Occupational Health Guideline for Nickel Carbonyl*

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: $Ni(CO)_4$
- Synonyms: None
- Appearance and odor: Colorless liquid with a musty odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for nickel carbonyl is 0.001 part of nickel carbonyl per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.007 milligram of nickel carbonyl per cubic meter of air (mg/m^3). NIOSH has recommended that the permissible exposure limit be retained, but has recommended that nickel carbonyl be regulated as an occupational carcinogen. The NIOSH Special Occupational Hazard Review for Nickel Carbonyl and the NIOSH Criteria Document for Inorganic Nickel should be consulted for more detailed information.

HEALTH HAZARD INFORMATION

- **Routes of exposure**

Nickel carbonyl can affect the body if it is inhaled or if it comes in contact with the eyes or skin. It can also affect the body if it is swallowed.

- **Effects of overexposure**

1. Short-term Exposure: Depending on the severity of inhalation exposure, both initial and delayed symptoms may develop. Initial symptoms include dizziness, headache, shortness of breath, and vomiting. These symptoms generally disappear when the individual is removed from exposure. The delayed symptoms may develop 12 to 36 hours after exposure. These symptoms include chest pain, cough, rapid breathing, shortness of breath, a bluish discoloration of the skin, and increased temperature. Delirium and other signs of nervous system problems usually appear at this time. In some cases the two stages may merge. In severe cases death may occur.

2. Long-term Exposure: Repeated or prolonged exposure to nickel carbonyl has been associated with an increased incidence of cancer of the lungs and sinuses.

3. Reporting Signs and Symptoms: A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to nickel carbonyl.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to nickel carbonyl at potentially hazardous levels:

1. Initial Medical Examination:

—A complete history and physical examination: The purpose is to detect pre-existing conditions that might place the exposed employee at increased risk, and to establish a baseline for future health monitoring. Examination of the lungs and upper respiratory tract should be stressed.

—14" x 17" chest roentgenogram: Nickel carbonyl causes human lung damage and is a suspected lung carcinogen. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Nickel carbonyl is a severe pulmonary irritant. Persons with decreased pulmonary function may be at increased risk from exposure.

—Sputum cytology: Nickel carbonyl is associated with an increase of lung cancer in humans.

—Urinalysis: Since kidney damage has been observed from exposure, a urinalysis should be performed to include, at a minimum, specific gravity, albumin, glucose, and a microscopic on centrifuged sediment. Examination of the urine for nickel should be conducted on a monthly basis.

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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2. Periodic Medical Examination: The aforementioned medical examinations should be repeated on an annual basis, with the exception that a urinalysis should be conducted on a monthly basis.

• **Summary of toxicology**

Nickel carbonyl vapor is a severe pulmonary irritant and probably causes cancer of the paranasal sinuses and the lungs in animals and man. Initial symptoms of overexposure usually include frontal headache, vertigo, nausea, vomiting, and sometimes substernal and epigastric pain; generally these early effects disappear when the individual is removed to fresh air. There may be an asymptomatic interval between recovery from initial symptoms and the onset of delayed symptoms, which tend to develop 12 hours or more following exposure; constrictive pain in the chest is characteristic of the delayed onset of pulmonary effects, followed by cough, hyperpnea and cyanosis, leading to profound weakness; gastrointestinal symptoms may also occur. The temperature seldom rises above 101 F, and leukocytosis above 12,000 per mg/m^3 is infrequent. Physical signs compatible with pneumonitis or bronchopneumonia are elicited in the chest. Except for the pronounced weakness and hyperpnea, the physical findings and symptoms resemble those of a viral or influenzal pneumonia. Terminally, delirium and convulsions frequently occur; death has occurred from 3 to 13 days after exposure to nickel carbonyl. In subjects who recover from nickel carbonyl intoxication, convalescence is usually protracted (2 to 3 months) and is characterized by excessive fatigue on slight exertion. Exposure of rats to nickel carbonyl has caused pulmonary carcinomata; multiple intravenous injection of nickel carbonyl in rats has caused carcinomata and sarcomata in diverse organs, including the liver and kidneys. Several epidemiologic studies have shown an increased incidence of cancer of the paranasal sinuses and lungs among workers in nickel refineries and factories; suspicion of carcinogenicity has been focused primarily on nickel carbonyl vapor, although there are usually concurrent exposures to respirable particles of nickel, nickel subsulfide, and nickel oxide.

CHEMICAL AND PHYSICAL PROPERTIES

• **Physical data**

1. Molecular weight: 170.7
2. Boiling point (760 mm Hg): 43 C (109 F)
3. Specific gravity (water = 1): 1.32
4. Vapor density (air = 1 at boiling point of nickel carbonyl): 5.89
5. Melting point: −25 C (−13 F)
6. Vapor pressure at 20 C (68 F): 321 mm Hg
7. Solubility in water, g/100 g water at 20 C (68 F): 0.018
8. Evaporation rate (butyl acetate = 1): Data not available

• **Reactivity**

1. Conditions contributing to instability: Liquid nickel carbonyl may explode when heated above 60 C (140 F). In the presence of air, nickel carbonyl forms a deposit which becomes peroxidized. This tends to decompose and ignite.
2. Incompatibilities: Contact with nitric acid, chlorine, and other oxidizers may cause fires and explosions. The vapor of nickel carbonyl may promote the ignition of mixtures of combustible vapors (such as gasoline) and air.
3. Hazardous decomposition products: Toxic gases and vapors (such as nickel oxide fume and carbon monoxide) may be released in a fire involving nickel carbonyl.
4. Special precautions: Liquid nickel carbonyl will attack some forms of plastics, rubber, and coatings.

• **Flammability**

1. Flash point: Lower than −20 C (−4 F) (closed cup)
2. Autoignition temperature: May ignite spontaneously
3. Flammable limits in air, % by volume: Lower: 2; Upper: Data not available
4. Extinguishant: Foam, carbon dioxide, dry chemical

• **Warning properties**

1. Odor Threshold: Patty states that the odor of nickel carbonyl is detectable at between 1 and 3 ppm.
2. Eye Irritation Level: According to the AIHA *Hygienic Guide*, the effect of eye contact with nickel carbonyl is unknown. This substance is not known to be an eye irritant, however.
3. Evaluation of Warning Properties: Since the odor threshold of nickel carbonyl is over 1000 times greater than the permissible exposure limit, nickel carbonyl is treated as a material with poor warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Method**

Measurement of nickel carbonyl may be done by sampling with a bubbler containing alcoholic-iodine solution, followed by chemical treatment and colorimetric analysis. The NIOSH Special Occupational Hazard Review for Nickel Carbonyl suggests a detailed method which may be employed for sampling and analyzing nickel carbonyl.

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

PERSONAL PROTECTIVE EQUIPMENT

• Employees should be provided with and required to use impervious clothing, gloves, face shields (eight-inch minimum), and other appropriate protective clothing necessary to prevent any possibility of skin contact with liquid nickel carbonyl.

• Any clothing which becomes wet with liquid nickel carbonyl should be removed immediately and not reworn until the nickel carbonyl is removed from the clothing.

• Clothing wet with liquid nickel carbonyl should be placed in vapor-tight, sealed containers for storage until it can be discarded or until provision is made for the removal of nickel carbonyl from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the nickel carbonyl, the person performing the operation should be informed of nickel carbonyl's hazardous properties.

• Employees should be provided with and required to use splash-proof safety goggles where there is any possibility of liquid nickel carbonyl contacting the eyes.

SANITATION

• Skin that becomes wet with liquid nickel carbonyl should be immediately washed or showered to remove any nickel carbonyl.

• Eating and smoking should not be permitted in areas where nickel carbonyl is handled, processed, or stored.

• Employees who handle nickel carbonyl should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to nickel carbonyl may occur and control methods which may be effective in each case:

Operation	Controls
Use in Mond process for nickel refining	Process enclosure; local exhaust ventilation; personal protective equipment
Use in plating operations on foundry patterns, steel, and electronics manufacture	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a reagent in synthesis of acrylic esters; use as a catalyst or reagent in organic synthesis	Process enclosure; local exhaust ventilation; personal protective equipment
Use in petroleum and petrochemical processing (including methanation of ammonia synthesis gas)	Process enclosure; local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• **Eye Exposure**

If liquid nickel carbonyl gets into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. If irritation is present after washing, get medical attention. Contact lenses should not be worn when working with this chemical.

• **Skin Exposure**

If liquid nickel carbonyl gets on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If liquid nickel carbonyl soaks through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. Get medical attention immediately.

• **Breathing**

If a person breathes in large amounts of nickel carbonyl, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• **Swallowing**

When liquid nickel carbonyl has been swallowed and the person is conscious, give the person large quantities of water immediately. After the water has been swallowed, try to get the person to vomit by having him touch the back of his throat with his finger. Do not make an unconscious person vomit. Get medical attention immediately.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

SPILL, LEAK, AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of spills or leaks until cleanup has been completed.

• If nickel carbonyl is spilled or leaked, the following steps should be taken:

1. Remove all ignition sources.
2. Ventilate area of spill or leak.
3. For small quantities, absorb on paper towels. Evaporate in a safe place (such as a fume hood). Allow sufficient time for evaporating vapors to completely clear the hood ductwork. Burn the paper in a suitable location away from combustible materials. Large quantities can be collected and atomized in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device. Nickel carbonyl should not be allowed to enter a confined space, such as a sewer, because of the possibility of an explosion.

• Waste disposal method:

Nickel carbonyl may be disposed of by atomizing in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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* SPECIAL NOTE

Nickel carbonyl appears on the OSHA "Candidate List" of chemicals being considered for further scientific review regarding its carcinogenicity (*Federal Register*, Vol. 45, No. 157, pp. 5372-5379, 12 August 1980). The International Agency for Research on Cancer (IARC) has evaluated the data on this chemical and has concluded that it causes cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 11, 1976.

RESPIRATORY PROTECTION FOR NICKEL CARBONYL

Condition	Minimum Respiratory Protection* Required Above 0.001 ppm
Greater than 0.001 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against nickel carbonyl. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.