

Location	Date	Time	Contaminant	Concentration (ppm)
Bldg. 12, C-18 Oxide Process, End of Calciner No. 12	3-2	0730	инз	15-20
Bldg. 12, Ball Wheel Room for C84-3	3-2	0740	инз	<5
Bldg. 12, At Moly Dipping Operation While Dipping was Ongoing	3-2	0800	NH3	10
Bldg. 12, Calciner No. 12 at Midpoint of the Calciner	3-2	1010	инз	>50
Oven Near C12 Tab Bay	3-2	1200 (noon)	NOX	15-30
Bldg. 1, Low Bay 4' From Utility Dryer Near Cl2 Tab Bay	3-3	1020	NO <sub>2</sub>	1-2
Bldg. 1, Low Bay 30' From Utility Dryer Near C12 Tab Bay	3-3	1022	NO <sub>2</sub>	1
Bldg. 1, Nickel Carb. Area	3-3 3-3	1040 1042	NH3 NH3	30 40
Bldg. 1, Near Leak In Ammonia Mixture (Tank No. 2) Storage Tank	3-3	1045	NH3	>50
Bldg. 1, Near Leak in Tank No. 4 Which Contains Scrubber Water	3-3	1050	инз	>50

Expiration date for  $\mathrm{NO}_\mathrm{X}$  tubes was October 1982. Tubes had been refrigerated since they were purchased.

<sup>\*</sup> Detector tube went off scale during the 7th stroke.

## TABLE XII

## Area Total Exposure Rate Readings From Alpha, Beta, and Gamma Radiation

United Catalysts Inc. West Plant Louisville, Kentucky HETA 83-075

March 3, 1983

Time	Reading (millirem/hour)
1430	0.5
1432	0-0.5
1634	<0.5
1753	0.0-0.5
1755	0.25
1758	0.25
	1432 1634 1753

Environmental Criteria (NRC): 2 millirem in any hour (unrestricted area)

TABLE XIII
Airborne Concentrations of Metals

Personal Samples

Louisville, Kentucky HETA 83-075

June 28-29, 1983

	C7-		Vallen	Concentration (ug/m3)		
Job/Location	Sample Time	<u>Da te</u>	Volume (Liters)	Cu	Cr	Ni
C-18 Tab Bay, Oper. 4	0555-1725	6-28	1035	3190	LLD	42.5
C-18 Tab Bay, Oper. 4	0602-1700	6-29	987	7900	LLD	44.6
C-18 Tab Bay, Oper. 2	0546-1731	6-28	1058	3210	LLD	33
C-18 Tab Bay, Oper. 2	0557-1702	6-29	998	481	LLD	23
C-79 Spray Dryer Oper.	0607-1705	6-28	987	2630	5,1	12.2
C-79 Spray Dryer Oper.	0604-1705	6-29	992	4340	3	17.1
Screening, C-12 Being Run, Screens 1,2	0615-1717	6-28	993	78.5	121	252

TABLE XIII (continued)

	6 - 3		W 7	Concentr	ation (u	g/m3)
Job/Location	Sample <u>Time</u>	Date	Volume (Liters)	Cu	Cr	Ni
Screening, C-12 Being Run, Screens 1,2	0614-1645	6-29	947	75	327	65.5
Fork Lift Oper.	0616-1714	6-28	987	25.3	LLD	28.4
Environmental cri normal workshift, OSHA AND ACGIH an for NIOSH.	8 hr. for		OSHA NIOSH ACGIH	1000 N 1000	1000 N 500	1000 15 1000
Environmental cri workshift (12 hou West Plant). The equals the normal by the hours the by the hours wo shift.	rs at the adjusted crit criteria mult normal criteri	eria iplied a is base		667 N 667	667 N 333	667 12.5 667

For example:

OSHA copper criteria =

 $\frac{1000 \text{ ug/m}^3 \text{ X 8hrs}=}{12-\text{hrs}} 667 \text{ ug/m}^3$ 

Note: Lead was analyzed for but not found on any sample.

Cu = Copper, Cr = Chromium-Total, Ni= Nickel

LLD = Below the laboratory limit of detection (2 ug/filter for Cu, 3 ug/filter for Ni and Cr).

N = No specific criterion for this material.

Table XIV

Demographic Characteristics of Workers

	South Plant	West Plant
Number of workers:	98	235
Age (years) Range Mean	21-65 39	19-65 36
Number and percent male	87 (89)	201 (85)
Number of percent of current smokers	60 (61)	150 (64)

 $\label{eq:table_XV} \textbf{Numbers and Percentages of Workers Reporting Symptoms}$ 

South	Plant (98	Workers)	West Plant (	235 Workers)	Signific	ance
Symptom	Number	26	Number	Z	Chi-Square	P-Value
Cough	48	(49)	106	(45)	0.42	> 0.5
Burning, itchy, watery eyes	40	(41)	81	(34)	1.20	> 0.25
Itchy burning nose	38	(39)	97	(41)	0.18	> 0.5
Nasal sores	34	(35)	47	(20)	8.11	< 0.01
Shortness of breath	33	(34)	70	(30)	0.49	> 0.25
Chest tight- ness	28	(29)	61	(26)	0.24	> 0.5
Skin rash	26	(27)	92	(39)	4.81	< 0.05
Wheezing	24	(25)	60	(26)	0.04	> 0.75
One or more symptoms	68	(70)	169	(72)	0.22	> 0.5

Table XVI Locations of Skin Rashes

Sout	h Plant	(26 Workers)	West Plant	(92 Worker	s) Signifi	Significance			
Location	Number	%	Numbe	r %	Chi-Square	P-Value			
Hands	26	(100)	71	(77)	7.16	< 0.1			
Face and neck	20	(80)	50	(54)	4.32	< 0.05			
Arms	19	(73)	42	(46)	6.19	< 0.025			
Chest, back and abdomen	15	(58)	36	(39)	2.90	> 0.05			
Legs	13	(50)	33	(36)	1,70	> 0.1			
Neck and underarms	9	(35)	30	(33)	0.04	> 0.75			
Feet	8	(31)	24	(26)	0.22	> 0.5			

Table XVII
Characteristics of Skin Rashes

South Pl	an <b>t</b> (26 )	Workers)	West Plant	(92 Workers)	Significance			
Location	Number	%	Number	%	Chi-Square	P-Value		
Red itchy skin	20	(77)	57	(61)	1.93	> 0.1		
Dry cracked skin	19	(73)	70	(76)	0.1	> 0.75		
Red skin and blisters	11	(43)	17	(18)	6.26	< 0.025		
Patches of thickened skin	6	(23)	15	(16)	0.64	> 0.25		
Color change	6	(23)	15	(16)	0.64	> 0.25		
Frequent skin sores	4	(15)	8	(9)	-	0.30*		
Cracked deformed fingernails	3	(12)	20	(22)	1,34	> 0.1		

<sup>\*</sup> Fisher's Exact Test, 2-Tailed

Table XVIII Number and Percentage of Workers with Respiratory Symptoms

	South Plant							West Plant								
	2000	rrent oker	Fori	ner (ers		on- okers	To	tal		rrent oker		rmer okers	No.	n- kers	Tota	1
Number of workers	(	50	1	26		12	91	8	1	150		22	(	61	23	5
Cough	27	(45)A	14	(54)	7	(58)A	48	(49)	72	(48)E,F	6	(27)E	23	(37)F	101	(43)
Shortness of breath	23	(38) <sup>B</sup>	7	(27)	2	(17) <sup>B</sup>	32	(33)	47	(31) <sup>H</sup>	10	(45)G,H	13	(21) <sup>G</sup>	70	(30)
Nheezing	18	(30)C	7	(27)	1	(8)C	26	(27)	41	(27) <sup>J</sup>	8	(36)I,J	11	(17)1	60	(26)
Chest tight- ness	19	(32)D	5	(19)	1	(8)D	25	(26)	41	(27) <sup>K</sup>	6	(27)	14	(22) <sup>K</sup>	61	(26)

 $A \cdot X^2 = 0.68, p > 0.25$ 

B - P = 0.2 (Fisher's exact test, 2-tailed)

C - P = 0.16 (Fisher's exact test, 2-tailed)

D - P = 0.15 (Fisher's exact test, 2-tailed)

 $E - \chi^2 = 30.05$ , p < 0.001

 $F - \chi^2 = 1.83$ , p > 0.1 G -  $\chi^2 = 4.69$ , p < 0.05

 $H - X^2 = 2.13, p > 0.1$ 

 $I - X^2 = 3.16$ , p > 0.05  $J - X^2 = 2.02$ , p > 0.1  $K - X^2 = 0.42$ , p > 0.5

Table XIX
Workers Reporting Symptoms In High, Medium and Low Exposure Groups

			Exposure C	roups*			Significance						
	H1gh (88	workers)	Hedium (92	workers)	Low (49 W	orkers)	High -vs- Lo	w Exposure	Medium -vs-	Low Exposure			
Symptoms	Number	2	Number	2	Number	2	Ch1-Square	P-Value	Chi-Square	P-Value			
Itchy burning	48	(55)	48	(52)	8	(16)	18.94	< 0.001	17.27	< 0.001			
ough	48	(55)	19	(53)	10	(20)	15.02	< 0.001	14.17	< 0.001			
Burning itchy watery eyes	37	(42)	47	(51)	7	(14)	11.14	< 0.001	18.42	< 0,001			
St In rash	34	(39)	34	(39)	8	(16)	7.37	< 0.01	6.51	< 0.025			
dortness of breath	33	(38)	. 33	(30)	5	(10)	11.70	0,001	10.70	< 0.01			
theez ing	26	(30)	20	(30)	5	(10)	6.73	< 0.01	7.30	< 0.01			
hest tight-	24	(27)	32	(35)	5	(10)	5.50	< 0.025	9.08	< 0.01			
lesal sores	23	(26)	10	(11)	2	(14)	10.26	< 0.001	6.93	< 0.01			
lone	8	(9)	10	(21)	33	(67)	50.94	< 0.001	29.82	< 0.001			

<sup>\*</sup> Exposure groups are defined in the lest

Table XX

Personal Summary of Airborne Sampling Results
Full-Shift Samples

Material	Lowest Evaluation Criteria-Adjusted for 12-hour Shift	Number of . Samples	Exposures Range	Number and % of Samples Exceeding Lowest Criteria	Average Exposure (Stan. Deviation		
Nickel	12.5 ug/m <sup>3</sup> - NIOSH	38	8 to 1780 ug/m <sup>3</sup>	22 (58%)	99.4 (296)		
Chromiun- Total	333 ug/m³ - OSHA, ACGIH	38	LLD to 327 ug/m <sup>3</sup>	0 (-)	37.3 (72.4)		
Copper	667 ug/m <sup>3</sup> - OSHA, ACGIH	38	25.3 to 7900 ug/m <sup>3</sup>	12 (32%)	1170 (1980)		
Lead	33 ug/m <sup>3</sup> - OSHA	28	1 to 34 ug/m <sup>3</sup>	1 (5%)	3.9 (6.7)		
Zinc	4170 ug/m <sup>3</sup> - NIOSH	19	1 to > $10700 \text{ ug/m}^3$	1 (5%)	879 (2430)		
Cobalt	67 ug/m <sup>3</sup> - OSHA,	29	LLD to 7 ug/m <sup>3</sup>	0 (-)	2.2 (*)		
Particulates- Total	6.7 mg/m <sup>3</sup> - ACGIH	Z	$0.53$ to $24.2 \text{ mg/m}^3$	1 (50%)	12.4 (16.7)		
Particulates- Respirable	3.3 $mg/m^3 = \frac{OSHA}{ACGIH}$	12	0.39 to 3.63 $mg/m^3$	1 (8%)	1.68 (1.04)		
Phosphoric Acid	$0.66 \text{ mg/m}^3 = \frac{\text{OSHA}}{\text{ACCIII}}$	8	LLD to 0.84 mg/m <sup>3</sup>	1 (13%)	0.2 (*)		
Ammonia	12 mg/m3 - ACGIH	7	$2.55$ to $13.5 \text{ mg/m}^3$	1 (147)	7.3 (4.2)		
Nitric Oxide	20 mg/m <sup>3</sup> - ACGIII	3	0.18 to 0.39 $m\eta/m^3$	0 (-)	0.29 (0.1)		
Nitrogen Dioxide	4 mg/m3 - ACGIII	3	0.96 to 1.04 $mg/m^3$	0 (-)	0.99 (0.01)		

<sup>- =</sup> Not applicable

\*

<sup>\* =</sup> Standard deviation not calculated due to percentage of samples with non-detected values.

LLD = Below the laboratory limit of detection.

Note: For calculating  $\vec{x}$  and S.D. for samples with LLD values, used mid point between 0.0 and highest concentration possible, which was determined using laboratory limit of detection  $\vec{x}$  volume.

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