

# Occupational Health Guideline for Chromic Acid and Chromates\*

## 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.

## APPLICABILITY

The general guidelines contained in this document apply to all chromic acid and chromates. Physical and chemical properties of several specific compounds are provided for illustrative purposes.

## SUBSTANCE IDENTIFICATION

### Chromic acid

- Formula:  $\text{CrO}_3$
- Synonyms: Chromic anhydride; chromium trioxide
- Appearance and odor: Dark red, deliquescent, odorless solid.

### Sodium dichromate

- Formula:  $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$
- Synonyms: Sodium bichromate (dihydrate)
- Appearance and odor: Red-orange, odorless solid.

### Potassium chromate

- Formula:  $\text{K}_2\text{CrO}_4$
- Synonyms: Chromate of potash
- Appearance and odor: Yellow, odorless solid.

## PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for chromic acid or chromates is a ceiling of 0.1 milligram of chromic acid or chromates per cubic meter of air ( $\text{mg}/\text{m}^3$ ). Certain

forms of chromium (VI) have been found to cause increased respiratory cancer among workers. Certain other forms of chromium (VI) are currently believed to be non-carcinogenic: The non-carcinogenic forms include the monochromates and bichromates (dichromates) of hydrogen, lithium, sodium, potassium, rubidium, cesium, and ammonium, and chromium (VI) oxide (chromium acid anhydride). NIOSH has not conducted an in-depth study of the toxicity of chromium metal or compounds containing chromium in an oxidation state other than 6. NIOSH recommends that the permissible exposure limit for carcinogenic chromium (VI) compounds be reduced to  $0.001 \text{ Cr (VI) mg}/\text{m}^3$  and that these compounds be regulated as occupational carcinogens. NIOSH also recommends that the permissible exposure limit for non-carcinogenic chromium (VI) be reduced to  $0.025 \text{ Cr (VI) mg}/\text{m}^3$  averaged over a work shift of up to 10 hours per day, 40 hours per week, with a ceiling level of  $0.05 \text{ Cr (VI) mg}/\text{m}^3$  averaged over a 15-minute period. It is further recommended that chromium (VI) in the workplace be considered carcinogenic, unless it has been demonstrated that only the non-carcinogenic chromium (VI) compounds mentioned above are present. The NIOSH Criteria Documents for Chromic Acid and Chromium (VI) should be consulted for more detailed information.

## HEALTH HAZARD INFORMATION

### • Routes of exposure

Chromic acid or chromates can affect the body if they are inhaled or if they come in contact with the eyes or skin. They can also affect the body if they are swallowed.

### • Effects of overexposure

*1. Short-term Exposure:* Chromic acid mist and chromate dusts may cause severe irritation of the nose, throat, bronchial tubes, and lungs. Chromic acid splashed in the eyes may cause severe injury. If swallowed, chromates and sodium and potassium dichromates may cause stomach and kidney problems. These

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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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compounds, if swallowed, often cause vomiting. Skin exposure to chromic acid or chromates may cause ulceration of the skin.

**2. Long-term Exposure:** Repeated or prolonged exposure to chromic acid or chromate dust or mist may cause an ulceration and perforation of the nasal septum. Respiratory irritation may occur with symptoms resembling asthma. Liver damage with yellow jaundice has been reported. Prolonged or repeated exposure of the skin may cause a skin rash. Allergic skin rash may also occur. An increased amount of lung cancer has been found in employees in the chromate-producing industry.

**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 chromic acid or chromates.

• **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to chromic acid or chromates 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. Persons with a history of asthma, allergies, or known sensitization to chromic acid or chromates would be expected to be at increased risk from exposure. Examination of the respiratory system, blood, liver, and kidneys should be stressed. The skin should be examined for evidence of chronic disorders.

—A complete blood count: Chromates have been shown to cause blood changes in humans. A complete blood count should be performed including a red cell count, a white cell count, a differential count of a stained smear, as well as hemoglobin and hematocrit.

—14" x 17" chest roentgenogram: Chromates may cause human lung damage and are associated with a high incidence of lung cancer. Surveillance of the lungs is indicated.

—FVC and FEV (1 sec): Chromates are reported to cause decreased pulmonary function. Periodic surveillance is indicated.

—Urinalysis: Since chromates may cause kidney damage, a urinalysis should be obtained, including at a minimum specific gravity, albumin, glucose, and a microscopic on centrifuged sediment.

—Liver function tests: Chromates may cause liver damage. A profile of liver function should be obtained by utilizing a medically acceptable array of biochemical tests.

—Skin disease: Chromates are defatting agents and can cause dermatitis on prolonged exposure. Persons with pre-existing skin disorders may be more susceptible to the effects of these agents.

**2. Periodic Medical Examination:** The aforementioned medical examinations should be repeated on an annual basis. Emphasis should be placed on observation for

changes in the mucous membranes of the upper respiratory tract, ulceration of the skin, and surveillance for malignancy of the respiratory tract and lungs.

• **Summary of toxicology**

Chromic acid mist and chromate dusts are severe irritants of the nasopharynx, larynx, lungs, and skin. Chromium compounds, especially the hexavalent compounds are associated with a high incidence of lung cancer in humans. Administered subcutaneously to rabbits and guinea pigs, chromates produce kidney damage, with albuminuria and cylindruria; fatal nephritis occurred in a human treated with chromic acid to cauterize a wound. Workers exposed to chromic acid or chromates in concentrations of 0.11 to 0.15 mg/m<sup>3</sup> developed ulcers of the nasal septum and irritation of the conjunctiva, pharynx and larynx, as well as asthmatic bronchitis. A worker exposed to unmeasured but massive amounts of chromic acid mist for 4 days developed severe frontal headache, wheezing, dyspnea, cough, and pain on inspiration; after 6 months there was still chest pain on inspiration and cough. In an industrial plant where the airborne chromic acid concentrations measured from 0.18 to 1.4 mg/m<sup>3</sup>, moderate irritation of the nasal septum and turbinates was observed after 2 weeks of exposure, ulceration of the septum after 4 weeks, and perforation of the septum after 8 weeks. A worker exposed to an unmeasured concentration of chromic acid mist for 5 years developed jaundice and was found to be excreting significant amounts of chromium; liver function in four other workers with high urinary chromium excretion was mildly to moderately impaired. Other studies of chromate workers have not found any unusual incidence of liver diseases or other systemic diseases except for lung cancer. Erosion and discoloration of the teeth has been attributed to chromic acid exposure. Blood changes were observed in chromate plant workers, including leukocytosis or leukopenia, monocytosis, and eosinophilia. A markedly increased incidence of bronchogenic carcinoma occurs in workers exposed to chromate dust. The latent period is relatively short, suggesting the presence of a potent carcinogen. Calcium chromate and zinc chromate have been demonstrated to be carcinogenic in rats, and the risk of lung cancer is reportedly increased in chrome pigment workers. Papillomata of the oral cavity and larynx were found in 15 of 77 chrome platers exposed for an average of 6.6 years to chromic acid mist at air concentrations of chromium of 0.4 mg/m<sup>3</sup>. There is no positive evidence that chromic acid in the workplace has contributed to an increase in lung cancer, neither is there definitive evidence that absolves chromic acid. A concentrated solution of chromic acid in the eye causes severe corneal injury; chronic exposure to the mist causes conjunctivitis. Chrome ulcer, a penetrating lesion of the skin, occurs chiefly on the hands and forearms where there has been a break in the epidermis; it is believed to be due to a direct necrotizing effect of the chromate ion. The ulcer is relatively painless, heals slowly, and produces a characteristic depressed scar.

Prolonged exposure to chromic acid mist causes dermatitis, which varies from a dry erythematous eruption to a weeping eczematous condition. Cutaneous sensitization to chromate compounds is a common problem in industrial practice.

## CHEMICAL AND PHYSICAL PROPERTIES

### • Physical data—Chromic acid

1. Molecular weight: 100
2. Boiling point (760 mm Hg): Decomposes when it melts
3. Specific gravity (water = 1): 2.7
4. Vapor density (air = 1 at boiling point of chromic acid): Not applicable
5. Melting point: 197 C (387 F) (decomposes)
6. Vapor pressure at 20 C (68 F): Data not available (very low)
7. Solubility in water, g/100 g water at 20 C (68 F): 63
8. Evaporation rate (butyl acetate = 1): Not applicable

### • Physical data—Sodium dichromate

1. Molecular weight: 298
2. Boiling point (760 mm Hg): 400 C (752 F) (decomposes)
3. Specific gravity (water = 1): 2.34
4. Vapor density (air = 1 at boiling point of sodium dichromate): Not applicable
5. Melting point: 357 C (674 F) (loses water at 85 C (185 F))
6. Vapor pressure at 20 C (68 F): Zero (except for water of crystallization)
7. Solubility in water, g/100 g water at 20 C (68 F): 236
8. Evaporation rate (butyl acetate = 1): Not applicable

### • Physical data—Potassium chromate

1. Molecular weight: 194
2. Boiling point (760 mm Hg): Data not available
3. Specific gravity (water = 1): 2.7
4. Vapor density (air = 1 at boiling point of potassium chromate): Not applicable
5. Melting point: 971 C (1780 F)
6. Vapor pressure at 20 C (68 F): Zero
7. Solubility in water, g/100 g water at 20 C (68 F): 39
8. Evaporation rate (butyl acetate = 1): Not applicable

### • Reactivity—Chromic acid or chromates

1. Conditions contributing to instability: None
2. Incompatibilities: Contact with any combustible, organic, or other readily oxidizable materials such as paper, wood, sulfur, aluminum, plastics, etc. may cause fires and explosions.
3. Hazardous decomposition products: None
4. Special precautions: Chromic acid or chromates will attack most forms of metals, cloth, leather, plastics, rubber, and coatings and may cause spontaneous igni-

tion.

### • Flammability

1. Chromic acid is not combustible in itself, but is a powerful, oxidizing material. It will ignite on contact with acetic acid and alcohol.

### • Warning properties

Grant states that "contact with the solid material or with concentrated solution (of chromic acid) by splash in the eye causes severe corneal injury characterized by infiltration, vascularization, and opacification of the cornea.

"More commonly, exposure to chromic acid occurs in less serious form as a result of spraying of fine droplets into the air from electroplating baths or by transfer to the eyes on the fingers. After chronic exposure to such conditions, the ocular changes seen are chronic conjunctival inflammation, analogous to the well-known irritation of the nasal mucosa which leads to perforation of the nasal septum." In addition, Grant states that "dichromates (bichromates) as ammonium, sodium, or potassium salts are water-soluble, crystalline substances which have a peculiar injurious effect on the cornea, causing great swelling of the corneal stroma."

The *Documentation of TLV's* states that "Vigliani and Zurlo reported . . . irritation of the mucous membranes of the larynx, pharynx, and conjunctiva . . . in a group of workers allegedly exposed to chromates or chromic acid in concentrations ranging from 0.11 to 0.15 mg/m<sup>3</sup>."

## MONITORING AND MEASUREMENT PROCEDURES

### • Ceiling Evaluation

Measurements to determine employee ceiling exposure are best taken during periods of maximum expected airborne concentrations of chromic acid or chromates. Each measurement should consist of a fifteen (15) minute sample or series of consecutive samples totalling fifteen (15) minutes in the employee's breathing zone (air that would most nearly represent that inhaled by the employee). A minimum of three (3) measurements should be taken on one work shift and the highest of all measurements taken is an estimate of the employee's exposure.

### • Method

Sampling and analyses may be performed by collection of chromic acid or chromates on a filter, followed by chemical treatment and colorimetric analysis. An analytical method for chromic acid and chromates is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 3, 1977, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00261-4).

## 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 solids or liquids containing chromic acid or chromates.

- If employees' clothing may have become contaminated with solids or liquids containing chromic acid or chromates, employees should change into uncontaminated clothing before leaving the work premises.

- Clothing contaminated with chromic acid or chromates should be placed in closed containers for storage until it can be discarded or until provision is made for the removal of substance from the clothing. If the clothing is to be laundered or otherwise cleaned to remove the chromic acid or chromates, the person performing the operation should be informed of chromic acid or chromates' hazardous properties.

- Where there is any possibility of exposure of an employee's body to solids or liquids containing chromic acid or chromates, facilities for quick drenching of the body should be provided within the immediate work area for emergency use.

- Non-impervious clothing which becomes contaminated with chromic acid or chromates should be removed immediately and not reworn until the substance is removed from the clothing.

- Employees should be provided with and required to use dust- and splash-proof safety goggles where there is any possibility of solids or liquids containing chromic acid or chromates contacting the eyes.

- Where there is any possibility that employees' eyes may be exposed to solids or liquids containing chromic acid or chromates, an eye-wash fountain should be provided within the immediate work area for emergency use.

## SANITATION

- Skin that becomes contaminated with chromic acid or chromates should be immediately washed or showered with soap or mild detergent and water to remove any such substance.

- Workers subject to skin contact with solids or liquids containing chromic acid or chromates should wash with soap or mild detergent and water any areas of the body which may have contacted such a substance at the end of each work day.

- Eating and smoking should not be permitted in areas where solids or liquids containing chromic acid or chromates are handled, processed, or stored.

- Employees who handle solids or liquids containing chromic acid or chromates should wash their hands thoroughly with soap or mild detergent and water before eating, smoking, or using toilet facilities.

- Areas in which exposure to a carcinogenic form of chromium (VI) may occur should be identified by signs or other appropriate means, and access to these areas should be limited to authorized personnel only.

## COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to chromic acid or chromates may occur and control methods which may be effective in each case:

| Operation   | Controls   |
|---|--|
| Use in metal finishing in chrome plating, anodizing, conversion coatings, and for corrosion resistance  | Local exhaust ventilation; personal protective equipment |
| Use in leather finishing for shoe uppers, glove and garment leathers, and bag leather   | Local exhaust ventilation; personal protective equipment |
| Use as corrosion inhibitors in radiator coolants, internal combustion and gas turbine engines, refrigerator and air conditioning systems, and water-cooled nuclear reactors | Local exhaust ventilation; personal protective equipment |
| Use in photoreproduction processes as sensitizing agents for photoengraving, photography, lithography, and blueprinting   | Local exhaust ventilation; personal protective equipment |

| <b>Operation</b>   | <b>Controls</b>   |
|--|---|
| Use as corrosion-inhibiting and coloring pigments, artists' colors, jointing pastes, inks, rubber, and ceramics, and color blending  | Process enclosure; local exhaust ventilation; personal protective equipment |
| Use in dyeing of fur, leather, fabrics, wool, and nylon; oxidizing of dyes; aftertreating on cotton, and in textile and paper printing; use in manufacture of glue used in shoes, furniture, and packaging | Local exhaust ventilation; personal protective equipment                    |
| Use as fungicides; use in aqueous preservatives and fire retardants for wood; for protection of textiles and seed  | Local exhaust ventilation; personal protective equipment                    |
| Use in battery manufacture to increase shelf life; to provide corrosion resistance and for battery depolarization  | Local exhaust ventilation; personal protective equipment                    |
| Use in manufacture of safety matches and explosives  | Local exhaust ventilation; personal protective equipment                    |
| Use as a chemical reagent, oxidizing agent, catalyst, indicator, in bleaching of fats, oils, and waxes, in chemical synthesis, and in analytical chemistry   | Local exhaust ventilation; personal protective equipment                    |
| Use in manufacture and packaging of cement   | 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 solids or liquids containing chromic acid or chromates get into the eyes, wash eyes immediately with large amounts of water, lifting the lower and upper lids occasionally. Get medical attention immediately. Contact lenses should not be worn when working with these chemicals.

### • Skin Exposure

If solids or liquids containing chromic acid get on the skin, immediately flush the contaminated skin with soap or mild detergent and water. If chromic acid soaks through the clothing, remove the clothing immediately and flush the skin with water. If irritation persists after washing, get medical attention. If chromates get on the skin, immediately wash the contaminated skin using soap or mild detergent and water. If solids or liquids containing chromic acid or chromates penetrate through the clothing, remove the clothing immediately and wash the skin using soap or mild detergent and water. If irritation persists after washing, get medical attention.

### • Breathing

If a person breathes in large amounts of chromic acid or chromates, 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 solids or liquids containing chromic acid or chromates have been swallowed, 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 AND DISPOSAL PROCEDURES

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

• If chromic acid or chromates are spilled, the following steps should be taken:

1. Ventilate area of spill.
2. Collect spilled material in the most convenient and safe manner and deposit in sealed containers for reclamation or for disposal in a secured sanitary landfill. Liquid containing chromic acid or chromates should be absorbed in vermiculite, dry sand, earth, or a similar material.

• Waste disposal method:

Chromic acid or chromates may be disposed of in sealed containers in a secured sanitary landfill.

## REFERENCES

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#### \* SPECIAL NOTE

The International Agency for Research on Cancer (IARC) has evaluated the data on these chemicals and has concluded that they cause cancer. See *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man*, Volume 2, 1973, and Volume 23, 1980.

- Warning properties

## RESPIRATORY PROTECTION FOR CHROMIC ACID AND CHROMATES

| Condition   | Minimum Respiratory Protection*<br>Required Above 0.1 mg/m <sup>3</sup>   |
|---|---|
| Particulate Concentration   |   |
| 5 mg/m <sup>3</sup> or less   | A high efficiency particulate filter respirator with a full facepiece.<br>Any supplied-air respirator with a full facepiece, helmet, or hood.<br>Any self-contained breathing apparatus with a full facepiece.  |
| 30 mg/m <sup>3</sup> or less  | A powered air-purifying respirator with a full facepiece and a high efficiency particulate filter.<br>A Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure mode or with a full facepiece, helmet, or hood operated in continuous-flow mode.  |
| Greater than 30 mg/m <sup>3</sup> or entry and escape from unknown concentrations | Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.<br>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  | A high efficiency particulate filter respirator.<br>Any escape self-contained breathing apparatus.  |

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

