

## Chromium Hexavalent Compounds\*

Known to be human carcinogens

First Listed in the *First Annual Report on Carcinogens* (1980)

### Carcinogenicity

Chromium hexavalent (VI) compounds are *known to be human carcinogens* based on sufficient evidence of carcinogenicity in humans. Epidemiological studies in various geographical locations have consistently reported increased risks of lung cancer among workers engaged in chromate production, chromate pigment production, and chromium plating. Epidemiological studies of lung cancer among ferrochromium workers were inconclusive. Exposure to specific chromium compounds varies by industry. Chromate production workers are exposed to a variety of chromium compounds, including chromium(VI) and trivalent (III) compounds. Chromate pigment workers are exposed to chromates in the pigment and to soluble chromium(VI) compounds used in pigment production. Chrome platers are exposed to soluble chromium(VI) compounds and possibly to nickel. Ferrochromium workers are exposed mainly to chromium(III) compounds and possibly to chromium(VI) compounds. Epidemiological studies of stainless-steel welders exposed to chromium(VI) compounds also found an increased risk of lung cancer; however, these studies are of limited use for evaluation of chromium's carcinogenicity, because the welders were co-exposed to other potential carcinogens. In addition, epidemiological studies of chromate production workers, chromate pigment workers, and chrome platers found an increased risk of a rare cancer of the sinonasal cavity. The data for cancer at sites other than the lung and sinonasal cavity were unclear. The International Agency for Research on Cancer (IARC) concluded that there was sufficient evidence in humans for the carcinogenicity of chromium(VI) compounds as encountered in the chromate production, chromate pigment production, and chromium plating industries (IARC 1990).

Some studies published since the reviews for listing in the *First Annual Report on Carcinogens* and by the IARC (1990) suggested that exposure to chromium among workers such as chromium-exposed arc welders, chromate pigment workers, chrome platers, and chromium tanning workers may be associated with cancer at other tissue sites, including leukemia and bone cancer (reviewed by Costa 1997).

The findings in humans are supported by studies in experimental animals. Chromium(VI) compounds have been tested for carcinogenicity in rats exposed by inhalation, intrabronchial, intrapleural, intratracheal, intramuscular, or subcutaneous administration. They also have been tested in mice exposed by inhalation, intramuscular, or intratracheal administration and in hamsters, guinea pigs, and rabbits exposed by intratracheal instillation. Benign and malignant lung tumors were observed in rats in a number of studies with calcium chromate, chromium trioxide, sodium dichromate, lead chromates, strontium chromate, or zinc chromates. In addition, malignant tumors were observed at the injection or implantation site in rats following intrapleural, subcutaneous, or intramuscular administration of these compounds. When administered to mice by inhalation, calcium chromate caused benign lung tumors, and chromium trioxide caused malignant lung tumors; a benign nasal tumor also was observed in a mouse exposed to chromium trioxide. Exposure of hamsters, guinea pigs, and rabbits to chromium(VI) compounds by intratracheal instillation did not cause lung tumors (IARC 1980, 1990). IARC (1990) concluded that there was sufficient evidence for the carcinogenicity of calcium chromate, lead chromates, strontium chromate, and zinc chromates in experimental animals and limited evidence for the carcinogenicity of chromium trioxide and sodium dichromate.

### Additional Information Relevant to Carcinogenicity

Chromosomal aberrations (changes in chromosome structure or number), sister chromatid exchange, and aneuploidy (extra or missing chromosomes) were observed in workers exposed to chromium(VI) compounds. Chromium(VI) compounds also caused genetic damage in a variety of test systems. Most caused mutations and DNA damage in bacteria; however, the poorly soluble compounds had to be dissolved in acids or alkalis to produce genetic effects. A few compounds also caused mutations in yeast and insects. Many chromium(VI) compounds caused genetic damage in cultured human and other animal cells and in experimental animals exposed *in vivo*. The compounds tested included ammonium chromate and dichromate, calcium chromate, chromium trioxide, sodium chromate and dichromate, potassium chromate and dichromate, strontium chromate, and the industrial product basic zinc chromate (zinc yellow). Among the types of genetic damage observed were gene mutations (including dominant lethal mutations), DNA damage, sister chromatid exchange, chromosomal aberrations, and cell transformation (a step in tumor formation) (IARC 1990).

IARC (1990) concluded that there was sufficient evidence for the carcinogenicity of chromium(VI) compounds in humans based on the combined results of epidemiological studies, carcinogenicity studies in experimental animals, and evidence that chromium(VI) ions generated at critical sites in the target cells are responsible for the carcinogenic action observed.

### Properties

Elemental chromium is a transition-group metal belonging to group VIB of the periodic table and has oxidation states ranging from  $-2$  to  $+6$ , of which the divalent, trivalent, and hexavalent forms are the most important. Elemental chromium does not occur naturally in the environment. The divalent (chromous) state is readily oxidized to the more stable trivalent (chromic) state. Although the hexavalent (including chromates) state is more stable than the divalent state, it is rarely found in nature. Chromium(VI) compounds are strong oxidizing agents and are highly corrosive. In the environment, they generally are reduced to chromium(III) compounds. The chromium(VI) compounds most commonly encountered in industry are calcium chromate, chromium trioxide, sodium chromate and dichromate, potassium chromate and dichromate, lead chromate, strontium chromate, and zinc chromate (IARC 1990, Costa 1997). However, this listing applies to all hexavalent chromium compounds, not just to those listed above.

Calcium chromate occurs as yellow crystals or a bright-yellow powder. It has a molecular weight of 156.1 and a density of  $2.89 \text{ g/cm}^3$ . It is slightly soluble in water and soluble in dilute acids, and it reacts with acids and ethanol. Although calcium chromate is not flammable, toxic chromium fumes may be formed in fires, and mixtures with boron burn violently when ignited (ATSDR 2000, HSDB 2003).

Chromium trioxide occurs as dark-red or brown crystals, flakes, or granular powder. It has a molecular weight of 100, a density of  $2.7 \text{ g/cm}^3$  at  $25^\circ\text{C}$ , and a melting point of  $197^\circ\text{C}$ . It is soluble in water, ethyl alcohol, ethyl ether, sulfuric acid, and nitric acid. Contact of chromium trioxide with organic chemicals may result in violent or explosive reactions, and fires with chromium trioxide may produce irritating, corrosive, and toxic gases (ATSDR 2000, HSDB 2003).

Sodium chromate occurs as yellow crystals, with a molecular weight of 162.0, a density of 2.71 to  $2.74 \text{ g/cm}^3$ , and a melting point of  $792^\circ\text{C}$ . It is soluble in water and slightly soluble in methanol. Although sodium chromate is not flammable, toxic chromium oxide fumes may be formed in fires with sodium chromate (ATSDR 2000, HSDB 2003).

Sodium dichromate occurs as bright orange-red or red hygroscopic crystals, with a molecular weight of 262 and a density of

2.52 g/cm<sup>3</sup> at 13°C. It melts at 356.7°C, decomposes at 400°C, and is soluble in water and methanol. Sodium dichromate reacts explosively with hydrazine, acetic anhydride, boron, silicon, and other materials (IARC 1980, HSDB 2003).

Potassium chromate occurs as yellow crystals, with a molecular weight of 194.2, a density of 2.73 g/cm<sup>3</sup> at 18°C, and a melting point of 968°C. It is soluble in water and insoluble in ethanol (ATSDR 2000, HSDB 2003).

Potassium dichromate occurs as red or orange-red crystals, with a molecular weight of 294.2 and a density of 2.68 g/cm<sup>3</sup> at 25°C. It melts at 398°C, decomposes at 500°C, and is soluble in water and insoluble in ethanol and acetone. Potassium dichromate poses a dangerous fire risk when in contact with organic materials or finely divided combustible materials, such as sawdust (ATSDR 2000, HSDB 2003).

Lead chromate occurs as yellow, orange, or red crystals or a yellow or orange-yellow powder. It has a molecular weight of 323.2, a density of 6.12 g/cm<sup>3</sup> at 15°C, and a melting point of 844°C. It is insoluble in water, acetic acid, and ammonia and soluble in dilute nitric acid. When heated, lead chromate emits highly toxic fumes, and it may react explosively with azo dyes (IARC 1980, HSDB 2003). The term "lead chromate" also is used to refer to a variety of commercial lead chromate pigments (IARC 1990).

Strontium chromate occurs as yellow monoclinic crystals or a yellow powder, with a molecular weight of 203.6 and a density of 3.9 g/cm<sup>3</sup> at 15°C. It is slightly soluble in water and soluble in dilute hydrochloric acid, nitric acid, and acetic acid. Strontium chromate is not flammable but reacts explosively with hydrazine (HSDB 2003).

Zinc chromate occurs as lemon-yellow crystals or powder, with a molecular weight of 181.4 and a density of 3.40 g/cm<sup>3</sup>. It is insoluble in cold water and acetone, sparingly soluble in hot water, and soluble in acid and liquid ammonia. Zinc chromate reacts explosively with hydrazine (HSDB 2003). The term "zinc chromate" also is used to refer to a variety of commercial zinc and zinc potassium chromates (IARC 1990).

## Use

Chromium(VI) compounds are widely used as corrosion inhibitors, in the manufacture of pigments, in metal finishing and chrome plating, in stainless-steel production, in leather tanning, and in wood preservatives (Costa 1997, ATSDR 2000). In 1996, about 52% of all chromium compounds used in the United States chemical industry were used in production of wood preservatives; the rest were used in leather tanning (13%), metals finishing (13%), pigments (12%), refractories (linings for high-temperature industrial furnaces) (3%), and other uses (7%) (ATSDR 2000). The use of chromium(VI) compounds in wood preservatives increased dramatically from the late 1970s to the early 2000s; however, this use is expected to decrease because of a voluntary phase-out of all residential uses of wood treated with chromated copper arsenate (CCA, or pressure-treated wood) that went into effect December 31, 2003 (Brooks 2002). Chromium(VI) compounds also are used in textile dyeing processes, printing inks, drilling muds, pyrotechnics, water treatment, and chemical synthesis (HSDB 2003). Uses of specific chromium(VI) compounds are summarized below.

Calcium chromate is used primarily as a corrosion inhibitor and as a depolarizer in batteries. Chromium trioxide is used primarily in chrome plating and other metal finishing (particularly in the production of automobiles and military aircraft), in production of wood preservatives, as a corrosion inhibitor, and in the production of organic chemicals and catalysts. Sodium chromate is used as a corrosion inhibitor and in textile dyeing processes, inks, paints, leather tanning, wood preservatives, drilling muds, cutting oils, water treatment, and production of other chromium compounds. Sodium dichromate is the primary base material for the production of chromium compounds and is used as a

corrosion inhibitor, in metal treatments, in drilling muds, and in the production of dyes, wood preservatives, synthetic organic chemicals, and catalysts. Potassium chromate is used in production of dyes and in textile dyeing processes. Potassium dichromate has largely been replaced by sodium dichromate in many applications; however, it is still used in photomechanical processes and production of pigments and wood preservatives. Lead chromate has been used in paints and printing inks and as a colorant in vinyl, rubber, and paper. Strontium chromate is used as a corrosion inhibitor and metal conditioner, in aluminum flake coatings, as a colorant in polyvinyl chloride, in pyrotechnics, in chrome plating, and for sulfate ion control in electrochemical processes. Zinc chromates are used as corrosion inhibitors and metal conditioners and in paints, varnishes, and oil colors (IARC 1973, 1990, HSDB 2003).

The steel industry is the major consumer of chromium. In 1996, estimated consumption of chromium ferroalloys and metals by end use was 74% in stainless and heat-resisting steel, 10% in full-alloy steel, 3% in superalloys, and 13% in other end uses (USGS 1997). Alloys of stainless steel and chromium typically contain between 11.5% and 30% chromium (ATSDR 2000).

## Production

The United States is one of the world's leading producers of chromium compounds. Chromium metal, sodium chromate, and sodium dichromate are produced in the United States from imported chromite ore, and most other chromium compounds are produced from sodium chromate and dichromate (ATSDR 2000). Although chromite ore has not been mined in the United States since 1961 (ATSDR 2000), the United States does have a small reserve base of chromium ore, containing an estimated 7 million metric tons (15.4 billion pounds) of chromium that could be exploited in the future. The only domestic source of chromium is recycling (Papp 2003). Between 1940 and 2001, annual imports of chromite ore ranged from about 207,000 to 640,000 metric tons (460 to 1,400 million pounds) (Goonan and Papp 2003). Production, import, and export data for specific chromium(VI) compounds are summarized below.

U.S. production of calcium chromate in 1977 was at least 5,450 kg (12,000 lb); no other production data and no import or export data were found. In the late 1970s and early 1980s, annual U.S. production of chromium trioxide was around 30 million kilograms (66 million pounds). Annual production capacity was 52 million kilograms (115 million pounds) in 1988; more recent data were not found. Annual imports of chromium trioxide ranged from 200,000 kg (440,000 lb) in 1977 to 16.5 million kilograms (36.4 million pounds) in 2002, and exports were 4.1 million kilograms (9 million pounds) in 1977, 11.6 million kilograms (25.6 million pounds) in 2000, and 8.4 million kilograms (18.5 million pounds) in 2002 (IARC 1990, ITA 2001, HSDB 2003, ITA 2003).

The United States produced 139,000 short tons (126 million kilograms) of sodium chromate and dichromate combined in 1998 and 140,700 short tons (128 million kilograms) in 1999 (HSDB 2003). Imports of these compounds ranged from 4.2 million kilograms (9.3 million pounds) in 1982 (chromate and dichromate) to 18.8 million kilograms (41.4 million pounds) in 2002 (dichromate only). Exports were 8.8 million kilograms (19.4 million pounds) in 1985 (chromate and dichromate), 26.3 million kilograms (58 million pounds) in 1999 (chromate and dichromate), and 12.6 million kilograms (27.8 million pounds) in 2002 (dichromate only) (HSDB 2003, ITA 2003).

U.S. production of potassium chromate and dichromate combined were estimated to be 2.6 to 3.8 million kilograms (5.7 to 8.4 million pounds) in 1966. Production of potassium dichromate declined throughout the 1970s from 3.2 million kilograms (7.1 million pounds) in 1972 to 1.0 million kilograms (2.2 million pounds) in 1978 (IARC 1990). No more recent production data for potassium

chromate or dichromate were found. In the mid 1980s, combined annual imports of potassium chromate and dichromate ranged from 580,000 kg (1.3 million lb) to 1.0 million kilograms (2.2 million pounds) (IARC 1990). In 2002, the United States imported 189,000 kg (416,000 lb) of potassium dichromate and exported 26,000 kg (57,000 lb) (ITA 2003).

The United States produced 30.6 million kilograms (67 million pounds) of lead chromate in 1972 (HSDB 2003). In 1976 and 1977, 20 million kilograms (44 million pounds) of lead chromate was used annually to produce chrome yellow and chrome orange pigments (IARC 1990). No production data were found for zinc chromate. U.S. imports of lead and zinc chromate combined were 289,000 kg (638,000 lb) in 2000 and 135,500 kg (300,000 lb) in 2002, and exports were 287,500 kg (634,000 lb) in 2000 and 125,000 kg (275,000 lb) in 2002 (ITA 2001, 2003).

The United States produced 680,000 kg (1.5 million pounds) of strontium chromate in 1970 (IARC 1990); no other production data were found. Imports of strontium chromate were 300,000 kg (660,000 lb) in 1978, 250,000 kg (550,000 lb) in 1982, 180,000 kg (400,000 lb) in 1984, 390,000 kg (860,000 lb) in 1985, and 120,000 kg (265,000 lb) in 1986 and 1987 (IARC 1990, HSDB 2003). No export data were found.

## Exposure

Chromium, in the form of unidentified chromium compounds, occurs naturally in the earth's crust and is widely distributed in air, water, soil, and food. Chromium(III) is an essential trace element in humans. The general population is exposed to some chromium(VI) compounds, but the levels of exposure vary. Environmental exposure specifically to chromium(VI) compounds is difficult to quantify, because specific forms of chromium seldom are identified in exposure studies. Although chromium(VI) compounds in the environment may be reduced to chromium(III) compounds, hexavalent forms can persist under some conditions. The general population may be exposed to chromium(VI) compounds through inhalation of ambient air, ingestion of water, or dermal contact with products that contain chromium(VI) compounds, such as pressure-treated wood. People who live near industrial facilities that use chromium(VI) compounds or near chromium waste disposal sites have the greatest potential for exposure (ATSDR 2000).

Most occupational exposure to chromium(VI) compounds is through inhalation or dermal contact. Occupational exposures to chromium generally exceed non-occupational exposures. However, concentrations of airborne chromium in workplaces have declined significantly since the 1980s because of improved emission controls. Typical concentration ranges for airborne chromium(VI) in industries that use chromium(VI) compounds are as follows: stainless-steel welding, 50 to 400  $\mu\text{g}/\text{m}^3$ ; chromate production, 100 to 500  $\mu\text{g}/\text{m}^3$ ; chrome plating, 5 to 25  $\mu\text{g}/\text{m}^3$ ; ferrochrome alloy production, 10 to 140  $\mu\text{g}/\text{m}^3$ ; and chromate pigment production, 60 to 600  $\mu\text{g}/\text{m}^3$  (IARC 1990, ATSDR 2000). In the tanning industry, hides are soaked with chromium(VI) compounds in the presence of other chemicals that reduce them to chromium(III) compounds (Costa 1997); therefore, exposure in the tanning industry is almost exclusively to soluble chromium(III) (ATSDR 2000). In a study assessing chromium exposure among stainless-steel welders and mild-steel welders, chromium levels in blood, plasma, and urine were higher among the stainless-steel welders, particularly those engaged in manual metal arc welding, which produces fumes with high concentrations of total water-soluble chromium, mainly chromium(VI) (which constituted up to 61% of total soluble chromium) (Edme *et al.* 1997).

The National Occupational Hazard Survey (1972–1974) estimated that 16,576 workers were exposed to chromium (types and compounds not specified), 42,043 to potassium dichromate, and 3,519 to calcium chromate (NIOSH 1976). The National Occupational Exposure

Survey (1981–1983) estimated that 386,142 workers (including 10,433 women) potentially were exposed to chromium, 61,073 (including 19,198 women) to potassium dichromate, 32,129 (including 5,565 women) to calcium chromate, and 30,784 (including 8,856 women) to lead chromate (NIOSH 1984).

A 1990 study reported the average concentration of chromium(VI) to be 0.0012  $\mu\text{g}/\text{m}^3$  (ranging from less than 0.001 to 3  $\mu\text{g}/\text{m}^3$ ) in indoor air samples collected from residences in Hudson County, New Jersey (ATSDR 2000). Other reports of exposure to chromium were not specific for chromium(VI) compounds, but provide general information on exposure to chromium and chromium compounds. Between 1977 and 1984, typical total chromium concentrations in ambient air in the United States were less than 0.01  $\mu\text{g}/\text{m}^3$  in rural areas and 0.01 to 0.03  $\mu\text{g}/\text{m}^3$  in urban areas. Average atmospheric concentrations of chromium from more than 2,100 monitoring stations ranged from 0.005 to 0.525  $\mu\text{g}/\text{m}^3$ . A survey of more than 3,800 tap water samples in 1974 and 1975 found chromium concentrations ranging from 0.4 to 8.0  $\mu\text{g}/\text{L}$ , with a mean value of 1.8  $\mu\text{g}/\text{L}$ . In surveys of U.S. surface waters, chromium concentrations in rivers ranged from less than 1 to 30  $\mu\text{g}/\text{L}$ , and concentrations in lakes typically were less than 5  $\mu\text{g}/\text{L}$ . Typical chromium levels in most fresh foods are low; chromium was detected in vegetables, fruits, grains, cereals, eggs, meat, and fish at concentrations between 20 and 520  $\mu\text{g}/\text{kg}$ . The mean daily dietary intake of chromium was estimated to be less than 0.2 to 0.4  $\mu\text{g}$  from air, 2.0  $\mu\text{g}$  from water, and 60  $\mu\text{g}$  from food (ATSDR 2000).

EPA's Toxics Release Inventory listed 2,006 industrial facilities that released a total of 14 million pounds (6,400 metric tons) of chromium into the environment in 2001 and 1,762 facilities that released 116 million pounds (52,600 metric tons) of chromium compounds. About 90% of the total amounts released were reported by the top 100 facilities. Environmental releases of chromium compounds in 2001 were the lowest since reporting began in 1988 and were about half the average annual amount released from 1988 to 2000 (TRI01 2003).

## Regulations

### EPA

#### Clean Air Act

Mobile Source Air Toxics: Chromium Compounds listed as Mobile Source Air Toxics for which regulations are to be developed

NESHAP: Chromium Compounds listed as Hazardous Air Pollutants (HAPs)

Urban Air Toxics Strategy: Chromium Compounds identified as one of 33 HAPs that present the greatest threat to public health in urban areas

#### Clean Water Act

Biosolids Rule: Ceiling concentration of total chromium for land application = 3,000 mg/kg

Effluent Guidelines: Listed as a Toxic Pollutant (chromium and compounds)

#### Comprehensive Environmental Response, Compensation, and Liability Act

Reportable Quantity (RQ) = 5,000 lb (chromium); 10 lb (chromic acid, sodium chromate, ammonium chromate, potassium chromate, strontium chromate, calcium chromate, lithium chromate, potassium bichromate, ammonium bichromate, sodium bichromate)

#### Emergency Planning and Community Right-To-Know Act

Toxics Release Inventory: Chromium and chromium compounds are listed substances subject to reporting requirements

#### Federal Insecticide, Fungicide, and Rodenticide Act

Almost all registrations for chromated copper arsenate products for residential uses have been voluntarily cancelled

#### Resource Conservation and Recovery Act

Characteristic Toxic Hazardous Waste: TCLP Threshold = 5.0 mg/L (chromium)

Listed Hazardous Waste: Waste codes in which listing is based wholly or partly on substance - F006, F019, K002, K003, K004, K005, K006, K007, K008, K048, K049, K050, K051, K061, K062, K069, K086, K100 (all listed based on hexavalent chromium); U032 (based on calcium chromate)

Listed as a Hazardous Constituent of Waste (chromium, calcium chromate, chromium compounds)

#### Safe Drinking Water Act

Maximum Contaminant Level (MCL) = 0.1 mg/L (total chromium)

### FDA

Maximum permissible level of chromium in bottled water = 0.1 mg/L

Specified color additives may contain chromium (as chromates) under certain restrictions

Specified color additives may contain chromium at levels no greater than 50 ppm

Chromium may be used in hydrolyzed leather meal used in feed for animals provided it contains chromium at levels not to exceed 2.75% of the total by weight

#### OSHA

Permissible Exposure Limit (PEL) = 0.1 mg/m<sup>3</sup> (based on chromic acid & chromates listing)

### Guidelines

#### ACGIH

Threshold Limit Value - Time-Weighted Average Limit (TLV-TWA) = 0.05 mg/m<sup>3</sup> (water soluble Chromium(VI) compounds); 0.01 mg/m<sup>3</sup> (insoluble Chromium(VI) compounds)

#### NIOSH

Immediately Dangerous to Life and Health (IDLH) = 15 mg/m<sup>3</sup> (as Chromium(VI)) (For chromic acid & chromates listing)

Recommended Exposure Limit (time-weighted-average workday) = 0.001 mg/m<sup>3</sup> (for chromic acid & chromates and chromyl chloride listings)

Listed as a potential occupational carcinogen (based on chromic acid & chromates and chromyl chloride listings)

**\*No separate CAS registry number is assigned to chromium hexavalent compounds.**

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