

Chromium Hexavalent Compounds

CAS No. 18540-29-9

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 from studies in humans.

Cancer Studies 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 hexavalent (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 also 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 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 1973, 1979, 1990).

Cancer Studies in Experimental Animals

Exposure to chromium(VI) compounds (calcium chromate, chromium trioxide, or sodium dichromate) via inhalation or intratracheal or intrabronchial implantation caused benign and/or malignant lung tumors in rats and/or mice. Intrabronchial implantation of zinc chromate or strontium chromate also caused bronchial tumors in rats, and inhalation exposure to chromium trioxide caused benign nasal tumors in mice. In addition, cancer at the injection site was observed in rats following administration of chromium compounds (calcium chromate, lead chromate, basic lead chromate, zinc chromate, or strontium chromate) by intrapleural, subcutaneous, or intramuscular injection and in mice following intramuscular injection of calcium chromate (IARC 1980, 1990). IARC (1990) concluded that there was sufficient evidence in experimental animals for the carcinogenicity of calcium chromate, lead chromates, strontium chromate, and zinc chromates and limited evidence for the carcinogenicity of chromium trioxide and sodium dichromate.

Since chromium hexavalent compounds were reviewed for listing in the *First Annual Report on Carcinogens* and reviewed by IARC in 1990, the National Toxicology Program has conducted two-year cancer studies of sodium dichromate in rats and mice. Sodium dichromate administered in the drinking water caused cancer of the

oral cavity (squamous-cell carcinoma of the oral mucosa) in rats and increased the combined incidence of benign and malignant tumors (adenoma and carcinoma) of the small intestine (duodenum, jejunum, or ileum) in mice (NTP 2008).

Studies on Mechanisms of Carcinogenesis

Chromosomal aberrations, sister chromatid exchange, and aneuploidy 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 (IARC 1990).

IARC (1990) concluded that there was sufficient evidence in humans for the carcinogenicity of chromium(VI) compounds based on the combined results of epidemiological studies, cancer studies in experimental animals, and evidence that chromium(VI) ions generated at critical sites in the target cells were 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 (+2, II), trivalent (+3, III), and hexavalent (+6, VI) 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 state (including chromates) 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 specified above.

Calcium chromate occurs as yellow crystals or a bright-yellow powder. 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. Chromium trioxide (also known as chromic trioxide) occurs as dark-red or brown crystals, flakes, or granular powder and 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 2009). Lead chromate occurs as yellow, orange, or red crystals or a yellow or orange-yellow powder that is insoluble in water, acetic acid, and ammonia but soluble in dilute nitric acid. When heated, it emits highly toxic fumes, and it may react explosively with azo dyes. The term "lead chromate" is also used to refer to various commercial lead chromate pigments (IARC

1980, 1990, HSDB 2009). Potassium chromate occurs as yellow crystals and is soluble in water but insoluble in ethanol. Potassium dichromate occurs as red or orange-red crystals and is soluble in water but insoluble in ethanol and acetone. It poses a dangerous fire risk when in contact with organic materials or finely divided combustible materials, such as sawdust (ATSDR 2000, HSDB 2009).

Sodium chromate occurs as yellow crystals and is soluble in water and slightly soluble in methanol. Although it is not flammable, toxic chromium oxide fumes may be formed in fires with sodium chromate (ATSDR 2000, HSDB 2009). Sodium dichromate occurs as bright orange-red or red hygroscopic crystals and is soluble in water and methanol. It reacts explosively with hydrazine, acetic anhydride, boron, silicon, and other materials (IARC 1980, HSDB 2009). Strontium chromate occurs as yellow monoclinic crystals or a yellow powder. It is slightly soluble in water and soluble in dilute hydrochloric acid, nitric acid, and acetic acid. It is not flammable but reacts explosively with hydrazine (HSDB 2009). Zinc chromate occurs as lemon-yellow crystals or powder. 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. The term “zinc chromate” is also used to refer to various commercial zinc and zinc potassium chromates (IARC 1990, HSDB 2009). Physical and chemical properties of these chromium(VI) compounds are listed in the table below, along with their chemical formulas.

Use

The steel industry is the major consumer of chromium. In 2007, estimated consumption of chromium in the United States by end use was 78% in stainless and heat-resisting steel, 13.8% for other steel uses, 3.7% in superalloys, and 4.5% in other alloys and end uses (Papp 2009). Alloys of stainless steel and chromium typically contain between 11.5% and 30% chromium (ATSDR 2000). 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 U.S. 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 (pressure-treated wood) that went into effect December 31, 2003 (Brooks 2009). Chromium(VI) compounds are also used in textile-dyeing processes, printing inks, drilling muds, pyrotechnics, water treatment, and chemical synthesis (HSDB 2009).

Calcium chromate is used primarily as a corrosion inhibitor and as a depolarizer in batteries (IARC 1973, 1990, HSDB 2009). Chro-

mium 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 production of organic chemicals and catalysts. Lead chromate has been used in paints and printing inks and as a colorant in vinyl, rubber, and paper. 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. 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. 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.

Production

The United States is one of the world's leading producers of chromium compounds. U.S. primary production levels of chromium (i.e., mine production of chromite ore) have not been reported since 1961 (Papp 2007). One surface mine was developed in the United States in the mid to late 2000s (Papp 2009, USGS 2010), but production levels from that mine were not reported. Other domestic sources of chromium include recycled stainless-steel scrap, industry stocks, and the Defense National Stockpile. Overall U.S. production of chromium metal decreased between 2000 and 2008 (Papp 2009, USGS 2010), but production in 2015 (shown in the table on the next page) was similar to that in 2000. Apparent chromium consumption in 2017 (about 1.2 billion pounds) also was similar to that in 2000. In contrast, U.S. imports and exports of chromium metal were lower in 2017 than in 2000 (when they each totaled about 1 billion pounds) (USGS 2005, 2019).

The table also shows the production, import, and export data available for specific hexavalent chromium compounds. The United States has produced or imported several chromium compounds in quantities of at least 1 million pounds for decades, and some compounds have also been exported in large quantities. Production of sodium chromate and dichromate combined was about 280 million pounds in the late 1990s (HSDB 2009), similar to the figure reported in 2015 for production plus imports of sodium dichromate. In contrast, chromium trioxide production increased from around 66 million pounds in the late 1970s through the 1980s (IARC 1990, HSDB 2009) to over 100 million pounds in 2015. U.S. production of potassium chromate

Compound	Formula	Molec. wt.	Density (g/cm ³) ^a	Melting pt.	Dec.
Calcium chromate	CaCrO ₄	156.1	2.89	NR	NR
Chromium trioxide	CrO ₃	100.0	2.70	197°C	yes
Lead chromate	PbCrO ₄	323.2	6.12	844°C	yes
Potassium chromate	K ₂ CrO ₄	194.2	2.73	975°C	NR
Potassium dichromate	K ₂ Cr ₂ O ₇	294.2	2.68	398°C	~500°C
Sodium chromate	Na ₂ CrO ₄	162.0	2.72	792°C	NR
Sodium dichromate	Na ₂ Cr ₂ O ₇	262.0	2.52	357°C	400°C
Strontium chromate	SrCrO ₄	203.6	3.90	NR	NR
Zinc chromate	ZnCrO ₄	181.4	3.40	NR	NR

Source: HSDB 2009. ^aSource specifies the temperature at which density was determined for some but not all of the compounds. Dec. = decomposes; NR = not reported.

Chromium category	Quantity (lb)		
	Production (2015)	Imports (2017)	Exports (2017)
Metal (excluding alloys)	1 billion to 5 billion	32.0 million ^a	1.4 million ^a
Hexavalent compounds			
Chromium trioxide	100 million to 250 million	8.0 million	–
Potassium dichromate	–	66,313	4.7 million
Sodium dichromate	100 million to 250 million	200,984	–
Strontium chromate	1 million to 10 million	–	–

Sources: EPA 2016 (production volume = production + imports), USITC 2018 (imports and exports).

– = no data found.

^aThe reported value is for the sum of the following chromium metal categories: unwrought chromium (powders), chromium waste and scrap, and chromium and articles thereof, not elsewhere specified or included.

and dichromate combined or separately and of strontium chromate was generally less than 10 million pounds in the 1960s to 1970s (IARC 1990, HSBB 2009) and remained below 10 million pounds in 2015.

Chromium compounds that have been imported in quantities of at least 1 million pounds since the 1970s include sodium chromate and dichromate (over 40 million pounds in 2002 and 2008), chromium trioxide (over 35 million pounds in 2002), and potassium chromate and dichromate (about 1 to 2 million pounds in the mid 1980s) (IARC 1990, HSDB 2009), but only chromium trioxide imports exceeded 1 million pounds in 2017.

U.S. exports of sodium chromate and dichromate exceeded 50 million pounds in 1999, but no export data specific for either of these compounds were reported in 2017 (HSDB 2009, USITC 2018). U.S. exports of chromium trioxide were less than 10 million pounds in 1977, but approached 40 million pounds by 2008 (HSDB 2009, USITC 2009); however, no export data specific for chromium trioxide were reported in 2017. U.S. exports of potassium dichromate were only 170,000 lb in 2008 (USITC 2009), but approached 5 million pounds in 2017 (as shown in the table above).

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).

A 1990 study reported the average concentration of chromium(VI) to be 0.0012 $\mu\text{g}/\text{m}^3$ (range = < 0.001 to 3 $\mu\text{g}/\text{m}^3$) in indoor air samples collected from residences in Hudson County, New Jersey. 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 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 of 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 μg from air, 2.0 μg from water, and 60 μg from food (ATSDR 2000).

Evidence that people in the United States are exposed to some form of chromium is provided by the National Health and Nutrition Examination Survey for 2015–2016, which found that the 95th-percentile concentration of chromium in whole blood for the U.S. general population was 1.08 $\mu\text{g}/\text{L}$, based on samples from 3,442 individuals of all ages, both genders, and all race and ethnicity groups (CDC 2018).

According to the U.S. Environmental Protection Agency's Toxics Release Inventory, environmental releases of chromium compounds since reporting began in 1988 were lowest in 2001 (about half the average from 1988 to 2000). In 2007, 1,384 facilities released 12 million pounds of chromium, and 1,147 facilities released 51 million pounds of chromium compounds. The 100 facilities with the largest releases accounted for most of the total amounts released (TRI 2008).

Most occupational exposure to chromium(VI) compounds is through inhalation or dermal contact. Exposure to specific chromium compounds varies by industry. Chromate production workers are exposed to a variety of chromium compounds, including chromium(VI) and chromium(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.

Occupational exposure to chromium generally exceeds non-occupational exposure. 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 (conducted from 1972 to 1974) estimated that 16,576 workers potentially 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 (conducted 1981 to 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 cal-

cium chromate; and 30,784, including 8,856 women, to lead chromate (NIOSH 1990).

Regulations

Department of Transportation (DOT)

Chromium hexavalent compounds are considered hazardous materials, and special requirements have been set for marking, labeling, and transporting these materials.

Environmental Protection Agency (EPA)

Clean Air Act

Mobile Source Air Toxics: Chromium compounds are listed as mobile source air toxics for which regulations are to be developed.

National Emission Standards for Hazardous Air Pollutants: Chromium compounds are listed as hazardous air pollutants.

Urban Air Toxics Strategy: Chromium compounds have been identified as one of 33 hazardous air pollutants that present the greatest threat to public health in urban areas.

Clean Water Act

Numerous hexavalent chromium compounds are designated as hazardous substances.

Effluent Guidelines: Chromium and chromium compounds are listed as toxic pollutants.

Comprehensive Environmental Response, Compensation, and Liability Act

Reportable quantity (RQ) = 5,000 lb for chromium; = 10 lb for chromic acid, sodium chromate, ammonium chromate, potassium chromate, strontium chromate, calcium chromate, lithium chromate, potassium bichromate, ammonium bichromate, sodium bichromate; = 1,000 lb for chromic acetate, chromic sulfate.

Emergency Planning and Community Right-To-Know Act

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

Federal Insecticide, Fungicide, and Rodenticide Act

Wood intended to be used in residential settings cannot be treated with chromated copper arsenate.

Resource Conservation and Recovery Act

Characteristic Hazardous Waste: Toxicity characteristic leaching procedure (TCLP) threshold = 5.0 mg/L for chromium.

Listed Hazardous Waste: Waste codes for which the listing is based wholly or partly on the presence of chromium hexavalent compounds = F006, F019, K002, K003, K004, K005, K006, K007, K008, K048, K049, K050, K051, K061, K062, K069, K086, K100; on the presence of chromium = F032, F034, F035, F037, F038.

Chromium compounds are listed as hazardous constituents of waste.

Safe Drinking Water Act

Maximum contaminant level (MCL) = 0.1 mg/L for total chromium.

Food and Drug Administration (FDA, an HHS agency)

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.

Hydrolyzed leather meal used in the feed of animals may contain chromium at levels not to exceed 2.75% of the total by weight; finished feeds may not contain more than 1% hydrolyzed leather meal by weight.

Occupational Safety and Health Administration (OSHA, Dept. of Labor)

While this section accurately identifies OSHA's legally enforceable PELs for this substance in 2018, specific PELs may not reflect the more current studies and may not adequately protect workers.

Permissible exposure limit (PEL) = 0.005 mg/m³ for hexavalent chromium and compounds;

= 0.1 mg/m³ where the limit of 0.005 mg/m³ has been stayed or otherwise is not in effect.

Comprehensive standards have been developed for occupational exposure to hexavalent chromium in any form and in any compound.

Guidelines

American Conference of Governmental Industrial Hygienists (ACGIH)

Threshold limit value – time-weighted average (TLV-TWA) = 0.0002 mg/m³ for water-soluble chromium(VI) compounds; = 0.01 mg/m³ for insoluble chromium(VI) compounds.

Threshold limit value – short-term exposure limit (TLV-STEL) = 0.0005 mg/m³ for water-soluble chromium(VI) compounds.

Biological exposure index (BEI) (end of shift at end of workweek) = 25 µg/L for total chromium in urine; (increase during shift) = 10 µg/L for total chromium in urine.

National Institute for Occupational Safety and Health (NIOSH, CDC, HHS)

Immediately dangerous to life and health (IDLH) limit = 15 mg/m³ as hexavalent chromium for chromic acid and chromates.

Recommended exposure limit (REL) (time-weighted-average workday) (8-h TWA) = 0.0002 mg/m³ (as hexavalent chromium).

NIOSH considers all hexavalent chromium compounds to be potential occupational carcinogens (based on listings for chromic acid and chromates and for chromyl chloride).

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