CHROMIUM COMPOUNDS

1. Introduction

The first chromium compound was discovered in the Ural mountains of Russia, during the latter half of the eighteenth century. Crocoite [14654-05-8], a natural lead chromate, found immediate and popular use as a pigment because of its beautiful, permanent orange-red color. However, this mineral was very rare, and just before the end of the same century, chromite was identified as a chrome bearing mineral and became the primary source of chromium [7440-47-3] and its compounds (1) (see CHROMIUM AND CHROMIUM ALLOYS).

Around 1800, the attack of chromite [53293-42-8] ore by lime and alkali carbonate oxidation was developed as an economic process for the production of chromate compounds, which were primarily used for the manufacture of pigments (qv). Other commercially developed uses were: the development of mordant dyeing using chromates in 1820, chrome tanning in 1828 (2), and chromium plating in 1926 (3) (see DYES AND DYE INTERMEDIATES; ELECTROPLATING; LEATHER). In 1824, the first chromyl compounds were synthesized followed by the discovery of chromous compounds 20 years later. Organochromium compounds were produced in 1919, and chromium carbonyl was made in 1927 (1,2).

Kazakhstan and the Republic of South Africa account for more than half the world's chromite ore production. Almost all of the world's known reserves of chromium are located in the southeastern region of the continent of Africa. South Africa has 84% and Zimbabwe 11% of these reserves. The United States is completely dependent on imports for all of its chromium (4). The chromite's constitution varies with the source of the ore, and this variance can be important to processing. Typical ores are from 20 to 26 wt% Cr, from 10 to 25 wt% Fe, from 5 to 15 wt% Mg, from 2 to 10 wt% Al, and between 0.5 and 5 wt% Si. Other elements that may be present are Mn, Ca, Ti, Ni, and V. All of these elements are normally reported as oxides; iron is present as both Fe(II) and Fe(III) (5,6).

2. Properties

Chromium compounds number in the thousands and display a wide variety of colors and forms. Examples of these compounds and the corresponding physical properties are given in Table 1. More detailed and complete information on solubilities, including some solution freezing and boiling points, can be found in References 7–10, and 13. Data on the thermodynamic values for chromium compounds are found in References 7,8,10, and 13.

Chromium is able to use all of its 3*d* and 4*s* electrons to form chemical bonds. It can also display formal oxidation states ranging from Cr(−II) to Cr(VI). The most common and thus most important oxidation states are Cr(II), Cr(III), and Cr(VI). Although most commercial applications have centered around Cr(VI) compounds, environmental concerns and regulations in the early 1990s suggest that Cr(III) may become increasingly important, especially where the use of Cr(VI) demands reduction and incorporation as Cr(III) in the product.

Preparation and chemistry of chromium compounds can be found in several standard reference books and advanced texts (7,11,12,14). Standard reduction potentials for select chromium species are given in Table 2 whereas Table 3 is a summary of hydrolysis, complex formation, or other equilibrium constants for oxidation states II, III, and VI.

2.1. Low Oxidation State Chromium Compounds.

Cr(0) compounds are π-bonded complexes that require electron-rich donor species such as CO and C_6H_6 to stabilize the low oxidation state. A direct synthesis of $Cr(CO)_6$, from the metal and CO, is not possible. Normally, the preparation requires an anhydrous Cr(III) salt, a reducing agent, an arene compound, carbon monoxide that may or may not be under high pressure, and an inert atmosphere (see CARBONYLS).

$$CrCl_3 + 6\,CO \xrightarrow[4^\circ C,\ 101\ kPa,\ H_2O]{C_6H_5MgBr,\ (C_2H_5)_2O} Cr(CO)_6 + 3\,HCl \tag{1}$$

In equation 1, the Grignard reagent, C_6H_5MgBr, plays a dual role as reducing agent and the source of the arene compound (see GRIGNARD REACTION). The $Cr(CO)_6$ is recovered from an apparent phenyl chromium intermediate by the addition of water (19,20). Other routes to chromium hexacarbonyl are possible, and an excellent summary of chromium carbonyl and derivatives can be found in

Table 1. **Physical Properties of Chromium Compounds**[a]

Compound	CAS Registry number	Formula	Appearance
chromium(0) hexacarbonyl	[13007-092-6]	$Cr(CO)_6$	colorless crystals
dibenzene chromium(0)	[1271-54-1]	$(C_6H_6)_2Cr$	brown crystals
bis(biphenyl) chromium(I) iodide	[12099-17-1]	$(C_{12}H_{10})_2CrI$	orange plates
chromium(II) acetate dihydrate	[628-52-4]	$Cr_2(C_2H_3O_2)_4 \cdot 2H_2O$	red crystals
chromium(II) chloride	[10049-05-5]	$CrCl_2$	white crystals
ammonium chromium(II) sulfate hexahydrate	[25638-51-1]	$(NH_4)_2Cr(SO_4)_2 \cdot 6H_2O$	blue crystals
chromium(III) chloride	[10025-73-7]	$CrCl_3$	bright purple plates
chromium(III) acetylacetonate	[13681-82-8]	$Cr(C_5H_7O_2)_3$	red-violet crystals
potassium chromium(III) sulfate dodecahydrate	[7788-99-0]	$KCr(SO_4)_2 \cdot 12H_2O$	deep purple crystals
chromium(III) chloride hexahydrate	[10060-12-5]	$[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$	bright green crystals
		$[Cr(H_2O)_6]Cl_3$	violet crystals
chromium(III) oxide	[1308-38-9]	Cr_2O_3	green powder or crystals
chromium(IV) oxide	[12018-01-8]	CrO_2	dark brown or black powder
chromium(IV) fluoride	[10049-11-3]	CrF_4	very dark greenish black powder
barium chromate(V)	[12345-14-1]	$Ba_3(CrO_4)_2$	black-green crystals
chromium(VI) oxide	[1333-82-0]	CrO_3	dark red crystals
chromium(VI) dioxide dichloride	[14977-61-8]	CrO_2Cl_2	cherry-red liquid
ammonium dichromate(VI)	[7789-09-5]	$(NH_4)_2Cr_2O_7$	red-orange crystals
potassium dichromate(VI)	[7778-50-9]	$K_2Cr_2O_7$	orange-red crystals
sodium dichromate(VI) dihydrate	[7789-12-0]	$Na_2Cr_2O_7 \cdot 2H_2O$	orange-red crystals
potassium chromate(VI)	[7789-00-6]	K_2CrO_4	yellow crystals
sodium chromate(VI)	[7775-11-3]	Na_2CrO_4	yellow crystals
potassium chlorochromate(VI)	[16037-50-6]	$KCrO_3Cl$	orange needles
silver chromate(VI)	[7784-01-2]	Ag_2CrO_4	maroon crystals
barium chromate(VI)	[10295-40-3]	$BaCrO_4$	pale yellow crystals
strontium chromate(VI)	[7789-06-2]	$SrCrO_4$	yellow crystals
lead chromate(VI)	[7758-97-6]	$PbCrO_4$	yellow crystals
			orange crystals
			red crystals

[a] Refs. 7–12.

reference 2. The only access to the less stable Cr(−II) and Cr(−I) oxidation states is by reduction of $Cr(CO)_6$.

The preparation of disodium pentacarbonylchromide [51233-19-3], $Na_2[Cr(CO)_5]$, is performed in solvents such as liquid ammonia, diglyme, or tetrahydrofuran. The Cr(O) in the $Cr(CO)_6$ solution is reduced to Cr(−II) by the addition of Na, sodium amalgam, Li, Ca, or Ba. If $NaBH_4$ is used as the reducing agent, then the Cr(−I) compound disodium decacarbonyldichromide [15616-67-8],

Crystal system	Density[b] g/cm^3	Mp, °C	Bp, °C	Solubility
orthorhombic	1.77_{18}	148.5	210^c	sl sol CCl_4; insol H_2O, $(C_2H_5)_2O$, C_2H_5OH, C_6H_6
cubic	1.519	284–285	sub 150^d	insol H_2O; sol C_6H_6
	1.617_{16}	178	dec	sol C_2H_5OH, C_5H_5N
monoclinic	1.79			sl sol H_2O, C_2H_5OH; sol acids
tetragonal	2.88	815	1300	sol H_2O to blue soln, absorbs O_2
monoclinic				sol H_2O to blue soln, absorbs O_2
hexagonal	2.76_{15}	877	sub 947	insol H_2O; sol H_2O+Cr(II), Zn or Mg
monoclinic	1.34	216	340	insol H_2O; sol C_6H_6
cubic	1.826_{25}	89^e	400^f	sol H_2O
triclinic or monoclinic	1.835_{25}	95		sol H_2O, green soln turning green-violet
rhombohedral		90		sol H_2O, violet soln turning green-violet
rhombohedral	5.22_{25}	2330	3000	insol H_2O; sol hot 70% $HClO_4$ dec
tetragonal	4.98^g	dec	dec 300 to Cr_2O_3	sol acids with dec to Cr(III) and Cr(VI)
amorphous	2.89	ca 277	ca 400	sol H_2O, dec; insol organic solvents
same as $Ca_3(PO_4)_2$				sl dec H_2O; sol acids with dec to Cr(III) and Cr(VI)
orthorhombic	2.7_{25}	197	dec	v sol H_2O; sol CH_3COOH, $(CH_3CO)_2O$
	1.9145_{25}	–96.5	115.8	insol H_2O, hydrolyzes; sol CS_2, CCl_4
monoclinic	2.155_{25}	dec 180		sol H_2O
triclinic	2.676_{25}	398	dec 500	sol H_2O
monoclinic	2.348_{25}	356; 84.6^f	dec 400	v sol H_2O
orthorhombic	2.732_{18}	975		sol H_2O
orthorhombic	2.723_{25}	792		sol H_2O
monoclinic	2.497_{39}	dec		sol H_2O, hydrolyzes
monoclinic	5.625_{25}			v sl sol H_2O; sol dilute acids
orthorhombic	4.498_{25}	dec		v sl sol H_2O; sol strong acids
monoclinic	3.895_{15}	dec		sl sol H_2O; sol dilute acids
orthorhombic				
tetragonal				
monoclinic	6.12_{15}	844		insol H_2O; sol strong acids

[b] Measurement taken at temperature in °C noted in subscript.

[c] Explodes.

[d] In vacuum.

[e] Incongruent.

[f] Loses all water at temperature indicated.

[g] Calculated value.

$Na_2[Cr_2(CO)_{10}]$, is produced (21,22). The coordination number for chromium in the carbonyls and most of the derivatives is six, with octahedral geometry around the metal. However, the geometry of Cr in some organochromium(0) compounds, eg, $(C_6H_6)_2Cr$, is very different. In dibenzene chromium(0), the Cr atom is sandwiched between the two centers of high electron density provided by the benzene molecules. The π-orbitals of C_6H_6 donate electrons as the π^* orbitals

Table 2. **Standard Reduction Potentials for Chromium Species**[a]

Half-cell reaction	E°, V
$\mathrm{Cr^{3+}} + 3\,e^- \longrightarrow \mathrm{Cr}$	-0.74
$\mathrm{Cr(OH)^{2+}} + \mathrm{H^+} + 3\,e^- \longrightarrow \mathrm{Cr} + \mathrm{H_2O}$	-0.58[b]
$\mathrm{Cr^{2+}} + 2\,e^- \longrightarrow \mathrm{Cr}$	-0.91
$\mathrm{Cr^{3+}} + e^- \longrightarrow \mathrm{Cr^{2+}}$	-0.41
$\mathrm{Cr_2O_7^{2-}} + 14\,\mathrm{H^+} + 6\,e^- \longrightarrow 2\,\mathrm{Cr^{3+}} + 7\,\mathrm{H_2O}$	1.33
$\mathrm{Cr_2O_7^{2-}} + 10\,\mathrm{H^+} + 6\,e^- \longrightarrow 2\,\mathrm{Cr(OH)_2^+} + 3\,\mathrm{H_2O}$	1.10[b]
$\mathrm{CrO_4^{2-}} + 4\,\mathrm{H_2O} + 3\,e^- \longrightarrow \mathrm{Cr(OH)_3} + 5\,\mathrm{OH^-}$	-0.13
$\mathrm{CrO_4^{2-}} + e^- \longrightarrow \mathrm{CrO_4^{3-}}$	0.1[c]
$\mathrm{Cr^{6+}} + e^- \longrightarrow \mathrm{Cr^{5+}}$	0.6[c,d]
$\mathrm{Cr^{5+}} + e^- \longrightarrow \mathrm{Cr^{4+}}$	1.3[c,d]
$\mathrm{Cr^{4+}} + e^- \longrightarrow \mathrm{Cr^{3+}}$	2.0[c,d]

[a] Ref. 12.

[b] Calculated from free energy data, Ref. 13.

[c] Ref. 13.

[d] In acid solutions.

simultaneously accept electrons. This back donation of electron density lowers the formal oxidation state of the metal.

The normal preparation of organochromium(0) compounds is indirect. First the organochromium(I) compound is formed

$$3\,\mathrm{CrCl_3} + \mathrm{AlCl_3} + 6\,\mathrm{C_6H_6} + 2\,\mathrm{Al} \xrightarrow[\mathrm{C_6H_6}]{\mathrm{AlCl_3}} 3\,[(\mathrm{C_6H_6})_2\mathrm{Cr}]^+ + 3\,\mathrm{AlCl_4^-} \tag{2}$$

Table 3. **Hydrolysis, Equilibrium, and Complex Formation Constants**

Reaction	$\log K$	Ref.
$\mathrm{Cr^{2+}} + \mathrm{H_2O} \rightleftharpoons \mathrm{Cr(OH)^+} + \mathrm{H^+}$	5.3	15
$\mathrm{Cr^{3+}} + \mathrm{H_2O} \rightleftharpoons \mathrm{Cr(OH)^{2+}} + \mathrm{H^+}$	-4.2	16
$\mathrm{Cr^{3+}} + 2\,\mathrm{H_2O} \rightleftharpoons \mathrm{Cr(OH)_2^+} + 2\,\mathrm{H^+}$	-10.4	16
$\mathrm{Cr^{3+}} + 3\,\mathrm{H_2O} \rightleftharpoons \mathrm{Cr(OH)_3} + 3\,\mathrm{H^+}$	-18.7	16
$\mathrm{Cr^{3+}} + 4\,\mathrm{H_2O} \rightleftharpoons \mathrm{Cr(OH)_4^-} + 4\,\mathrm{H^+}$	-27.8	16
$2\,\mathrm{Cr^{3+}} + 2\,\mathrm{H_2O} \rightleftharpoons [\mathrm{Cr_2(OH)_2}]^{4+} + 2\,\mathrm{H^+}$	-5.3	16
$3\,\mathrm{Cr^{3+}} + 4\,\mathrm{H_2O} \rightleftharpoons [\mathrm{Cr_3(OH)_4}]^{5+} + 4\,\mathrm{H^+}$	-8.7	17
$4\,\mathrm{Cr^{3+}} + 6\,\mathrm{H_2O} \rightleftharpoons [\mathrm{Cr_4(OH)_6}]^{6+} + 6\,\mathrm{H^+}$	-13.9	17
$\mathrm{Cr^{3+}} + 3\,\mathrm{C_2O_4^{2-}} \rightleftharpoons [\mathrm{Cr(C_2O_4)_3}]^{3-}$	15.4	16
$\mathrm{Cr^{3+}} + \mathrm{H_2EDTA^{2-}} \rightleftharpoons [\mathrm{CrEDTA}]^- + 2\,\mathrm{H^+}$	23.4[a]	16
$\mathrm{Cr^{3+}} + \mathrm{SO_4^{2-}} \rightleftharpoons \mathrm{CrSO_4^+}$	1.8	18
$\mathrm{H_2CrO_4} \rightleftharpoons \mathrm{HCrO_4^-} + \mathrm{H^+}$	0.61	12
$\mathrm{HCrO_4^-} \rightleftharpoons \mathrm{CrO_4^{2-}} + \mathrm{H^+}$	-5.9	12
$2\,\mathrm{HCrO_4^-} \rightleftharpoons \mathrm{Cr_2O_7^{2-}} + \mathrm{H_2O}$	2.2	12
$\mathrm{H_2CrO_4} + \mathrm{Cl^-} \rightleftharpoons \mathrm{CrO_3Cl^-} + \mathrm{H_2O}$	1.0	13
$\mathrm{HCrO_4^-} + \mathrm{HSO_4^-} \rightleftharpoons \mathrm{CrSO_7^{2-}} + \mathrm{H_2O}$	0.60	13

[a] $\mathrm{H_2EDTA^{2-}}$ is $[(\mathrm{HOOCCH_2})_2\mathrm{NCH_2CH_2N}(\mathrm{CH_2COO})_2]^{2-}$, dihydrogen ethylenediamine tetraacetate.

then the salt is reduced using dithionite in the presence of base (23,24)

$$2\left[(C_6H_6)_2Cr\right]^+ + S_2O^{2-}{}_4 + 4\,OH^- \longrightarrow 2\,(C_6H_6)_2Cr + 2\,SO_3^{2-} + 2\,H_2O \qquad (3)$$

The reductant of equation 3 can also be hypophosphite. Mixed organocarbonyl compounds of Cr(0) and other oxidation states are also possible. These mixed compounds make the preparation of highly unstable chromium hydrides, eg, tricarbonyl(η^5-2,4-cyclopentadien-1-yl)hydrochromium [36495-37-1], $C_5H_5Cr(CO)_3H$, possible (25). Equation 2 represents a typical preparation for organochromium(I) compounds. The orange–yellow dibenzene chromium(I) cation forms sparingly soluble salts with large anions, eg, $B(C_6H_5)_4^-$.

2.2. Chromium(II) Compounds. The Cr(II) salts of nonoxidizing mineral acids are prepared by the dissolution of pure electrolytic chromium metal in a deoxygenated solution of the acid. It is also possible to prepare the simple hydrated salts by reduction of oxygen-free, aqueous Cr(III) solutions using Zn or Zn amalgam, or electrolytically (2,7,12). These methods yield a solution of the blue $Cr(H_2O)_6^{2+}$ cation. The isolated salts are hydrates that are isomorphous with FE^{2+} and Mg^{2+} compounds. Examples are chromous sulfate heptahydrate [7789-05-1], $CrSO_4 \cdot 7H_2O$, chromous chloride hexahydrate [83082-80-8], $CrCl_2 \cdot 6H_2O$, and $(NH_4)_2Cr(SO_4)_2 \cdot 6H_2O$.

The standard reduction potential of Cr^{2+} (Table 2) shows that this ion is a strong reducing agent, and Cr(II) compounds have been used as reagents in analytical chemistry procedures (26). The reduction potential also explains why Cr(II) compounds are unstable in aqueous solutions. In the presence of air, the oxidation to Cr(III) occurs by reaction with oxygen. However, Cr(II) also reacts with water in deoxygenated solutions, depending on acidity and the anion present, to produce H_2 and Cr(III) (27,28).

The anhydrous halides, chromium(II) fluoride [10049-10-2], CrF_2, chromium(II) bromide [10049-25-9], $CrBr_2$, chromium(II) chloride [10049-05-5], $CrCl_2$, and chromium(II) iodide [13478-28-9], CrI_2, are prepared by reaction of the hydrohalide and pure Cr metal at high temperatures, or anhydrous chromium(II) acetate [15020-15-2], $Cr_2(CH_3COO)_4$, at lower temperatures, or by hydrogen reduction of the Cr(III) halide at about 500–800°C (2,12). These halides generally display a coordination number of six, have a distorted octahedral geometry, are moisture sensitive, and are easily oxidized when exposed to humid air.

When organic acids, RCOOH, are added to aqueous Cr(II) solutions, compounds having the general formula $Cr_2(RCOO)_4L_2$ where $L = H_2O$ are formed. The dimeric red molecules contain a quadruple Cr-Cr bond and are diamagnetic (29). They are stable in dry air but rapidly oxidize under humid conditions. Each Cr atom has a coordination number of six and an octahedral geometry. The $RCOO^{2-}$ anion serves to bridge the interpenetrating octahedra. Compounds containing quadrupole Cr-Cr bonds and octahedral geometries are also obtained from XYZ ligands such as acetanilide [103-84-4], $CH_3CONHC_6H_5$, where the Y, in this case the carbonyl carbon, connects electron-rich centers X, the carbonyl oxygen, and Z, the nitrogen. The Cr-Cr bond is part of a five-membered ring system that has one Cr bonded to X and the other to Z (30,31).

Chromium(II) also forms sulfides and oxides. Chromium(II) oxide [12018-00-7], CrO, has two forms: a black pyrophoric powder produced from the action of nitric acid on chromium amalgam, and a hexagonal brown-red crystal made from reduction of Cr_2O_3 by hydrogen in molten sodium fluoride (32). Chromium(II) sulfide [12018-06-3], CrS, can be prepared upon heating equimolar quantities of pure Cr metal and pure S in a small, evacuated, sealed quartz tube at 1000°C for at least 24 hours. The reaction is not quantitative (33). The sulfide has a coordination number of six and displays a distorted octahedral geometry (34).

The Cr^{2+} ion is extensively hydrolyzed in aqueous solutions (Table 3) and is not easily complexed in this medium. However, many complexes, such as those of cyanide, bipyridine, phenanthroline, acetylacetone, and propylenediamine, have been prepared. The first three of these ligands form octahedral complexes, acetylacetone produces a square complex, and propylenediamine forms a trigonal bipyramidal complex (35).

2.3. Chromium(III) Compounds. Chromium(III) is the most stable and most important oxidation state of the element. The E° values (Table 2) show that both the oxidation of Cr(II) to Cr(III) and the reduction of Cr(VI) to Cr(III) are favored in acidic aqueous solutions. The preparation of trivalent chromium compounds from either state presents few difficulties and does not require special conditions. In basic solutions, the oxidation of Cr(II) to Cr(III) is still favored. However, the oxidation of Cr(III) to Cr(VI) by oxidants such as peroxides and hypohalites occurs with ease. The preparation of Cr(III) from Cr(VI) in basic solutions requires the use of powerful reducing agents such as hydrazine, hydrosulfite, and borohydrides, but Fe(II), thiosulfate, and sugars can be employed in acid solution. Cr(III) compounds having identical counterions but very different chemical and physical properties can be produced by controlling the conditions of synthesis.

The anhydrous halides, chromium(III) fluoride [7788-97-8], CrF_3, chromium(III) chloride [10025-73-7], $CrCl_3$, chromium(III) bromide [10031-25-1], $CrBr_3$, and chromium(III) iodide [13569-75-0], CrI_3, can be made by the reaction of Cr metal and the corresponding halogen at elevated temperatures (12,36). Other methods of synthesis for the halides are also possible (36–38). All of the halides have a layer structure and contain Cr(III) in an octahedral geometry. They are only slightly soluble in water but dissolve slowly when Cr(II) or a reducing agent such as Zn or Mg is added.

An unusual crystal arrangement is exhibited by the isomorphous compounds $CrCl_3$ and CrI_3. The close-packed cubic array of Cl or I atoms has two-thirds of the octahedral holes between every other pair of chlorine or iodine planes filled with chromium atoms. Alternate layers of the halogen compounds are held together by van der Waals' forces (39,40).

The chemistry of Cr(III) in aqueous solution is coordination chemistry (see COORDINATION COMPOUNDS). It is dominated by the formation of kinetically inert, octahedral complexes. The bonding can be described by d^2sp^3 hybridization, and literally thousands of complexes have been prepared. The kinetic inertness results from the $3d^3$ electronic configuration of the Cr^{3+} ion (41). This type of orbital charge distribution makes ligand displacement and substitution reactions very slow and allows separation, persistence, and/or isolation of Cr(III) species under thermodynamically unstable conditions.

The simple hexaaquachromium(III) ion, $Cr(H_2O)_6^{3+}$, obtained from chromium(III) nitrate [26679-46-9], $Cr(NO_3)_3 \cdot 9H_2O$, crystals, or chromium(III) perchlorate [25013-81-4], $Cr(ClO_4)_3 \cdot 9H_2O$, is stable at room temperature. This violet ion displays strong dichroism, ie, solutions are blue by reflected light and reddish blue by transmitted light. If these solutions are heated, the color changes to green indicating hydrolysis (Table 3) and the formation of basic trivalent cations. A general equation for hydrolysis of the trivalent ion Cr^{3+} is

$$x\,Cr^{3+} + y\,H_2O \longrightarrow \left[Cr_x(OH)_y\right]^{(3x-y)+} + y\,H^+ \qquad (4)$$

The term basic used with Cr^{3+} defines the hydroxyl ion's displacement of H_2O in the primary coordination sphere of Cr(III). This displacement effectively lowers the positive charge on the cation. Aqueous solutions of other Cr(III) salts that contain the hexaaqua ion also show some tendency by the anion of the salt to displace the coordinated water molecule, even without heating.

Figure 1 illustrates the complexity of the Cr(III) ion in aqueous solutions. The relative strength of anion displacement of H_2O for a select group of species follows the order perchlorate $\leq$ nitrate $<$ chloride $<$ sulfate $<$ formate $<$ acetate $<$ glycolate $<$ tartrate $<$ citrate $<$ oxalate (42). It is also possible for any anion of this series to displace the anion before it, ie, citrate can displace a coordinated tartrate or sulfate anion. These displacement reactions are kinetically slow, however, and several intermediate and combination species are possible before equilibrium is obtained.

The carboxylic acids or anions in the displacement series prevent the formation of basic complexes whenever present in large excess. This is not true of the acids of inorganic anions. Chromium(III) acetate [1066-30-4], $Cr(CH_3COO)_3$, is not isomorphous with the Cr(II) salt and shows no tendency to form Cr–Cr bonds. Rather, the structure depends on the ratio of acetate to Cr (43). The

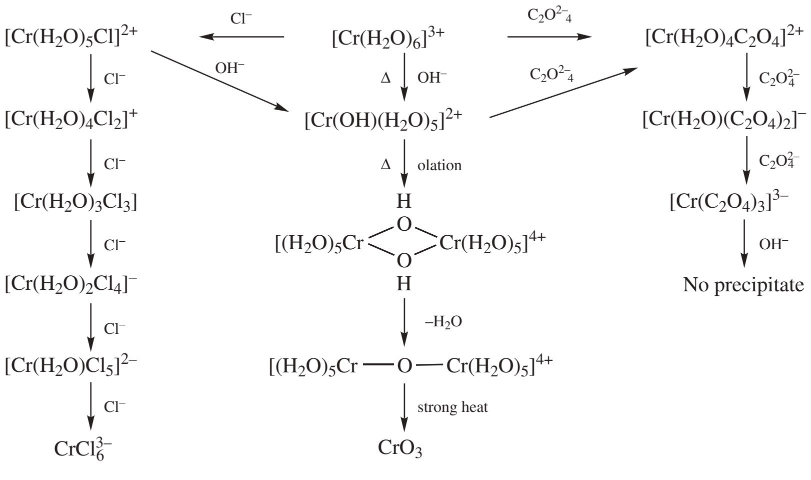


Fig. 1. Complexity of the aqueous Cr(III) ion system.

hydroxy carboxylates, eg, tartrate, may show bonding through both the alcohol and the carboxylic groups, yielding a cage-type structure (44).

The hydrolysis of Cr^{3+} (eq. 4) and the addition of less than equivalent amounts of hydroxide ion to aqueous solutions of Cr^{3+}, followed by aging, yields basic cationic polymers containing multiple chromium centers (45). The existence and formation of these polymers is of interest (17,46–49). Chromium polymers that consist of OH bridged octahedra linked via edges and/or faces, can be isolated by ion-exchange chromatography. The fraction of bridged polynuclear complexes present is proportional to the amount of hydroxide added (17,45).

When sufficient hydroxide is added to an aqueous solution of the trivalent chromium ion, the precipitation of a hydrous chromium(III) oxide, $Cr_2O_3 \cdot nH_2O$, of indefinite composition occurs. This compound is commonly misnamed as chromic or chromium(III) hydroxide [1308-14-1], $Cr(OH)_3$. A true hydroxide, chromium(III) hydroxide trihydrate [41646-40-6], $Cr(OH)_3 \cdot 3H_2O$, does exist and is prepared by the slow addition of alkali hydroxide to a cold aqueous solution of hexaaquachromium(III) ion (40). The fresh precipitate is amphoteric and dissolves in acid or in excess of hydroxide to form the metastable $Cr(OH)_4^-$. This ion decomposes upon heating to give the hydrous chromium(III) oxide. However, if the precipitate is allowed to age, it resists dissolution in excess hydroxide.

The trivalent chromium ion coordinates with almost all chelating agents (qv) and strong Lewis bases. Mixed ligand complexes of Cr(III) can yield stereoisomers. When the coordination number is 6, and J and Q are monodentate ligands, the formulas $[CrJ_4Q_2]^z$, $[CrJ_2Q_4]^z$, and $[CrJ_3Q_3]^z$, and the octahedral geometry of Cr^{3+}, allow for both cis and trans isomers. If only J is a bidentate ligand, then the formula $[CrJ_2Q_2]^z$ allows cis and trans isomers. However, if both J and Q are bidentate, then optical isomers are possible from the formulas $[CrJ_2Q]^z$, $[CrJQ_2]^z$, $[CrJ_3]^z$, and $[CrQ_3]^z$. The possible formation of binuclear complexes, eg, $[J_2Cr(OH)_2CrJ_2]^z$, allows for tartrate-type isomerism, ie, *d, l,* and *meso*. If the bidentate ligand is not symmetrical with respect to the coordination centers then structural isomers based on this asymmetry are also possible (50). The charge of the complex, z, depends on the charge of the ligands and can be positive, negative, or zero.

Chromium(III) oxide, Cr_2O_3, may be prepared by heating the hydrous chromium(III) oxide to completely remove water, as the final product of the calcination of chromium(VI) oxide, CrO_3, or by calcining chromium(III) salts that contain anions of volatile acids, eg, acetates. The Cr_2O_3 structure is isomorphous with α-alumina and α-Fe_2O_3. The best way to prepare pure chromium(III) oxide is by the decomposition of $(NH_4)_2Cr_2O_7$.

$$(NH_4)_2Cr_2O_7 \xrightarrow{200^\circ C} Cr_2O_3 + N_2 + 4\ H_2O \qquad (5)$$

When Cr_2O_3 is introduced as an impurity into the α-Al_2O_3 lattice, as occurs in the semiprecious mineral ruby, the color is red rather than the normal green. This color anomaly is the result of ligand field splitting of the Cr(III) ion (51,52). Chromium(III) also colors other minerals (53).

Compounds that have the empirical formulas $MCrO_2$ and DCr_2O_4 where M is a monovalent and D a divalent cation, are known as chromites. These are actually mixed oxides and probably are better written as $M_2O \cdot Cr_2O_3$ and $DO \cdot Cr_2O_3$, respectively. The oxides of D are largely spinels, ie, the oxygen atoms define a close-packed cubic array having the octahedral holes occupied by the Cr(III) cation and the tetrahedral holes occupied by D (54). Chromite ore is an important member of this class of oxides.

2.4. Chromium(IV) and Chromium(V) Compounds. The formal oxidation states Cr(IV) and Cr(V) show some similarities. Both states are apparently intermediates in the reduction of Cr(VI) to Cr(III). Neither state exhibits a compound that has been isolated from aqueous media, and Cr(V) has only a transient existence in water (55). The majority of the stable compounds of both oxidation states contain either a halide, an oxide, or a mixture of these two. As of this writing, knowledge of the chemistry is limited.

Chromium(IV) fluoride [10049-11-3], CrF_4, and chromium(V) fluoride [14884-42-5], CrF_5, can be prepared by fluorinating Cr, CrF_3, or $CrCl_3$. The Cr(IV) compound is quite stable, but the fluoride of Cr(V) decomposes at 117°C and is easily hydrolyzed. The fluoride of Cr(IV) forms complexes of the type M_2CrF_6 and $DCrF_6$. These complexes are easily hydrolyzed. The K^+ salt, potassium hexafluorochromate(IV) [19652-00-7], K_2CrF_6, decomposes to potassium hexafluorochromate(III) [13822-82-7], K_3CrF_6, and CrF_5 when heated to 300°C. Although Cr(V) displays no other halides, chromium(IV) chloride [15597-88-3], $CrCl_4$, chromium(IV) bromide [51159-56-9], $CrBr_4$, and chromium(IV) iodide [23518-77-6], CrI_4, have been identified in the vapor phase of high temperature, high respective halogen vapor pressure systems.

The pure, crystalline chromium(V) oxide trifluoride can be prepared by the reaction of xenon(II) difluoride and chromium(VI) dioxide difluoride [7788-96-7], also known as chromyl fluoride, CrO_2F_2 (56):

$$XeF_2 + 2\ CrO_2F_2 \longrightarrow 2\ CrOF_3 + Xe + O_2 \qquad (6)$$

Other methods of preparation, eg, the reaction of ClF_3 or BrF_3 and CrO_3, yield the oxyfluoride contaminated with reactants and side reaction products. The crystal structure of $CrOF_3$ has been found to be an infinite three-dimensional array of corner shared $CrOF_5$ octahedra (57). The species $[CrOX_4]^-$, $X = F$, Cl, and Br, contains the oxochromium(V) cation [23411-25-8], CrO^{3+}, exhibits a square pyramidal geometry. Compounds containing this cation are among the most stable Cr(V) compounds.

Chromium(IV) oxide [12018-01-8], CrO_2, is obtained from the hydrothermal decomposition of mixed oxides of Cr(III) and Cr(VI). A mixed oxide of the empirical formula Cr_xO_y, where the ratio of $2y$ to x is greater than 4 and less than 6, is heated at high pressure and in the presence of water to between 250 and 500°C (58). The resulting CrO_2 has an undistorted rutile structure, is ferromagnetic, and has metallic conductance. The chromium(V) oxide [12218-36-9], Cr_2O_5, is prepared by the thermal decomposition of CrO_3. It is always deficient in oxygen, giving an O to Cr mole ratio of about 2.4.

Both Cr(IV) and Cr(V) form mixed metal oxides. The blue-black and unstable tetrasodium chromate(IV) [50811-44-4], Na_4CrO_4, is formed when sodium chromite [12314-42-0], $NaCrO_2$, is heated in the presence of Na_2O to 1000°C. Compounds that have the formula D_2CrO_4 are prepared by heating the divalent metal's chromate(VI), the corresponding hydrate, and chromium(III) oxide to 1000°C. The emerald green, air-stable compounds of Sr and Ba contain the tetrahedral CrO_4^{4-} ions. Chromium(IV) mixed metal oxide species having the formulas $DCrO_3$, D_3CrO_5, and D_4CrO_6 are also known. The mixed metal oxides of chromium(V) are dark green, hygroscopic compounds of formula M_3CrO_4 or $D_3(CrO_4)_2$. The divalent cation's compound is prepared by heating a mixture of the divalent carbonate and the chromate in O_2 free nitrogen to temperatures at or above 1000°C. Both the monovalent and the divalent compounds contain the tetrahedral CrO_4^{3-} ion. Calcium chromate(V) [12205-18-4], $Ca_3(CrO_4)_2$, is isomorphous with $Ca_3(PO_4)_2$, and the other metal chromate(V) compounds show some structural similarities to the phosphates (59,60). There is also a series of compounds that have the formula $(RE)CrO_4$, where RE = La, Pr, Nd, Y, and Sm through Lu (61).

Peroxy compounds of Cr(IV) and Cr(V) are known. The chromium(IV) diperoxide adduct with ammonia [7168-85-3], $Cr(O_2)_2 \cdot 3NH_3$, crystallizes as light brown needles that are unstable and may explode, if an ammoniacal solution of ammonium perchromate is heated to 50°C, and then cooled to 0°C (62). The crystals contain Cr(IV) having a coordination number of 7 and a pentagonal bipyramidal geometry (63). Potassium tetraperoxochromate(V) [12331-76-9], $K_3Cr(O_2)_4$, is obtained as stable red-brown crystals when H_2O_2 is added to a basic solution of K_2CrO_4 maintained at 0°C (64). The geometry of Cr(V) in these crystals is dodecahedral, and its coordination number is 8 (63).

2.5. Chromium(VI) Compounds. Virtually all Cr(VI) compounds contain a Cr–O unit. The chromium(VI) fluoride [13843-28-2], CrF_6, is the only binary Cr^{6+} halide known and the sole exception. This fluoride, prepared by fluorinating Cr at high temperature and pressure, easily disproportionates to CrF_5 and F_2 at normal pressures, even at −100°C. The fluorination of chromium(VI) oxide or the reaction of KrF_2 and CrO_2F_2 in liquid HF produces chromium(VI) oxide tetrafluoride [23276-90-6], $CrOF_4$ (65). Only fluorine displays an oxyhalide having this formula.

The other Cr(VI) halides have the formula CrO_2X_2, where X = F, Cl, or Br. The mixed oxyhalides CrO_2ClY, where Y = F or Br, have been prepared but are not well characterized (66). The formula CrO_2X_2 also describes nonhalide compounds, where $X = ClO_4^-$, NO_3^-, SO_3F^-, N_3^-, CH_3COO^-, etc (67). Compounds containing the theoretical cation CrO_2^{2+} are commonly named chromyl. All of the chromyl compounds are easily hydrolyzed to H_2CrO_4 and HX.

The primary Cr–O bonded species is chromium(VI) oxide, CrO_3, which is better known as chromic acid [1115-74-5], the commercial and common name. This compound also has the aliases chromic trioxide and chromic acid anhydride and shows some similarity to SO_3. The crystals consist of infinite chains of vertex-shared CrO_4 tetrahedra and are obtained as an orange-red precipitate from the addition of sulfuric acid to the potassium or sodium dichromate(VI). Completely dry CrO_3 is very dark red to red purple, but the compound is deliquescent and even traces of water give the normal ruby red color. Chromium(VI) oxide is a very powerful oxidizer and contact with oxidizable organic compounds may cause fires or explosions.

Chromium(VI) oxide dissolves in water to yield the theoretical H_2CrO_4, which is only superficially similar to H_2SO_4. The two acids are about the same size, and they both have a central atom that displays a formal oxidation state of VI and a tetrahedral geometry. However, H_2CrO_4 is a very weak acid compared to sulfuric acid; H_2CrO_4 is easily reduced, but sulfuric acid is very stable. Unlike H_2SO_4, the chromium(VI) acid cannot be isolated as a pure compound, and a $HCrO_4^-$ salt analogue of $NaHSO_4$ has not been prepared. The $HCrO_4^-$ ion shows a distinct tendency to dimerize to $Cr_2O_7^{2-}$ at low total Cr(VI) concentrations, but the corresponding anion $S_2O_7^{2-}$ has not been identified in dilute aqueous sulfuric acid solutions.

The hydrolysis equilibria for H_2CrO_4 given in Table 3 are only valid in HNO_3 or $HClO_4$ solutions. Other acids yield complexes such as those shown for chloride and bisulfate ions. The exact composition of chromate(VI) anion(s) present in aqueous solution is a function of both pH and hexavalent chromium concentration (68). However, at pH values above 8, virtually all the Cr(VI) is present as the CrO_4^{2-} anion. When the pH is between 2 and 6, an equilibrium mixture of $HCrO_4^-$ and $Cr_2O_7^{2-}$ is present; when the pH is below 1, the principal species is H_2CrO_4 (68,69). At very high Cr(VI) concentrations the polychromates $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$ may be present, but this has not been confirmed. The salts of these ions, called trichromates and tetrachromates respectively, do exist (70).

When a warm solution of $K_2Cr_2O_7$ and HCl is allowed to cool, orange needles of $KCrO_3Cl$ precipitate. The fluoride, bromide, and iodide analogues can be prepared in a similar manner. The expected oxidation of the halides by Cr(VI) is kinetically hindered allowing for the formation of CrO_3Cl^-, CrO_3Br^-, and CrO_3I^- ions. All of these compounds display a distorted octahedral geometry, hydrolyze easily, and decompose if heated (71).

The chromate(VI) salts containing the tetrahedral CrO_4^{2-} ion are a very important class of Cr(VI) compounds. Only the alkali metal, ammonium ion, and magnesium chromates show considerable water-solubility. Some cations, eg, Ag^+, Ba^{2+}, and Pb^{2+}, are so insoluble that they precipitate from acidic Cr(VI) solutions, demonstrating the labile equilibria of H_2CrO_4. Salts of colorless cations generally have a pure yellow color, but there are some useful exceptions: silver chromate(VI) [7784-01-2], Ag_2CrO_4, is a maroon color and lead chromate(VI) [15804-54-3], $PbCrO_4$, displays colors that indicate its trimorphism. The stable form is monoclinic and has and has an orange-yellow color. An unstable tetragonal orange-red form is isomorphous with, and stabilized by, $PbMoO_4$. A second unstable yellow form is orthorhombic, isomorphous with and stabilized by $PbSO_4$. The diversity shown by the lead salt is the key to its versatility as a pigment.

The dichromate(VI) salts may be obtained by the addition of acid to the chromate(VI) salts. However, they are better prepared by adding one-half the acid equivalent of a metal hydrate, oxide, or carbonate to an aqueous solution of CrO_3, then removing the water and/or CO_2. Most dichromates(VI) are water-soluble, and the salts contain water(s) of hydration. However, the normal salts of K, Cs, and Rb are anhydrous. Dichromate(VI) compounds of the colorless cations are generally orange-red. The geometry of $Cr_2O_7^{2-}$ is described as two tetrahedral CrO_4 linked by the shared odd oxygen (72).

Chromate(VI) esters and salts of organic bases are known. The esters are generally very unstable, especially those of primary alcohols. The rapid formation of chromate(VI) esters is thought to be the first step in the Cr(VI) oxidation of alcohols and aldehydes (qv) (73–75) (see ALCOHOLS, HIGHER ALIPHATIC; ALCOHOLS, POLYHYDRIC). The adduct $CrO_3 \cdot 2L$ describes the formula of virtually all the organic base salts. Examples of organic bases for the adduct L are pyridine, picolines, lutidines, and quinoline. All organic chromates(VI) are photosensitive and decompose when exposed to light.

When hydrogen peroxide is added to an acid solution of Cr(VI), a deep blue color, indicating the formation of chromium(VI) oxide diperoxide [35262-77-2], $CrO(O_2)_2$, is observed. This compound is metastable and rapidly decomposes to Cr(III) and oxygen at room temperature. The reaction sequence is unique and can be used to qualitatively confirm the presence of Cr(VI). The $CrO(O_2)_2$ species can be extracted from the aqueous solution with ether and is stable in this solvent. If pyridine is added to the ether extract, then the oxodiperoxy-(pyridine)-chromium(VI) [33361-75-0], $C_5H_5N \cdot CrO(O_2)_2$, adduct is prepared. When the acid Cr(VI) solution is at 0°C or below, the green cationic species $Cr_2(O_2)^{4+}$ and $Cr_3(O_2)_2^{5+}$ are obtained. If H_2O_2 is added to a neutral or slightly acid solution of potassium, ammonium, or thallium dichromate, the blue-violet species $[CrO(O_2)_2OH]^-$ is formed. The salts of this anion are violently explosive (63).

3. Manufacture

The primary industrial compounds of chromium made directly from chromite ore are sodium chromate, sodium dichromate, and chromic acid. Secondary chromium compounds produced in quantity include potassium dichromate, potassium chromate, and ammonium dichromate. The secondary trivalent compounds manufactured in quantity are chrome acetate, chrome nitrate, basic chrome chloride, basic chrome sulfate, and chrome oxide.

3.1. Sodium Chromate, Dichromate, and Chromic Acid.

The basic chemistry used to process chromite ore has not changed since the early nineteenth century. However, modern technologies have added many refinements to the manufacturing techniques (76,77), and plants have been adapted to meet health, safety, and environmental regulations. A generalized block flow diagram for the modern chromite ore processing plant is given in Figure 2. In the United States, chemical-grade ore from the Transvaal Region of The Republic of South Africa is employed. Historical procedures and equipment are discussed in Reference 78.

The chemical-grade ore, containing about 30% chromium, is dried, crushed, and ground in ball mills until at least 90% of its particles are less than 75 μm. It is then mixed with an excess of soda ash and, optionally, with lime and leached residue from a previous roasting operation. In American and European practice, a variety of kiln mixes have been used. Some older mixes contain up to 57 parts of lime per 100 parts of ore. However, in the 1990s manufacturers used no more than 10 parts of lime per 100 parts of the ore, and some used no lime at all (77). The roasting may be performed in one, two, or three stages, and there may be as much as three parts of leached residue per part of ore. These adaptations are responses to the variations in kiln roast and the capabilities of the furnaces used.

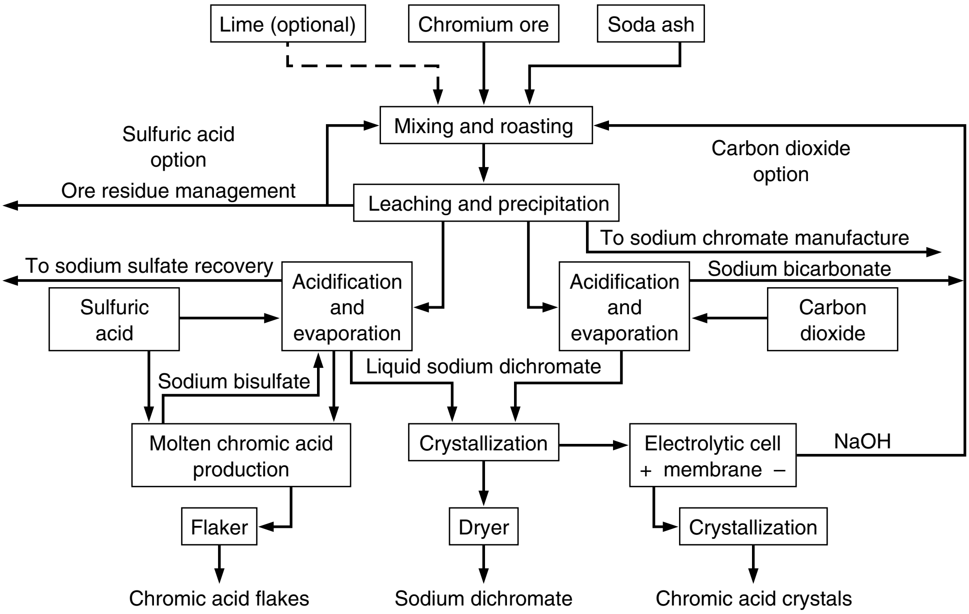


Fig. 2. Flow diagram for the production of sodium chromate, sodium dichromate, and chromic acid flake and crystals.

After thorough mixing, the mixture is roasted in a mechanical furnace, usually a rotary kiln. An oxidizing atmosphere is essential, and the basic reaction of a theoretical chromite is

$$4\ FeCr_2O_4 + 8\ Na_2CO_3 + 7\ O_2 \longrightarrow 2\ Fe_2O_3 + 8\ Na_2CrO_4 + 8\ CO_2 \qquad (7)$$

The temperature in the hottest part of the kiln is closely controlled using automatic equipment and a radiation pyrometer and generally is kept at about 1100–1150°C (see TEMPERATURE MEASUREMENT). Time of passage is about four hours, varying with the kiln mix being used. The rate of oxidation increases with temperature. However, the maximum temperature is limited by the tendency of the calcine to become sticky and form rings or balls in the kiln, by factors such as loss of Na_2O by volatilization, and by increased rate of attack on the refractory lining.

A gas-fired furnace with a revolving annular hearth also has been used to roast chrome ore (78). The mix is charged continuously at the outer edge of the hearth. A water-cooled helical screw moves it toward the inner edge where it is discharged. Mixes containing a much higher (28% Na_2CO_3) soda ash content can be handled in these furnaces. Also, the lower proportion of lime limits the formation of the suspected carcinogenic compound $Ca_3(CrO_4)_2$ (79).

Modern manufacturing processes quench the roast by continuous discharge into the leach water held in tanks equipped with agitators. At this point the pH of the leach solution is adjusted to between 8 and 9 to precipitate aluminum and silicon. The modern leaching operations are very rapid because no or little lime is used. After separation of the ore residue and precipitated impurities using rotary vacuum filters, the crude liquid sodium chromate may need to be treated to remove vanadium, if present, in a separate operation. The ore residue and precipitants are either recycled or treated to reduce hexavalent chromium to Cr(III) before disposal.

All stacks and vents attached to the process equipment must be protected to prevent environmental releases of hexavalent chromium. Electrostatic precipitators and baghouses are desirable on kiln and residue dryer stacks. Leaching operations should be hooded and stacks equipped with scrubbers (see AIR POLLUTION CONTROL METHODS). Recovered chromate values are returned to the leaching-water cycle.

Technical developments in the roasting and leaching area include refinements in pelletizing the mix fed to the kilns (80–82) and in the pre-oxidation of the ore prior to roasting (83). Both of these variants intend to increase the kiln capacity, the first through increasing the permissible fraction of soda ash in the mix, the second through increasing the effective rate of oxidation.

The neutralized, alumina-free sodium chromate solution may be marketed as a solution of 40° Bé (specific gravity = 1.38), evaporated to dryness, or crystallized to give a technical grade of sodium chromate or sodium chromate tetrahydrate [1003-82-9], $Na_2CrO_4 \cdot 4H_2O$. If the fuel for the kilns contains sulfur, the product contains sodium sulfate as an impurity. This compound is isomorphous with sodium chromate and hence difficult to separate. High purity sodium chromate must be made from purified sodium dichromate.

Sodium chromate can be converted to the dichromate by a continuous process treating with sulfuric acid, carbon dioxide, or a combination of these two (Fig. 2). Evaporation of the sodium dichromate liquor causes the precipitation of sodium sulfate and/or sodium bicarbonate, and these compounds are removed before the final sodium dichromate crystallization. The recovered sodium sulfate may be used for other purposes, and the sodium bicarbonate can replace some of the soda ash used for the roasting operation (76). The dichromate mother liquor may be returned to the evaporators, used to adjust the pH of the leach, or marketed, usually as 69% sodium dichromate solution.

Chromic acid may be produced by the reaction of sulfuric acid and sodium dichromate

$$Na_2Cr_2O_7 + 2\,H_2SO_4 \longrightarrow 2\,CrO_3 + 2\,NaHSO_4 + H_2O \tag{8}$$

This is the sulfuric acid option of Figure 2.

Traditionally, sodium dichromate dihydrate is mixed with 66° Bé (specific gravity = 1.84) sulfuric acid in a heavy-walled cast-iron or steel reactor. The mixture is heated externally, and the reactor is provided with a sweep agitator. Water is driven off and the hydrous bisulfate melts at about 160°C. As the temperature is slowly increased, the molten bisulfate provides an excellent heat-transfer medium for melting the chromic acid at 197°C without appreciable decomposition. As soon as the chromic acid melts, the agitator is stopped and the mixture separates into a heavy layer of molten chromic acid and a light layer of molten bisulfate. The chromic acid is tapped and flaked on water cooled rolls to produce the customary commercial form. The bisulfate contains dissolved CrO_3 and soluble and insoluble chromic sulfates. Environmental considerations dictate purification and return of the bisulfate to the treating operation.

Instead of the dihydrate and sulfuric acid, 20% oleum [8014-95-7] and anhydrous sodium dichromate may be used. In this case, the reaction requires little if any external heat, and liquid chromic acid is spontaneously produced. This procedure is the basis for a continuous process (84).

Molten chromic acid decomposes at its melting point at a significant rate. The lower oxides formed impart darkness and turbidity to the water solution. Accordingly, both temperature and time are important in obtaining a quality product.

Another process depends on the addition of a large excess of sulfuric acid to a concentrated solution or slurry of sodium dichromate. Under the proper conditions, a high purity chromic acid, may be precipitated and separated (77,85).

A newer technology for the manufacture of chromic acid uses ion-exchange (qv) membranes, similar to those used in the production of chlorine and caustic soda from brine (76) (see ALKALI AND CHLORINE PRODUCTS; CHEMICALS FROM BRINE; MEMBRANE TECHNOLOGY). Sodium dichromate crystals obtained from the carbon dioxide option of Figure 2 are redissolved and sent to the anolyte compartment of the electrolytic cell. Water is loaded into the catholyte compartment, and the ion-exchange membrane separates the catholyte from the anolyte (see ELECTROCHEMICAL PROCESSING).

When a potential is applied across the cell, the sodium and other cations are transported across the membrane to the catholyte compartment. Sodium hydroxide is formed in the catholyte compartment, because of the rise in pH caused by the reduction of water. Any polyvalent cations are precipitated and removed. The purified NaOH may be combined with the sodium bicarbonate from the sodium dichromate process to produce soda ash for the roasting operation. In the anolyte compartment, the pH falls because of the oxidation of water. The increase in acidity results in the formation of chromic acid. When an appropriate concentration of the acid is obtained, the liquid from the anolyte is sent to the crystallizer, the crystals are removed, and the mother liquor is recycled to the anolyte compartment of the cell. The electrolysis is not allowed to completely convert sodium dichromate to chromic acid (76). Patents have been granted for more electrolytic membrane processes for chromic acid and dichromates manufacture (86).

3.2. Other Chromates and Dichromates. The wet operations employed in the modern manufacture of the chromates and dichromates are completely enclosed and all stacks and vents equipped with scrubbers and entrainment traps to prevent contamination of the plant and its environment. The continuous process equipment that is used greatly facilitates this task. The trapped material is recycled.

Potassium and ammonium dichromates are generally made from sodium dichromate by a crystallization process involving equivalent amounts of potassium chloride or ammonium sulfate. In each case the solubility relationships are favorable so that the desired dichromate can be separated on cooling, whereas the sodium chloride or sulfate crystallizes out on boiling. For certain uses, ammonium dichromate, which is low in alkali salts, is required. This special salt may be prepared by the addition of ammonia to an aqueous solution of chromic acid. Ammonium dichromate must be dried with care, because decomposition starts at 185°C and becomes violent and self-sustaining at slightly higher temperatures.

Potassium chromate is prepared by the reaction of potassium dichromate and potassium hydroxide. Sulfates are the most difficult impurity to remove, because potassium sulfate and potassium chromate are isomorphic.

3.3. Water-Soluble Trivalent Chromium Compounds.

Most water-soluble Cr(III) compounds are produced from the reduction of sodium dichromate or chromic acid solutions. This route is less expensive than dissolving pure chromium metal, it uses high quality raw materials that are readily available, and there is more processing flexibility. Finished products from this manufacturing method are marketed as crystals, powders, and liquid concentrates.

The general method of production for aqueous trivalent compounds involves dissolving a Cr(VI) source in an acid solution of the desired anion, eg, nitric acid, in a reactor constructed of acid-resistant materials. Next, the reducing agent is added at a controlled rate until the Cr(VI) has been reduced to Cr(III). For some reducing agents it is necessary to complete the reduction at boiling or under reflux conditions. A simplified, general flow diagram for this process is given in Figure 3.

The product use determines the Cr(VI) source and limits the choice of reducing agents. High purity trivalent chromium compounds are produced from chromic acid and a variety of reducing agents that yield either the anion needed or a minimum of side reaction products. When a clean product is not required and the presence of sodium does not affect the intended application, solutions of sodium dichromate are reduced using sugars, starches, and/or other materials. Sodium-free products employ chromic acid and the same reducing agents. The reduction of Cr(VI) with sugar can be written

$$4\,Cr_2O_7^{2-} + 32\,H^+ + C_6H_{12}O_6 \longrightarrow 8\,Cr^{3+} + 6\,CO_2 + 22\,H_2O \qquad (9)$$

Although equation 9 is written as a total oxidation of sugar, this outcome is never realized. There are many intermediate oxidation products possible. Also, the actual form of chromium produced is not as simple as that shown because

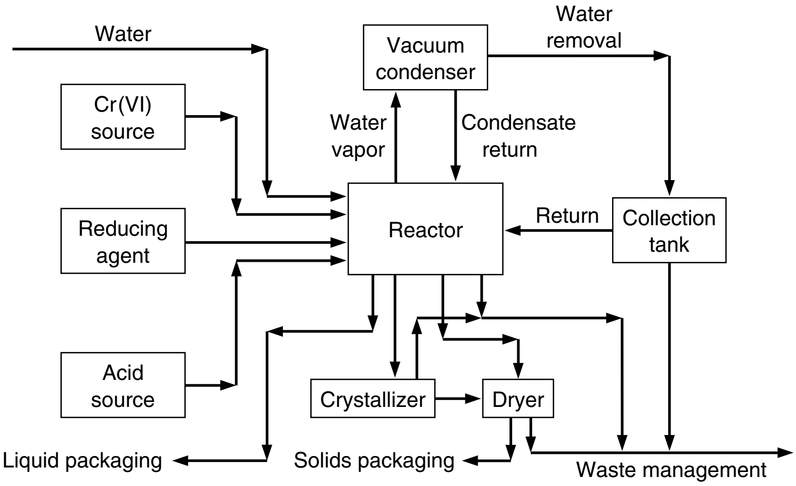


Fig. 3. Flow diagram for the manufacture of water-soluble Cr(III) compounds.

of hydrolysis, polymerization, and anion penetration. Other reducing agents are chosen to enhance the performance of the product.

The final consideration for the manufacture of Cr(III) compounds is the mole ratio of acid to Cr. This ratio determines the basicity value of the product. Basicity can also be stated as the amount of positive charge on chromium(III) neutralized by hydroxide. For example, Cr^{3+} is 0% basic, $Cr(OH)^{2+}$ is 33.3% basic, and $Cr_2(OH)_3^{3+}$ is 50% basic. The basicity value can vary continuously from 0% to 100%. It is unlikely that these formulas represent actual cationic species, but are rather simplistic images of the average charge. These formulas can be used, however, to determine the mole ratio of acid needed for manufacture of the compound. For a monovalent anion, the mole ratio of acid to Cr for 0% basicity is 3, for 33.3% basicity it is 2, and for 50% basicity it is 1.5.

Basic chrome sulfate [12336-95-7], $Cr(OH)SO_4$, is manufactured as a proprietary product under various trade names for use in leather tanning. It is generally made by reduction of sodium dichromate in the presence of sulfuric acid, and contains sodium sulfate, small amounts of organic acids if carbohydrate reducing agents are used, plus various additives. When sulfur dioxide is employed as the reducing agent, a 33.3% basic chromic sulfate is automatically obtained

$$Na_2Cr_2O_7 + 3\ SO_2 + H_2O \longrightarrow 2\ Cr(OH)SO_4 + Na_2SO_4 \qquad (10)$$

Pure sulfur dioxide is bubbled through the sodium dichromate solution in an acid-resistant tank, or sulfur burner gas is passed through a ceramic-packed tower countercurrent to descending dichromate solution. After reduction is complete, steam is bubbled through the solution to decompose any dithionate that may have formed, and to remove excess sulfur dioxide. Also, after reduction any desired additives, such as aluminum sulfate, are incorporated, and the solution is aged. It is then spray dried. Careful temperature control during drying is necessary to obtain a highly water-soluble, solid product.

The compounds are sold on a specification of chromic oxide content, 20.5–25% Cr_2O_3, and basicity, 30–58%. Solutions are also available.

4. Economic Aspects

In 2001, the total chrome ore consumption in the United States, including chemical, metallurgical (the principal use), and refractory grades, was 332,000 metric tons, having an average concentration of 42.6% Cr_2O_3. The world production of chromite in 2001 was 3,650,000 metric tons, down from the 2000 level of 4,380,000 metric tons (87).

In 2001, major producers of chromium chemicals were located in Kazakhstan, Russia, the United Kingdom and the United States. Moderate-size facilities were located in China, Japan, Romania, South Africa, and Turkey. Small-scale producers operated in China and India. Principal producers of chromium chemicals in the U.S. in 2001 were Elementis Chromium in Corpus Christi, Texas and Occidental Chemical Corp. in Castle Hayne, N. C. (87).

U.S. export data for chromium chemicals are given in Table 4. U.S. import data for chromium chemicals are given in Table 5.

Table 4. **U.S. Exports of Chromium Chemicals**[a,b]

Chromium chemicals, gross weight	2000		2001		Principal destinations, 2001
	Quantity, t	Value × 10^3 $	Quantity, t	Value × 10^3 $	
chromium trioxide	11,600	22,800	10,700	26,600	Canada (33%); New Zealand (10%); Australia (9%); Brazil (8%); Japan (8%); Mexico (8%); Hong Kong (5%); Germany (4%); Taiwan (4%); Korea, Republic of (3%); Thailand (2%); South Africa (1%).
chromium oxides, other	5,170	20,300	2,730	10,300	Canada (34%); Germany (18%); Belgium (11%); China (9%); Israel (3%); Japan (3%); Taiwan (3%); United Kingdom (3%); Australia (2%); Korea, Republic of (2%); Mexico (2%); Philippines (2%); Indonesia (1%).
chromium sulfates	23.5	32	13.1	200	United Kingdom (72%); Chile (18%); Hong Kong (10%).
zinc and lead chromate	287	620	158	416	Canada (7%); Chile (16%); Mexico (12%); Belgium (2%).
sodium dichromate	19,400	14,400	16,300	16,600	Canada (30%); Mexico (23%); Thailand (13%); Colombia (5%); Panama (5%); Peru (5%); Hong Kong (3%); Indonesia (3%); San Salvador (3%); Taiwan (3%); Brazil (2%); Philippines (2%).
potassium dichromate	95.4	144	18.6	44	Canada (33%); Japan (25%); New Zealand (24%); Korea, Republic of (14%); Brazil (1%); India (1%).
other chromates, dichromates, and peroxochromates	639	2,140	562	1,650	Korea, Republic of (49%); Canada (30%); Malaysia (5%); Mexico (5%); United Kingdom (5%); Saudi Arabia (3%); Japan (1%).
pigments and perparations	1,040	5,340	771	3,710	Canada (32%); Mexico (31%); Sweden (5%); Brazil (4%); Nigeria (4%); Venezuela (4%); Costa Rica (3%); Germany (2%); Guyana (2%); Trinidad and Tobago (2%); Korea, Republic of (1%); Philippines (1%).

[a] Ref. 87.

[b] Data are rounded to no more than three significant digits; may not add to totals shown.

Table 5. **U.S. Imports for consumption of Chromium Compounds**[a,b]

Chromium Chemicals, gross weight	2000		2001		
	Quantity, t	Value, × 10^3 $	Quantity, t	Value, × 10^3 $	Principal sources, 2001
chromium trioxide	8,030	13,700	10,500	17,200	Kazakhstan (57%); China (16%); Turkey (14%); United Kingdom (6%); Italy (3%); Russia (1%); South Africa (1%).
chromium oxides and hydroxides, other	3,220	12,100	2,820	10,500	Japan (31%); China (22%); Germany (22%); United Kingdom (13%); Colombia (4%); Belgium (1%); France (1%); Italy (1%); Netherlands (1%); Poland (1%); Russia (1%).
sulfates of chromium	239	227	155	151	United Kingdom (37%); Argentina (26%); Mexico (23%); Italy (14%).
chromates of lead and zinc	289	563	111	224	Norway (68%); China (20%); Japan (8%); Colombia (2%); Germany (2%).
sodium dichromate	16,900	10,500	14,800	7,760	United Kingdom (98%); China (1%); South Africa (1%).
potassium dichromate	205	392	152	322	United Kingdom (60%); Kazakhstan (26%); Netherlands (13%).
other chromates and dichromates; peroxochromates	56.9	183	110	291	Korea, Republic of (82%); United Kingdom (12%); Austria (4%); India (2%).
chromium carbide	182	2,010	267	2,900	China (45%); Germany (19%); Japan (17%); Canada (11%); United Kingdom (7%); Israel (1%).
		pigments and preparations based on chromium			
chrome yellow	7,000	18,700	5,870	16,300	China (69%); Mexico (11%); China (7%); Korea, Republic of (7%); Hungary (2%); Colombia (1%); Germany (1%); Japan (1%).
molybdenum orange	1,620	7,110	1,120	5,050	Canada (90%); Colombia (4%); Mexico (3%); Germany (1%); Philippines (1%).
zinc yellow	19	21	128	98	China (62%); Czech Republic (16%); Brazil (12%); Portugal (10%).
other	1,530	6,290	1,390	4,100	China (47%); France (41%); Germany (6%); Czech Republic (3%); Japan (2%); Poland (1%).

[a] Ref. 87.

[b] Data are rounded to no more than three significant digits; may not add to totals shown.

Most of the chromium consumed worldwide is used in steel production. Production of chemicals accounted for 10%.

Sodium dichromate is the starting material for all chromium compounds. Global consumption was estimated at 660×10^3 t in 1998 (a decline in consumption). Chromium sulfide used in leather tanning was the largest consumer of sodium dichromate (37%), followed by chromic acid production (32%), and chromic oxide production (21%). Miscellaneous uses make up the remaining 10%. Chromic acid is used in the preparation of wood preservatives and in metal finishing (88).

Environmental concerns have caused a slow down in the use of sodium dichromate and is expected to show a decline of 0.3% by 2003. Environmental regulations have also had a negative impact on the use of chromium products in tanning.

5. Specifications and Shipment

Chromates and dichromates are sold in both technical and reagent grades (89,90). Chlorides and sulfates are the principal impurities. Both manufacturers' and U.S. General Services Administration (GSA) specifications exist for the technical grades (91,92) and there are also producer specifications available for some trivalent chromium compounds (93). Specifications are shown in Tables 6 and 7.

Sodium dichromate, sodium chromate, and mixtures thereof are shipped as concentrated solutions in tank cars and trucks. The chloride and sulfate contents are usually somewhat higher than in the crystalline product. Sodium dichromate is customarily shipped at a concentration of 69% $Na_2Cr_2O_7 \cdot 2H_2O$, which is close to the eutectic composition freezing at −48.2°C.

Chromic acid is transported in steel drums and by rail in tank cars. Multiwall paper bags, fiber drums, as well as steel drums can be employed to ship the solid chromate salts, dichromate salts, and trivalent compounds. Trivalent

Table 6. **U.S. Government Specifications for Chromium(VI) Compounds**[a]

Specification	$Na_2Cr_2O_7 \cdot 2H_2O$	CrO_3[b]	Na_2CrO_4	$K_2Cr_2O_7$[c]	$(NH_4)_2Cr_2O_7$[d]
number	O-S-595B	O-C-303D	O-S-588C	O-P-559	O-A-498B
assay,[e] %	99.0[f]	99.5	98.5	99.0	99.7
Cl_- wt%[g]	0.1	0.1	0.1	0.1	0.005
SO_4^{2-}, wt %[g]	0.2	0.2	1.0	0.1	0.06
H_2O insol., wt %[g]	0.2	0.1		0.1	0.02
LOD[h] at 120°C, %[g]	12.5		0.5	0.2	

[a] Ref. 91.

[b] No more than 30% may pass a 600 μm (30 mesh) U.S. Sieve screen.

[c] All must pass 2000 μm (10 mesh) U.S. Sieve screen, and no more than 25% may pass a 149 μm (100 mesh) U.S. Sieve screen.

[d] Contains 13.5% NH_3 minimally. The pH of a 20% w/v soln is 3.2.

[e] Minimum value given.

[f] Actually % $Na_2Cr_2O_7$ after drying at 120°C.

Table 7. **Specifications for Trivalent Chromium Compounds**[a]

Specification	Chrome alum	Basic chrome chloride	Chrome acetate
formula	$KCr(SO_4) \cdot 12H_2O$	$Cr_5(OH)_6Cl_9 \cdot xH_2O$[b]	$Cr(C_2H_3O_2)_3$
form	violet crystals	green powder	green liquid
Cr, wt%	10.2–10.6	29.0–33.0	11.2–11.8
basicity, %		33.0–43.0	−5.0 – 5.0
Cl^-, wt%		33.0–39.0	<0.05
SO_4^{2-}, wt%			<0.05
Fe, wt%	<0.01		
Cu, wt%	<0.001		
Pb, wt%	<0.005		
H_2O insolubles, wt%	<0.1	<0.25	

[a] Ref. 93.

[b] Where $8.8 \leq x \leq 12$.

chromium liquid concentrates are also available in polyethylene drums. The U.S. Department of Transportation (DOT) requires all packages having a capacity ≤416.4 L (110 gallons) to be marked with the proper shipping name and identification number of the chemical contained. The Occupational Safety and Health Administration (OSHA) requires all compounds containing chromium to be labeled as hazardous and all Cr(VI) compounds are required to contain an additional cancer hazard warning.

6. Analytical Methods

The classical wet-chemical qualitative identification of chromium is accomplished by the intense red-violet color that develops when aqueous Cr(VI) reacts with (*S*)-diphenylcarbazide under acidic conditions (94). This test is sensitive to 0.003 ppm Cr, and the reagent is also useful for quantitative analysis of trace quantities of Cr (96). Instrumental qualitative identification is possible using inductively coupled argon plasma–atomic emission spectroscopy (icap/aes) having a sensitivity of <10 ppb using the 205.552 nm line; using optical atomic emission spectroscopy (oaes) having an arc sensitivity of 1 ppm for the persistent emission line at 425.43 nm; and using neutron activation analysis (naa) having a sensitivity of <0.5 microgram per sample.

The methods for quantitative analysis of chromium are dependent on the concentration and the nature of the chromium containing material. There are two types of samples: water-soluble and water-insoluble. The insoluble samples, eg, ores, refractories (qv), some organochromium compounds, and some pigments, need to be converted to water-soluble forms before analyzing. This can be accomplished by fusion using sodium peroxide or dissolution in an oxidizing acid mixture. Information on preparing chromium containing samples for analysis is available (92,96–99).

6.1. Wet-Chemical Determinations. Both water-soluble and prepared insoluble samples must be treated to ensure that all the chromium is present as Cr(VI). For water-soluble Cr(III) compounds, the oxidation is easily accomplished using dilute sodium hydroxide, dilute hydrogen peroxide, and heat. Any excess peroxide can be destroyed by adding a Ni^{2+} catalyst and boiling the alkaline solution for a short time (100). Appropriate aliquot portions of the samples are acidified and chromium is found by titration either using a standard ferrous solution or a standard thiosulfate solution after addition of potassium iodide to generate an iodine equivalent. The ferrous endpoint is found either potentiometrically or by visual indicators, such as ferroin, a complex of iron(II) and *o*-phenanthroline, and the thiosulfate endpoint is ascertained using starch as an indicator.

To determine moderate amounts of Cr(III) and Cr(VI) in samples that have both oxidation states present, Cr(VI) is analyzed by direct titration in one sample, and the total chromium is found in a second sample after oxidation of the Cr(III). The Cr(III) concentration is determined as the difference. Trace quantities of Cr(VI) in Cr(III) compounds can be detected and analyzed by (*S*)-diphenylcarbazide. Trace quantities of Cr(III) in Cr(VI) may be detected and analyzed either photometrically (101) or by ion chromatography using various modes of detection (102).

6.2. Instrumental Quantitative Analysis.

Methods such as x-ray spectroscopy, oaes, and naa do not necessarily require pretreatment of samples to soluble forms. Only reliable and verified standards are needed. Other instrumental methods that can be used to determine a wide range of chromium concentrations are atomic absorption spectroscopy (aas), flame photometry, icap-aes, and direct current plasma–atomic emission spectroscopy (dcp-aes). These methods cannot distinguish the oxidation states of chromium, and speciation at trace levels usually requires a previous wet-chemical separation. However, the instrumental methods are preferred over (*S*)-diphenylcarbazide for trace chromium concentrations, because of the difficulty of oxidizing very small quantities of Cr(III).

Impurities in industrial chromium compounds include chloride, sulfate, insoluble matter, and trace metals. The chloride ion-selective electrode can be used to determine chloride values; sulfate is found by barium precipitation, after the reduction of Cr(VI) to Cr(III) for hexavalent chromium compounds; and a variety of methods are available to determine the specified trace metals, eg, aas and icapaes. The standard methods of organizations and agencies such as the American Society for Testing and Materials (ASTM), the American Wood Preservers' Association, the General Services Administration (GSA), and the American Leather Chemists' Association (ALCA) contain procedures for the analysis of commercially available chromium formulations, pigments, and compounds. A wider variety of tests are required for reagent chemicals (89,90).

7. Health and Safety Factors

Chromium in its hexavalent oxidation state is identified by the United States Environmental Protection Agency as one of the seventeen high-priority toxic chemicals that can cause human health problems. Hexavalent chromium (chromium VI) is found in ammonium dichromate, chromic acid, sodium dichromate, sodium chromate, and potassium dichromate. Symptoms of acute dermal exposure to hexavalent chromium are irritated skin and mucous membranes.

Table 8. **Air Standards (mg/m^3) and Classification for Various Chromium Compounds**

Substance	ACGIH	OSHA	NIOSH
chromic acid and chromates (as CrO_3)		ceiling 0.01	0.001 as Cr carcinogen
chromite ore processing (chromate) as Cr	0.05, A1		
chromium (II) compounds as Cr	0.5	0.5	0.5
chromium (III) compounds as Cr	0.5	0.5	0.5
chromium (VI) compounds as Cr water soluble	0.05		
chromium (VI) compounds as Cr certain water insoluble	0.01, A1		
lead chromate as Cr	0.012, A2		
strontium chromate as Cr[a]	0.0005, A2		
zinc chromates as Cr	0.01, A1	ceiling 1 as CrO_3	0.001 carcinogen

[a] Proposed, 1992.

Ingestion can cause serious injury or death. Deep perforating nasal ulcers know as chrome holes can result form chronic inhalation. Chromium VI is mutagenic and carcinogenic in animals and is a Classification A human carcinogen.

All chromium compounds are considered hazardous substances under CERCLA (Comprehensive Response, Compensation and Liability Act (88).

7.1. Standards, Regulations, or Guidelines of Exposure.

For chromium (II) and chromium (III), the following are the exposure limits: ACGIH TLV TWA = 0.5 mg/m^3, OSHA PEL TWA = 1 mg/m^3, and NIOSH REL TWA = 0.5 mg/m^3, IDLH = 250 mg Cr(II)/m^3. ACGIH, OSHA, and NIOSH treat chromium and its compounds in slightly different ways, as shown in Table 8. It should be noted that both IARC and NTP classify certain chromium compounds as carcinogens (103). The ACGIH proposed lowering the TLV for strontium chromate to 0.0005 mg/m^3 because it is a significantly more potent carcinogen than other chromates (104). The exposure limits for the chromates (+6) is 0.1 mg/m^3 for OSHA as a ceiling value, and 0.001 mg/m^3 as a NIOSH REL. The ACGIH has a number of recommended TLVs depending upon the chromium compound.

The ACGIH biologic exposure determinants for water-soluble hexavalent chromium (the TLV is 0.05 mg/m^3) in the urine is 10 mg/g creatinine for an increase during the work shift and 30 mg/g of creatinine for the end of the shift at the end of the work week. The ACGIH noted that there is some background for those not occupationally exposed (105).

The ACGIH TLV for chromyl chloride is 0.025 mg/m^3. The NIOSH REL for chromyl chloride, which they treat as a carcinogen, is 0.001 mg/m^3 (106).

7.2. Nutrition.

Chromium, in the trivalent oxidation state, is recognized as an essential trace element for human nutrition, and the recommended daily intake is 50 to 200 micrograms (107). The transport of glucose via insulin's reaction with the cell membrane, a necessary mechanism of glucose metabolism, appears to be mediated by chromium (108,109). Increased coronary disease risk, glucose intolerance, elevated serum cholesterol and elevated insulin levels have been linked to chromium deficiency (110–113). Evidence is available that suggests dietary supplements of chromium(III) may improve glucose tolerance, and there is some indication that a correlation may exist between diabetes and chromium deficient diets (114,115).

8. Environmental Concerns

The EPA has set the National Interim Primary Drinking Water Standard at 50 μg/L total chromium and the current Maximum Contamination Level (MCL) is 120 μg/L. This agency has also issued a Cr(VI) ambient water quality standard of 50 μg/L and has proposed a Maximum Contamination Level Goal (MCLG) of 0.1 μg/L (116). Industrial discharges of total Cr(VI) are regulated by National Pollutant Discharge Elimination System (NPDES) permits, specific for the area that receives the waste or discharge.

8.1. Waste Management.

All chromium-bearing waste materials in the United States are regulated by the EPA. Best practicable technology is required by the EPA to control chromium effluent in discharged industrial waters. Wastes are also subjected to designation as hazardous waste under the Resource Conservation and Recovery Act (RCRA). Chromium compounds are tracked by the EPA's Toxic Release Inventory.

In Europe, chromium is considered as cause for environmental concern. Regulations differ from country to country. Environmental issues have been a long time concern of Western Europe's leather industry. Chromium waste is significant. Sludge has been a principal concern because of the limited availability of disposal sites. An increasing number of Western European tanneries are implementing chrome-free tanning procedures.

Environmental regulations are expected to tighten with regard to air and water emissions and waste disposal.

Chromium containing solids from manufacturing and wastewater treatment sludges are classified as hazardous wastes and must be handled as such (120). These wastewater treatment sludges are F006 from electroplating wastewaters; K002, K003, K005, K006, and K008 from pigment producers' wastewaters; K086 wastewaters generated as a result of cleaning process equipment used to make chromium containing inks (qv) from pigments, driers, soaps (qv) and stabilizers; U032 wastewaters from the production of calcium chromate. These solids are characterized as D007 wastes because they exceed the Resource Conservation and Recovery Act (RCRA) threshold of 5.0 mg/L Cr as determined by the extraction procedure (EP) toxic characteristic leaching procedure (TCLP) tests and may contain both Cr(VI) and Cr(III) (121).

The EPA has established exposure levels for both Cr(III) and Cr(VI) for the general population (117,118). For exposures of short duration that constitute an insignificant fraction of the lifespan the acceptable intake subchronic (AIS) by ingestion is 979 mg/d for trivalent chromium and 1.75 mg/d for hexavalent chromium. There was insufficient data to calculate an AIS by inhalation for Cr(III), and the EPA believes this type of standard is inappropriate for hexavalent chromium (124). For lifetime exposures, an acceptable intake chronic (AIC) of 103 mg/d Cr(III) and 0.35 mg/d Cr(VI) is established for ingestion. The inhalation AIC is estimated to be 0.357 mg/d Cr(III). The EPA has calculated an inhalation cancer potency for Cr(VI) of 41 $[\mathrm{mg}/(\mathrm{kg}\cdot\mathrm{d})]^{-1}$ risk for a lifetime exposure to 1 $\mu g/m^3$ hexavalent chromium (109,117–119).

Where appropriate, the direct precipitation of hexavalent chromium with barium, and recovery of the Cr(VI) value can be employed (122). Another recycling (qv) option is ion exchange (qv), a technique that works for chromates and Cr^{3+} (123). Finally, recovery of the chromium as the metal or alloy is possible by a process similar to the manufacture of ferrochromium alloy and other metals (123).

9. Uses

9.1. Metal Finishing and Corrosion Control. The exceptional corrosion protection provided by electroplated chromium and the protective film created by applying chromium surface conversion techniques to many active metals, has made chromium compounds valuable to the metal finishing industry. Cr(VI) compounds have dominated the formulas employed for electroplating (qv) and surface conversion, but the use of Cr(III) compounds is growing in both areas because of the health and safety problems associated with hexavalent chromium and the low toxicity of trivalent chromium (see CORROSION AND CORROSION INHIBITORS; METAL SURFACE TREATMENTS; METALLIC COATINGS).

Electroplating of Chromium. Until the middle to late 1970s, all of the commercially electroplated chromium was produced from plating baths prepared from chromic acid. Although these baths accounted for the majority of chromium electroplated products (124–127), decorative trivalent chromium baths are successfully operated in many installations (128).

Compositions and operating parameters for both Cr(VI) and Cr(III) baths are given in Table 9. Two types of trivalent baths result from different anode arrangement (129,130). The No. 1 bath uses a graphite anode that is in the bath during plating, and relies on proprietary additives combined with current

Table 9. **Chemical Composition and Operating Parameters for Chromium Electroplating Baths**

Parameter	Cr(III)[a] No. 1	Cr(III)[a] No. 2	Cr(VI)[a] decorative	Cr(VI)[b] functional
Cr, g/L	20–23	5–10	100–200	100–200
CrO_3, g/L			190–380	190–380
SO_4^{2-}, g/L	[c]	[c]	1.9–3.8	1.9–3.8
H_3BO_3, g/L	60–65	60–65		
temperature, °C	20–50	45–55	30–50	50–60
pH	2.3–2.9	3.5–3.9	<1	<1
anode type	internal	external	internal	internal
anode material	graphite	93%Pb/7%Sn	93%Pb/7%Sn	93%Pb/7%Sn
current density, A/dm^2	4–15	4–15	17.5–30	3.6–36
deposit thickness, μm	0.05–0.5	0.05–0.5	0.05–0.5	2.5–500

[a] Ref. (128–130).

[b] Ref. 131.

[c] No specifications, but may be present.

density control to limit the anodic oxidation of trivalent to hexavalent chromium. Bath No. 2 employs an anode that is isolated from the plating bath by a hydrogen ion-selective membrane that allows only H^+ to pass, and therefore any anodic oxidation of Cr(III) is prevented (130). Small amounts of hexavalent chromium reduces the efficiency of trivalent baths.

Because the thickness of the plate deposited from trivalent baths is limited, these have only been employed for decorative applications. However, the bluish white deposit obtained from chromic acid baths can be closely matched by trivalent chromium baths (129).

Unlike most metals, chromium can be plated from solutions in which it is present as an anion in a high oxidation state. The deposition of chromium from chromic acid solutions also requires the presence of a catalyst anion, usually sulfate, although fluoride, fluosilicate, and mixtures of these two with sulfate have been extensively used. The amount of catalyst must be carefully regulated. Neither pure chromic acid or solutions containing excess catalysts produce a satisfactory plate. Even using carefully controlled temperature, current density, and bath composition, chromium plating is one of the most difficult electroplating operations. Throwing power and current efficiency are notably poor, making good racking procedures and good electrical practices essential.

In 1979, a viable theory to explain the mechanism of chromium electroplating from chromic acid baths was developed (132). An initial layer of polychromates, mainly $HCr_3O_{10}^-$, is formed contiguous to the outer boundary of the cathode's Helmholtz double layer. Electrons move across the Helmholtz layer by quantum mechanical tunneling to the end groups of the polychromate oriented in the direction of the double layer. Cr(VI) is reduced to Cr(III) in one-electron steps and a colloidal film of chromic dichromate is produced. Chromous dichromate is formed in the film by the same tunneling mechanism, and the Cr(II) forms a complex with sulfate. Bright chromium deposits are obtained from this complex.

Decorative chromium plating, 0.2–0.5 μm deposit thickness, is widely used for automobile body parts, appliances, plumbing fixtures, and many other products. It is customarily applied over a nonferrous base in the plating of steel plates. To obtain the necessary corrosion resistance, the nature of the undercoat and the porosity and stresses of the chromium are all carefully controlled. Thus microcracked, microporous, crack-free, or conventional chromium may be plated over duplex and triplex nickel undercoats.

Functional or hard chromium plating (125,131) is a successful way of protecting a variety of industrial devices from wear and friction. The most important examples are cylinder liners and piston rings for internal combustion engines. Functional chromium deposits must be applied to hard substrates, such as steel, and are applied in a wide variety of thicknesses ranging from 2.5 to 500 μm.

Black and colored plates can also be obtained from chromic acid baths. The plates are mostly oxides (133). Black chromium plating bath compositions are proprietary, but most do not contain sulfate. The deposit has been considered for use in solar panels because of its high absorptivity and low emissivity (131).

Chromium Surface Conversion. Converting the surface of an active metal by incorporating a barrier film of complex chromium compounds protects the metal from corrosion, provides an excellent base for subsequent painting, provides a chemical polish, and/or colors the metal. This conversion is normally accomplished by immersion, but spraying, swabbing, brushing, and electrolytic methods are also employed (134) (see METAL SURFACE TREATMENTS). The metals that benefit from chromium surface conversion are aluminum, cadmium, copper, magnesium, silver, and zinc. Zinc is the largest consumer of chromium conversion baths, and more formulations are developed for zinc than for any other metal.

The compositions of the conversion baths are proprietary and vary greatly. They may contain either hexavalent or trivalent chromium (135,136), but baths containing both Cr(III) and Cr(VI) are rare. The mechanism of film formation for hexavalent baths has been studied (137,138), and it appears that the strength of the acid and its identity, as well as time and temperature, influences the film's thickness and its final properties, eg, color. The newly prepared film is a very soft, easily damaged gel, but when allowed to age, the film slowly hardens, assumes a hydrophobic character and becomes resistant to abrasion. The film's structure can be described as a cross-linked Cr(III) polymer, that uses anion species to link chromium centers. These anions may be hydroxide, chromate, fluoride, and/or others, depending on the composition of the bath (139).

Clear-bright and blue-bright chromium conversion colors are thin films (qv) and may be obtained from both Cr(III) and Cr(VI) conversion baths. The perceived colors are actually the result of interference phenomena. Iridescent yellows, browns, bronzes, olive drabs, and blacks are only obtained from hexavalent conversion baths, and the colors are listed in the order of increasing film thickness. Generally, the thicker the film, the better the corrosion protection (see FILM DEPOSITION TECHNIQUES).

Oxide films on aluminum are produced by anodizing in a chromic acid solution. These films are heavier than those produced by chemical conversion and thinner and more impervious than those produced by the more common sulfuric acid anodizing. They impart exceptional corrosion resistance and paint adherence to aluminum and were widely used on military aircraft assemblies during World War II. The films may be dyed. A typical anodizing bath contains 50 to 100 g/L CrO_3 and is operated at 35–40°C. The newer processes use about 20 volts dc and adjust the time to obtain the desired film thickness (140).

Dichromates and chromic acid are used as sealers or after-dips to improve the corrosion resistance of various coatings on metals. For example, phosphate coatings on galvanized iron or steel as well as sulfuric acid anodic coatings on aluminum can be sealed by hexavalent chromium baths.

Chromium compounds are used in etching and bright-dipping of copper and its alloys. A typical composition for the removal of scale after heat-treating contains 30 g/L $Na_2Cr_2O_7 \cdot 2H_2O$ and 240 mL/L concentrated H_2SO_4. It is used at 50–60°C.

Chromates are used to inhibit metal corrosion in recirculating water systems. When methanol was extensively used as an antifreeze, chromates could be successfully used as a corrosion inhibitor for cooling systems in locomotive diesels and automobiles (141).

Steel immersed in dilute chromate solutions does not rust. The exact mechanism of the inhibition is not known, although it is agreed that polarization of the local anodes that serve as corrosion foci is important. In the inhibition of iron and steel corrosion a film of τ-Fe_2O_3, in which some Cr is present, appears to form. The concentration of chromate required to inhibit corrosion may range from 50 to 20,000 ppm, depending on conditions, and a pH of 8–9 is usually optimum. The inclusion of chromium compounds in formulations permits the use of such corrosive salts as zinc chloride and copper sulfate in steel cylinders.

9.2. Pigments.

Chromium pigments can be divided into chromate color pigments based on lead chromate, chromium oxide greens, and corrosion inhibiting pigments based on difficulty soluble chromate. An excellent discussion of these pigments is given in Reference 142. An older reference is also useful (143) (see PIGMENTS, INORGANIC).

Chromate Pigments Based on Lead. Pigments based on lead can be further subdivided into primrose, lemon, and medium yellows, and chrome orange, molybdate orange, [12709-98-7] and normal lead silicochromates. Although earlier emphasis was on pure lead compounds, modern pigments contain additives to improve working properties, hue, light fastness, and crystal size and shape and to maintain metastable structures (144).

The chemical composition and ASTM specifications (145) of these pigments is given in Table 10. Details for commercial procedures are not disclosed. The pigments are characterized as follows: Medium yellows are orange–yellows that are essentially pure monoclinic lead chromate. Light lemon or primrose yellows containing up to 40% lead sulfate have some or all of the lead chromate in the metastable orthorhombic form, which is stabilized by lead sulfate and other additives. The higher the orthorhombic content, the greener the shade. Chrome oranges are basic lead chromate [18454-12-1], $PbCrO_4 \cdot PbO$. Molybdate oranges are tetragonal solid solutions of lead sulfate, lead chromate, and lead molybdate. An aging step is required in precipitation to permit development of the orange tetragonal form. Lead silicochromate, essentially medium chrome yellow precipitated on silica, has been developed for use in traffic paints where the silica gives better abrasion resistance. Chrome green, not to be confused with chromic oxide green, is a mixture of a light chrome yellow, ie, lemon or primrose, and a blue, usually iron blue. The pigment may be produced by grinding, mixing in suspension, or precipitating the yellow on the blue. The last method is the preferred. The first is hazardous because the pigment, containing both oxidizing (chromate) and reducing (ferrocyanide) components, may undergo spontaneous combustion. Phthalocyanine blues have replaced iron blues to some extent and organic greens and chromic oxide have displaced chrome green, which has poor acid and alkali resistance.

Chromium Oxide Greens. The chromium oxide green pigments comprise both the pure anhydrous oxide, Cr_2O_3, and hydrated oxide, or Guignet's green (146). The following manufacturing processes appear to be in use.

An alkali dichromate is reduced in self-sustaining dry reaction by a reducing agent such as sulfur, carbon, starch, wood flour, or ammonium chloride. For pigment use, the reducing agent is generally sulfur. When a low sulfur grade is needed in the manufacture of aluminothermic chromium, a carbonaceous reducing agent is employed:

$$Na_2Cr_2O_7 + S \longrightarrow Na_2SO_4 + Cr_2O_3 \tag{11}$$

$$Na_2Cr_2O_7 + 2C \longrightarrow Na_2CO_3 + Cr_2O_3 + CO \tag{12}$$

Table 10. **Chemical Composition and ASTM Specifications for Chromate Color Pigments**[a]

	Composition, wt%			
			Actual	
Analyte[b]	Spec[c]	Theory	Min	Max
	Primrose chrome yellow, D211-67 Type I			
$PbCrO_4$	50[d]	77.3	52.0	82.7
$PbSO_4$		22.7	4.2	25.9
TFM	8.0[e]			
	Lemon chrome yellow, D211-67 Type II			
$PbCrO_4$	65[d]	72.7	52.4	68.8
$PbSO_4$		27.3	17.4	39.0
TFM	10.0[e]			
	Medium chrome yellow, D211-67 Type III			
$PbCrO_4$	87[d]	100	82.4	98.2
TFM	10.0[e]			
	Light chrome orange, D211-67 Type IV			
$PbCrO_4$	55[d]	59.2		
PbO		40.8		
TFM	10.0[e]			
	Dark chrome orange, D211-67 Type V			
$PbCrO_4$	55[d]	59.2		
PbO		40.8		
TFM	3.0[e]			
	Chrome yellow for green, D211-67 Type VI			
$PbCrO_4$	75[d]			
TFM	8.0[e]			
	Pure chrome green, D212-80			
$PbCrO_4$	70[d]			
	Molybdate orange, D2218-67			
$PbCrO_4$	70[d]	82.3		
$PbMoO_4$	8[d]	14.9		
$PbSO_4$		2.8		
TFM	12[e]			

[a] Ref. 145.

[b] TFM = total foreign materials or total of all substances that are not insoluble lead compounds.

[c] Spec = specification

[d] Value is minimum.

[e] Value is maximum.

The mixture is ignited with an excess of reducing agent in a reverberatory furnace or small kiln, transferred to leaching tanks, filtered, washed, dried, and pulverized. The product is 99 + % Cr_2O_3, and the metallurgical grades contain less than 0.005% of sulfur.

Chromate–dichromate solutions are reduced by sulfur in a boiling alkaline suspension (147).

$$2\,Na_2CrO_4 + Na_2Cr_2O_7 + 6\,S + 2\,x\,H_2O \longrightarrow 2\,Cr_2O_3 \cdot x\,H_2O + 3\,Na_2S_2O_3 \quad (13)$$

Excess NaOH is used to start the reaction and not over 35% of the chromium is added as dichromate. At the end of the reaction, the thiosulfate is removed by filtration and recovered. The hydrous oxide slurry is then acidified to pH 3–4 and washed free of sodium salts. On calcination at 1200–1300°C, a fluffy pigment oxide is obtained, which may be densified and strengthened by grinding. The shade can be varied by changes in the chromate:dichromate ratio, and by additives.

A dichromate or chromate solution is reduced under pressure to produce a hydrous oxide, which is filtered, washed, and calcined at 1000°C. The calcined oxide is washed to remove sodium chromate, dried, and ground. Sulfur, glucose, sulfite, and reducing gases may be used as reducing agent, and temperatures may reach 210°C and pressures 4–5 MPa (600–700 psi).

A number of manufacturers around the world are using the decomposition of ammonium dichromate to produce chrome oxide (eq. 5) (78). Generally, an excess of finely ground ammonium sulfate is mixed with sodium dichromate, and the dry mixture is heated to form chrome oxide and sodium sulfate, evolving nitrogen and steam.

$$(NH_4)_2SO_4 + Na_2Cr_2O_7 \longrightarrow Cr_2O_3 + Na_2SO_4 + N_2 + 4\,H_2O \qquad (14)$$

This is a favorable process because the side reaction products, nitrogen and water, are not pollutants and the sodium sulfate can be recovered and sold. Also, all of the wash water used to remove the sodium sulfate from the chrome oxide can be recycled.

Chromic oxide green is the most stable green pigment known. It is used where chemical and heat resistance are required and is a valuable ceramic color (see COLORANTS FOR CERAMICS). It is used in coloring cement (qv) and granulated rock for asphalt (qv) roofing. An interesting application is in camouflage paints, as the infrared reflectance of chromic oxide resembles green foliage. A minor use is in the coloring of synthetic gem stones (see GEMS). Ruby, emerald, and the dichroic alexandrite all owe their color to chromic oxide (53).

Guignet's green, or hydrated chromic oxide green, is not a true hydrate, but a hydrous oxide, $Cr_2O_3 \cdot xH_2O$, in which x is about 2. It is obtained from the production of hydrous oxide at elevated temperature, and sometimes pressure, in a borax or boric acid melt. Although Guignet's green is permanent, it does not withstand use in ceramics. It has poor tinting strength but is a very clean, transparent, bluish green. It is used in cosmetics (qv) and metallic automotive finishes (see COLORANTS FOR FOOD, DRUGS, COSMETICS, AND MEDICAL DEVICES).

Corrosion Inhibiting Pigments. Pigments inhibiting corrosion derive effectiveness from the low solubility of chromate. The principal pigment of this group is zinc chromate or zinc yellow. Others include zinc tetroxychromate, basic lead silicochromate, strontium chromate, and barium potassium chromate (148). The chemical composition and ASTM specifications of some of these pigments are shown in Table 11.

Zinc yellow became an important corrosion-inhibiting pigment for aircraft during World War II. However, the war production rate of 11,000 t/yr has not since been reached. Now, zinc yellow is widely used for corrosion inhibition on

Table 11. **Chemical Compositions and Analytical Specifications for Chromate Corrosion Inhibiting Pigments**

	Composition, wt %		
Analyte[a]	Spec[b]	Theory	Typical
Basic lead silicochromate D 1648–81 Type 1			
CrO_3	5.1–5.7		5.4
PbO	46.0–49.0		47.0
SiO_2	45.5–48.5		47.0
SSD, μm	<8.5		
Basic lead silicochromate D 1648–81 Type 2			
CrO_3	6.3–7.2		
PbO	42.5–46.0		
SiO_2	47.5–50.5		
SSD, μm	<2.0		
Strontium chromate D 1649–82			
CrO_3	41[c]		
SrO	41[c]		
SO_3	0.2[d]		
Zinc yellow (zinc chromate) D 478–49 Type I			
CrO_3	41[c]	45.8	45.0
ZnO	35–40	37.2	36.0
K_2O	13[d]	10.8	10.0
SO_3	0.2[d]		0.05
Cl	0.1[d]		
Zinc yellow (zinc chromate) D 478–49 Type II			
CrO_3	41[c]	45.8	45.0
ZnO	35–40	37.2	36.0
K_2O	13[d]	10.8	10.0
SO_3	3.0[d]		1.0
Cl	0.8[d]		
[e]	1.0[d]		
Zinc tetroxychromate			
CrO_3			17.0
ZnO			71.0
H_2O			10.0

[a] SSD = selective surface diameter determined by ASTM D1366.

[b] Ref. 145.

[c] Value is minimum.

[d] Value is maximum.

[e] When SO_3 and Cl are below maximum, the expression $[(\%SO_3/3) + (\%Cl/0.8)]$ must be used to determine conformance to specifications.

auto bodies, light metals, and steel, and in combination with red lead and ferric oxide for structural steel painting.

Zinc yellow is not a normal zinc chromate, having the empirical formula $K_2O \cdot 4ZnO \cdot 4CrO_3 \cdot 3H_2O$ [12433-50-0]. It belongs to the group of salts having the general formula $M(I)_2O \cdot 4M(II)O \cdot 4CrO_3 \cdot 3H_2O$ (149). The sodium zinc salt has occasionally been used as a pigment. The sodium copper salt has been tested as an antifouling marine pigment and is an ingredient of dips for auto bodies (see Coatings, marine).

Zinc yellow is made by a variety of processes, all based on the reaction of zinc compounds, chromates, and potassium salts in aqueous solution. If products free of chloride and especially sulfate are desired, they are excluded from the system. In one process, for example, zinc oxide is swollen with potassium hydroxide and the chromates are added as a solution of potassium tetrachromate [12422-53-6] (150).

$$4\,\mathrm{ZnO} + \mathrm{K_2Cr_4O_{13}} + 3\,\mathrm{H_2O} \longrightarrow \mathrm{K_2O}\cdot 4\,\mathrm{ZnO}\cdot 4\,\mathrm{CrO_3}\cdot 3\,\mathrm{H_2O} \qquad (15)$$

The final pH is 6.0–6.6. Care must be taken in washing to avoid hydrolysis and loss of chromate.

Zinc tetroxychromate [13530-65-9], approximately $4ZnO \cdot ZnCrO_4 \cdot xH_2O$, has a somewhat lower chromate solubility than zinc yellow and has been used in wash primers.

Strontium chromate [12677-00-8], $SrCrO_4$, is used increasingly despite its high cost. It works well on light metals, and is compatible with some latex emulsions where zinc compounds cause coagulation (see LATEX TECHNOLOGY). It is also an ingredient of some proprietary formulations for chrome plating.

Basic lead silicochromate [11113-70-5] (National Lead Co. designation Pigment M-50) is a composite in which basic lead chromate, ie, chrome orange, is precipitated onto a lead silicate–silica base. It does not have an appreciable chromate solubility and depends on lead oxide for its effectiveness.

Table 12. **Chemical Composition and Specifications for Wood Preservatives**[a]

Type	Component	Composition, wt% Optimum	Min	Max
	Acid copper chromate (ACC)			
	CrO_3	68.2	63.3	
	CuO	31.8	28.0	
	Chromated copper arsenate (CCA)			
type A	CrO_3	65.5	59.4	69.3
	CuO	18.1	16.0	20.9
	As_2O_5	16.4	14.7	19.7
type B	CrO_3	35.3	33.0	38.0
	CuO	19.6	18.0	22.0
	As_2O_5	45.1	42.0	48.0
type C	CrO_3	47.5	44.5	50.5
	CuO	18.5	17.0	21.0
	As_2O_5	34.0	30.0	38.0
	Chromated zinc chloride (CZC)			
	CrO_3	20	19	
	ZnO	80	76	
	Fluor chrome arsenate phenol (FCAP)			
	CrO_3	37	33	41
	As_2O_5	25	22	28
	F	22	20	24
	DNP[b]	16	14	18

[a] Ref. 155.

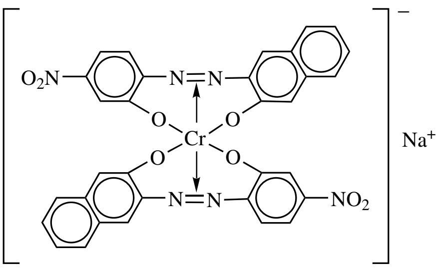
[b] DNP = dinitrophenol.

9.3. Leather Tanning and Textiles. Although chromium(VI) compounds are the most important commercially, the bulk of the applications in the textile and tanning industries depend on the ability of Cr(III) to form stable complexes with proteins, cellulosic materials, dyestuffs, and various synthetic polymers. The chemistry is complex and not well understood in many cases, but a common denominator is the coordinating ability of chromium(III) (see LEATHER; TEXTILES).

The chrome tanning is one step in a complicated series of leather operations leading from the raw hide to the finished products. Chrome tanning is the most important tannage for all hides except heavy cattle hides, which are usually vegetable tanned. In heavy shoe uppers and soles, a chrome tanned leather is frequently given a vegetable retan to produce chrome retan leather.

Sodium dichromate and various chromic salts are employed in the textile industry (151,152). The former is used as an oxidant and as a source of chromium, for example, to dye wool and synthetics with mordant acid dyes, oxidize vat dyes and indigosol dyes on wool, aftertreat direct dyes and sulfur dyes on cotton to improve washfastness, and oxidize dyed wool. Premetallized dyes are also employed. These are hydroxyazo or azomethine dyes in which chromium or other metals are combined in the dye (see AZINE DYES; AZO DYES).

Acid Black 63 [32517-36-5] (CI 12195) is a typical premetallized dye. The commercial product contains some of the 1:2 chelate shown.



Another use of chromium compounds is in the production of water- and oil-resistant coatings on textiles, plastic, and fiber glass. Trade names are Quilon, Volan, and Scotchgard (153,154) (see WATERPROOFING AND WATER/OIL REPELLANCY).

9.4. Wood Preservation. The use of chromium compounds in wood preservation is largely because of the excellent results achieved by chromated copper arsenate (CCA), available in three modifications under a variety of trade names. The treated wood (qv) is free from bleeding, has an attractive olive-green color, and is paintable. CCA is widely used, especially in treating utility poles, building lumber, and wood foundations. About 62% of all the chromic acid produced in the United States is consumed by the wood preservation industry (77) (see BUILDING MATERIALS, SURVEY).

Chromium compounds are also used in fire-retardant formulations where their function is to prevent leaching of the fire retardant from the wood and corrosion of the equipment employed.

Chromium-containing wood preservatives and their chemical compositions are listed in Table 12 (155). Chromium compounds have a triple function in wood preservation (156). Most importantly, after impregnation of the wood the Cr(VI) compounds used in the formulations react with the wood extractives and the other preservative salts to produce relatively insoluble complexes from which preservative leaches only very slowly. This mechanism has been studied in the laboratory (157) and the field (158). Finally, although most of the chromium is reduced to chromium(III), there is probably some slight contribution of the chromium(VI) to the preservative value (159).

9.5. Drilling Muds in the Petroleum and Natural Gas Industry.

Since 1941, chromium chemicals have been used in the drilling of wells to combat fatigue corrosion cracking of drill strings, with about one metric ton of sodium chromate being used annually for an average West Texas well. Other early uses were in gas-condensate wells in Louisiana and East Texas.

However, the petroleum (qv) industry has turned to proprietary drilling-mud formulations, specially designed to suit the aqueous environment and rock strata in which the well is located (see DRILLING FLUIDS AND OTHER OIL RECOVERY CHEMICALS). In addition to heavy minerals, such as barite, and both soluble and difficulty soluble chromates for corrosion control, many of these formulations contain chromium lignosulfonates. The latter Cr(III) compounds are prepared like a tanning formula from sodium dichromate, using lignosulfonate waste from sulfite pulp (qv) mills as the reducing agent. This use amounts to about 4% of the total chromium compound consumption (160,161).

Acrylamide–polymer/Cr(III)carboxylate gel technology has been developed and field tested in Wyoming's Big Horn Basin (162,163). These gels economically enhance oil recovery from wells that suffer fracture conformance problems. The Cr(III) gel technology was successful in both sandstone and carbonate formations, and was insensitive to H_2S, high saline, and hard waters (163).

9.6. Miscellaneous Uses.

A large number of chromium compounds have been sold in small quantities for a variety of uses, some of which are described in Table 13 (185–187).

Catalysts. A more important minor use of chromium compounds is in the manufacture of catalysts (Table 13). Chromium catalysts are used in a great variety of reactions, including hydrogenations, oxidations, and polymerizations (179–181). Most of the details are proprietary and many patents are available.

Chromia–alumina catalysts are prepared by impregnating τ-alumina shapes with a solution of chromic acid, ammonium dichromate, or chromic nitrate, followed by gentle calcination. Zinc and copper chromites are prepared by coprecipitation and ignition, or by thermal decomposition of zinc or copper chromates, or organic amine complexes thereof. Many catalysts have spinel-like structures (188–191).

Photosensitive Reactions. The reduction of chromium(VI) by organic compounds is highly photosensitive, and this property is used in photosensitive dichromate-colloid systems.

A dichromate-colloid system is applied to a metal pringing plate (192). This soluble material is exposed to an image, and, where light strikes, the photochemical reaction reduces the dichromate. The chromium(III) produced forms an insoluble complex with the colloid in a reaction similar to that of dye mordanting or leather tanning. The unreacted colloid is washed off exposing bare metal that can be etched. Some of the colloids used are shellac, glue, albumin, casein, gum

Table 13. **Chromium Compounds Properties and Uses**

Name	CAS Registry number	Molecular formula	Properties	Uses
Cr(VI) compounds				
ammonium chromate	[7788-98-9]	$(NH_4)_2CrO_4$	yellow crystals, 1.91, sol H_2O	textile printing, photography, dye mordant for wool, analytical reagent
barium chromate	[10294-40-3]	$BaCrO_4$	[a]	pyrotechnics, high temp. batteries, pigment for glasses and ceramics[b,c,d]
barium dichromate	[10031-16-0]	$BaCr_2O_7 \cdot 2H_2)$	bright red-yellow needles, $-2H_2O$ at 120°C, dec in H_2O	ceramics
barium potassium chromate	[27133-66-0]	$K_2Ba(CrO_4)_2$	yellow crystals, 3.65	corrosion inhibiting pigment[e]
cadmium chromate	[14312-00-6]	$CdCrO_4$	yellow crystals, insol H_2O	catalysts, pigments
cadmium dichromate	[69239-51-6]	$CdCr_2O_7 \cdot H_2O$	orange crystals, sol H_2O	metal finishing
calcium chromate	[13765-19-0]	$CaCrO_4$	yellow crystals, sl sol H_2O	metal primers, high temp. batteries, corrosion inhibitor[b,c]
calcium dichromate	[14307-33-6]	$CaCr_2O_7 \cdot 4.5H_2O$	orange crystals, 2.136, sol H_2O	metal finishing, catalyst, corrosion inhibitor[f]
cesium chromate	[13454-78-9]	Cs_2CrO_4	yellow crystals, 4.237, sol H_2O	electronics
chromic chromate	[11056-30-7]	variable	brown, amorphous, and hydrated	catalysts, mordants
chromyl chloride	[14977-61-8]	CrO_2Cl_2	[a]	Etard reaction, oxidation of organics, catalyst-polymerization of olefins[g]
cobalt chromate	[13455-25-9]	$CoCrO_4$	gray-black crystals, insol H_2O, sol acids	ceramics[h]
copper chromate, basic	[12433-14-6]	$4CuO \cdot CrO_3 \cdot xH_2O$	brown, amorphous	fungicides, catalysts
copper dichromate	[13675-47-3]	$CuCr_2O_7 \cdot 2H_2O$	black crystals, 2.283, very sol H_2O, sol acids and NH_4OH	catalysts, wood preservatives
copper sodium chromate	[68399-60-0]	$Na_2O \cdot 4CuO \cdot 4CrO_2 \cdot 3H_2O$	maroon crystals, 3.57, sl sol H_2O	antifouling pigment[i]
lithium chromate	[7789-01-7]	$Li_2CrO_4 \cdot 2H_2O$	yellow crystals, 2.149, sol H_2O, transition to anhydrous at 74.6°C	corrosion inhibitor esp. in air-conditioner and nuclear reactors[j]

Table 13 (*Continued*)

Name	CAS Registry number	Molecular formula	Properties	Uses
lithium dichromate	[10022-48-7]	$Li_2Cr_2O_7 \cdot 2H_2O$	orange-red crystals, 2.34, very sol H_2O	corrosion inhibitor[k]
magnesium chromate	[16569-85-0]	$MgCrO_4 \cdot 5H_2O$	yellow crystals, 1.954, sol H_2O, turns to 7 H_2O at 17.2°C	corrosion inhibitor in gas turbines, refractories
magnesium dichromate	[34448-20-9]	$MgCr_2O_7 \cdot 6H_2O$	orange-red crystals, 2.002, sol H_2O, tr to $5H_2O$ at 48.5°C	catalyst, refractories[l]
mercuric chromate	[13444-75-2]	$HgCrO_4$	red crystals, slightly sol	antifouling formulations
mercurous chromate	[13465-34-4]	Hg_2CrO_4	red crystals, very sl sol	antifouling formulations
morpholine chromate	[36969-05-8]	$(C_4H_{10}NO)_2CrO_4$	yellow oily material	vapor-phase corrosion inhibitor in catalysts
nickel chromate	[14721-18-7]	$NiCrO_4$	maroon to black crystals, very sl sol	catalyst
pyridine–chromic acid adduct	[26412-88-4]	$CrO_3 \cdot 2C_5H_5N$	dark red crystals, explodes on warming	research oxidant
pyridine dichromate	[20039-37-6]	$(C_5H_5NH)_2Cr_2O_7$	orange crystals	photosensitizer in photoengraving
silver chromate	[7784-01-2]	Ag_2CrO_4	[a]	catalyst
strontium chromate	[7789-06-2]	$SrCrO_4$	[a]	corrosion-inhibiting pigment, plating additive
tetramminecopper(II) chromate	[13870-96-7]	$Cu(NH_3)_4CrO_4$	dark green needles	catalyst, gas absorbant
zinc sodium chromate	[68399-59-7]	$Na_2O \cdot 4ZnO \cdot 4CrO_3 \cdot 3H_2O$	yellow crystals, sl sol 3.24	corrosion-inhibiting pigment
		Cr(III) compounds		
ammonium tetrathiocyanato diamminechromate(III)	[13573-16-5]	$NH_4(NH_3)_2Cr(SCN)_4$	red crystals	known as Reinecke's salt, analytical reagent for amines and alkaloids
basic chrome acetate	[39430-51-8]	$Cr_3(OH)_2(C_2H_3O_2)_7 \cdot xH_2O$	blue-green powder, sol H_2O	oil drilling muds, textile dye mordant, catalyst for organic oxidations[m,n]
basic chrome chloride	[50925-66-1]	$Cr_5(OH)_6Cl_9 \cdot xH_2O$	available as a green powder sol H_2O, hygroscopic	textile dye mordant, release adhesives, polymerization cross-linking agent[n]

basic chrome formate	[73246-98-7]	$Cr(OH)(OOCH)_2 \cdot 4H_2O$	green needles, example of rare crystalline basic Cr(III) salt, sol H_2O	skein printing of cotton tanning
chromic acetate	[1066-30-4]	$Cr(C_2H_3O_2)_3$	usually sold as a solution	printing and dyeing textiles[o]
chromic acetylacetonate	[13681-82-8]	$Cr(C_5H_7O_2)_3$	[a]	preparation Cr complexes, catalysts, antiknock compounds
chromic ammonium sulfate	[10022-47-6]	$NH_4Cr(SO_4)_2 \cdot 12H_2O$	violet crystals, 1.72, mp 94°C, sol water	Cr electrowinning salt
chromic chloride	[10025-73-7]	$CrCl_3$	[a]	chromizing, Cr metal organochromium compounds[p]
chromic fluoborate	[27519-39-7]	$Cr(BF_4)_3$	available as a solution	Cr plating, in catalysts
chromic fluoride	[7788-97-8]	CrF_3	green crystals, 3.78, insol H_2O	chromizing
chromic hydroxy dichloride	[14982-80-0]	$Cr(OH)Cl_2$	sold as a water solution, can be made as isopropanol solution	manufacturing Quilon, Volan, and Scotchgard[q]
chromic naphthenate	[61788-69-0]	no definite formula	sold as soln in petroleum solvents	textile preservative
chromic nitrate	[26679-46-9]	$Cr(NO_3)_2 \cdot 9H_2O$	violet crystals, 1.80, mp 66.3°C, sol in H_2O	catalysts, textiles, manufacturing CrO_2[r]
chromic phosphate	[27096-04-4]	$CrPO_4$	green powder, also available as a solution in H_3PO_4	pigments, phosphate coatings, wash primers
chromic potassium oxalate	[15275-09-9]	$K_3[Cr(C_2O_4)_3] \cdot 3H_2O$	violet crystals	dye mordant
chromic potassium sulfate	[7788-99-0]	$KCr_2(SO_4)_3 \cdot 12H_2O$	[a] also available as a green powder with <12 H_2O[m]	hardening photographic emulsions, dietary supplement
chromic sulfate	[15005-90-0]	$Cr_2(SO_4)_3 \cdot xH_2O$	green amorphous powder	insolubilizing gelatin
cobalt chromite	[12016-69-2]	$CoCr_2O_4$	turquoise blue crystals, spinel	ceramics, catalysts
copper chromite	[12018-10-9]	$CuCr_2O_4$	black crystals, distorted spinel	catalysts esp. automobile exhaust[r]
magnesium chromite	[12053-26-8]	$MgCr_2O_4$	brown crystals, spinel, 4.415	refractory
zinc chromite	[12018-19-8]	$ZnCr_2O_4$	green crystals, spinel, 5.30	catalyst[s]
Other oxidation states				
chromium(0) hexacarbonyl	[13007-92-6]	$Cr(CO)_6$	[a]	synthesis of organo-chromium and hydride compounds, preparation of CrO[t]
dicumene chromium(0)	[12001-89-7]	$[(CH_3)_2CHC_6H_5]_2Cr$	estd bp 300°C, explodes at 210°C	preparation of Cr carbides by vapor deposition[u]

Table 13 (*Continued*)

Name	CAS Registry number	Molecular formula	Properties	Uses
chromium(II) chloride	[10049-05-5]	$CrCl_2$	[a]	chromizing, preparation of Cr metal[v]
chromium(IV) oxide	[12018-01-8]	CrO_2	[a]	magnetic tapes[w]
calcium chromate(V)	[12205-18-4]	$Ca_3(CrO_4)_2$	green crystals, similar to $Ba_3(CrO_4)_2$[a]	corrosion inhibiting pigment, suspect carcinogen[x]

[a] See Table 1.
[b] Ref. 164.
[c] Ref. 165.
[d] Ref.166.
[e] Ref. 167.
[f] Ref. 168; Ref. 169.
[g] Ref. 170; Ref. 171.
[h] Ref. 172.
[i] Ref. 173.
[j] Ref. 174.
[k] Ref. 175.
[l] Ref. 176.
[m] Ref. 93.
[n] Ref. 162.
[o] Ref. 177.
[p] Ref. 178.
[q] Ref. 153; Ref. 154.
[r] Ref. 58.
[s] Ref. 179; Ref. 180; Ref. 181.
[t] Ref. 24; Ref. 182.
[u] Ref. 183.
[v] Ref. 184.
[w] Ref. 5; Ref. 185.
[x] Ref. 59.

arabic, and gelatin. The newer technology employs more consistent and readily controlled synthetic materials, such as poly(vinyl alcohol).

Batteries. The shelf life of dry batteries (qv) is increased from 50 to 80% by the use of a few grams of zinc chromate or dichromate near the zinc anode. This polarizes the anode on open circuit but does not interfere with current delivery.

Since World War II, the U.S. space program and the military have used small amounts of insoluble chromates, largely barium and calcium chromates, as activators and depolarizers in fused-salt batteries (165). The National Aeronautics and Space Administration (NASA) has also used chromium(III) chloride as an electrolyte for redox energy storage cells (194).

Magnetic Tapes. Chromium dioxide, CrO_2, is used as a ferromagnetic material in high fidelity magnetic tapes (qv). Chromium dioxide has several technical advantages over the magnetic iron oxides generally used (58,195).

Reagent-Grade Chemicals. Potassium dichromate is an important analytical standard, and other chromium chemicals, in reagent grades, find considerable laboratory use (89,90). This use, though small, is most important in wet analyses.

Alloys. A substantial amount of chromic oxide is used in the manufacture of chromium metal and aluminum–chromium master alloys.

Other. Recent patents describe a method for reducing cholesterol levels using proanthocyanidin and niacin-bound chromium complex (196); chromium picolinate compositions used for supplementing dietary chromium, lowering blood glucose levels and serum lipid levels and increasing lean body mass (197); heat treatable coated article with a chromium nitride ir-reflecting layer that enables the coated article to have good corrosion resistance to acid, good mechanical performance, and good color stability (198).

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