COBALT COMPOUNDS

1. Introduction

Cobalt [7440-48-4] forms numerous compounds and complexes of industrial importance. Nonmetallic cobalt usage represents 30% of total cobalt produced (1). Cobalt, at wt 58.933, is one of the three members of the first transition series of Group 9 (VIIIB). The electronic configuration is $[Ar]3d^7 4s^2$. There are thirteen known isotopes, but only three are significant: ^{59}Co is the only stable and naturally occurring isotope; ^{60}Co has a half-life of 5.3 years and is a common source of γ-radioactivity; and ^{57}Co has a 270-d half-life and provides the γ-source for Mössbauer spectroscopy (see COBALT AND COBALT ALLOYS).

Cobalt exists in the +2 or +3 valence states for the majority of its compounds and complexes. A multitude of complexes of the cobalt(III) ion [22541-63-5] exist, but few stable simple salts are known (2). Werner's discovery and detailed studies of the cobalt(III) ammine complexes contributed greatly to modern coordination chemistry and understanding of ligand exchange (3). Octahedral stereochemistries are the most common for the cobalt(II) ion [22541-53-3] as well as for cobalt(III). Cobalt(II) forms numerous simple compounds and complexes, most of which are octahedral or tetrahedral in nature; cobalt(II) forms more tetrahedral complexes than other transition-metal ions. Because of the small stability difference between octahedral and tetrahedral complexes of cobalt(II), both can be found in equilibrium for a number of complexes. Typically, octahedral cobalt(II) salts and complexes are pink to brownish red; most of the tetrahedral Co(II) species are blue (see COORDINATION COMPOUNDS).

Cobalt metal is significantly less reactive than iron and exhibits limited reactivity with molecular oxygen in air at room temperature. Upon heating, the black, mixed valence cobalt oxide [1308-06-1], Co_3O_4, forms; at temperatures above 900°C the olive green simple cobalt(II) oxide [1307-96-6], CoO, is obtained. Cobalt metal reacts with carbon dioxide at temperatures greater than 700°C to give cobalt(II) oxide and carbon monoxide.

In the absence of complexing agents and in acidic solution the cobalt(II) hexaaquo ion [15276-47-8] oxidizes with difficulty.

$$Co(H_2O)_6^{3+} + e^- \longrightarrow Co(H_2O)_6^{2+} \qquad E^0 = 1.86\ V$$

Indeed the cobalt(III) ion is sufficiently unstable in water to result in release of oxygen and formation of cobalt(II) ion. Under alkaline conditions the oxidation is much more facile and in the presence of complexing agents, eg, ammonia or cyanide, the oxidation may occur with ease or even spontaneously.

$$CoO(OH)(s) + H_2O + e^- \longrightarrow Co(OH)_2(s) + OH^- \qquad E^0 = 0.17\ V$$

$$Co(NH_3)_6^{3+} + e^- \longrightarrow Co(NH_3)_6^{2+} \qquad E^0 = 0.1\ V$$

$$Co(CN)_6^{3-} + H_2O + e^- \longrightarrow \left[Co(CN)_5(H_2O)\right]^{3-} + CN^- \qquad E^0 = -0.80\ V$$

2. Preparation and Properties

2.1. Cobalt(II) Salts. Cobalt(II) acetate tetrahydrate [71-48-7], $Co(C_2H_3O_2)_2 \cdot 4H_2O$, occurs as pink, deliquescent, monoclinic crystals. It can be prepared by reaction of cobalt carbonate or hydroxide and solutions of acetic acid, by reflux of acetic acid solutions in the presence of cobalt(II) oxide, or by oxygenation of hot acetic acid solutions over cobalt metal. The tetrahydrate is soluble in water, alcohol, and acidic solutions. Dehydration of the crystals occurs at about 140°C. It is used as a bleaching agent (see Bleaching Agents) and drier in inks (qv) and varnishes, and in pigments (qv), catalysis (qv), agriculture, and the anodizing industries (see Drying).

The mauve colored cobalt(II) carbonate [7542-09-8] of commerce is a basic material of indeterminate stoichiometry, $(CoCO_3)_x \cdot (CO(OH)_2)_y \cdot zH_2O$, that contains 45–47% cobalt. It is prepared by adding a hot solution of cobalt salts to a hot sodium carbonate or sodium bicarbonate solution. Precipitation from cold solutions gives a light blue unstable product. Dissolution of cobalt metal in ammonium carbonate solution followed by thermal decomposition of the solution gives a relatively dense carbonate. Basic cobalt carbonate is virtually insoluble in water, but dissolves in acids and ammonia solutions. It is used in the preparation of pigments and as a starting material in the preparation of cobalt compounds.

Cobalt(II) acetylacetonate [14024-48-7], cobalt(II) ethylhexanoate [136-52-7], cobalt(II) oleate [14666-94-5], cobalt(II) linoleate [14666-96-7], cobalt(II) formate [6424-20-0], and cobalt(II) resinate can be produced by metathesis reaction of cobalt salt solutions and the sodium salt of the organic acid, by oxidation of cobalt metal in the presence of the acid, and by neutralization of the acid using cobalt carbonate or cobalt hydroxide.

Cobalt(II) chloride hexahydrate [7791-13-1], $CoCl_2 \cdot 6H_2O$ is a deep red monoclinic crystalline material that deliquesces. It is prepared by reaction of hydrochloric acid with the metal, simple oxide, mixed valence oxides, carbonate, or hydroxide. A high purity cobalt chloride has also been prepared electrolytically (4). The chloride is very soluble in water and alcohols. The dehydration of the hexahydrate occurs stepwise:

$$CoCl_2 \cdot 6H_2O \xrightarrow[-4H_2C]{50^\circ C} CoCl_2 \cdot 2H_2O \xrightarrow[-H_2O]{90^\circ C} CoCl_2 \cdot H_2O \xrightarrow[-H_2O]{140^\circ C} CoCl_2$$

The anhydrous chloride is blue, ie, tetrahedral cobalt, and commonly used as a humidity indicator in desiccants (qv).

Cobalt(II) hydroxide [1307-86-4], $Co(OH)_2$, is a pink, rhombic crystalline material containing about 61% cobalt. It is insoluble in water, but dissolves in acids and ammonium salt solutions. The material is prepared by mixing a cobalt salt solution and a sodium hydroxide solution. Because of the tendency of the cobalt(II) to oxidize, antioxidants (qv) are generally added. Dehydration occurs above 150°C. The hydroxide is a common starting material for the preparation of cobalt compounds. It is also used in paints and lithographic printing inks and as a catalyst (see Paint).

Cobalt(II) nitrate hexahydrate [10026-22-9], $Co(NO_3)_2 \cdot 6H_2O$, is a dark reddish to reddish brown, monoclinic crystalline material containing about 20%

cobalt. It has a high solubility in water and solutions containing 14 or 15% cobalt are commonly used in commerce. Cobalt nitrate can be prepared by dissolution of the simple oxide or carbonate in nitric acid, but more often it is produced by direct oxidation of the metal with nitric acid. Dissolution of cobalt(III) and mixed valence oxides in nitric acid occurs in the presence of formic acid (5). The trihydrate forms at 55°C from a melt of the hexahydrate. The nitrate is used in electronics as an additive in nickel–cadmium batteries (qv), in ceramics (qv), and in the production of vitamin B_{12} [68-19-9] (see VITAMIN B_{12}).

Cobalt(II) oxalate [814-89-1], CoC_2O_4, is a pink to white crystalline material that absorbs moisture to form the dihydrate. It precipitates as the tetrahydrate on reaction of cobalt salt solutions and oxalic acid or alkaline oxalates. The material is insoluble in water, but dissolves in acid, ammonium salt solutions, and ammonia solution. It is used in the production of cobalt powders for metallurgy and catalysis, and is a stabilizer for hydrogen cyanide.

Cobalt(II) phosphate octahydrate [10294-50-5], $Co_3(PO_4)_2 \cdot 8H_2O$, is a red to purple amorphous powder. The product is obtained by reaction of an alkaline phosphate and solutions of cobalt salts. The material is insoluble in water or alkali, but dissolves in mineral acids. The phosphate is used in glazes, enamels, pigments (qv) and plastic resins, and in certain steel (qv) phosphating operations (see ENAMELS, PORCELAIN OR VITREOUS).

Cobalt(II) sulfamate [1407-41-5], $Co(NH_2SO_3)_2$, is generally produced and sold as a solution containing about 10% cobalt. The product is formed by reaction of sulfamic acid and cobalt(II) carbonate or cobalt(II) hydroxide, or by the aeration of sulfamic acid slurries over cobalt metal. Cobalt(II) sulfamate is used in the electroplating (qv) industry and in the manufacture of precision molds for record and compact discs (see INFORMATION STORAGE MATERIALS).

Cobalt(II) sulfate heptahydrate [10026-24-1], $CoSO_4 \cdot 7H_2O$, is a reddish pink monoclinic crystalline material that effloresces in dry air to form the hexahydrate. The dehydration–decomposition occurs according to the following:

$$CoSO_4 \cdot 7H_2O \xrightarrow[-H_2O]{41^\circ C} CoSO_4 \cdot 6H_2O \xrightarrow[-5H_2O]{71^\circ C} CoSO_2 \cdot H_2O \xrightarrow[-H_2O]{250^\circ C} CoSO_4$$

$$3\ CoSO_4 \xrightarrow{710^\circ C} Co_3O_4 + 3\ SO_2 + O_2$$

Cobalt(II) sulfate can be prepared by solution of cobalt(II) carbonate, cobalt(II) hydroxide, or cobalt(II) oxide in sulfuric acid. The digestion of the metal in sulfuric acid solution is assisted by air sparging. Also, cobalt(III) and mixed valence oxides in the presence of formic acid can be dissolved in sulfuric acid solution (5). High concentration (6) and high purity (7) cobalt sulfate solutions have been prepared electrolytically. Cobalt sulfate heptahydrate and cobalt(II) sulfate monohydrate [10124-43-3] are the most economical sources of cobalt ion and are used in feed supplements (see FEEDS AND FEED ADDITIVES) as well as in the electroplating industry, in storage batteries, in porcelain pigments, glazes, and as a drier for inks.

2.2. Cobalt Fluorides. *Cobalt Difluoride.* Cobalt difluoride [10026-17-2], CoF_2, is a pink solid having a magnetic moment of $4,266 \times 10^{-23}$ J/T (4.6 Bohr magneton) (8) and closely resembling the ferrous (FeF_2) compounds. Physical

Table 1. **Physical Properties of the Cobalt Fluorides**

Parameter	Cobalt difluoride[a]	Cobalt trifluoride
molecular weight	96.93	115.93
melting point, °C	1127	926
solubility, g/100 g[b]		
water	1.36	dec
anhydrous HF	0.036	
density, g/cm^3	4.43	3.88
ΔH_f, kJ/mol[c]	−672	−790
ΔG_f, kJ/mol[c]	−627	−719
S, J/(mol · K)[c]	82.4	95
C_p, J/(mol · K)[c]	68.9	92

[a] The bp of CoF_2 is 1739°C.
[b] CoF_2 is also soluble in mineral acids.
[c] To convert J to cal, divide by 4.184.

properties are listed in Table 1. Cobalt(II) fluoride is highly stable. No decomposition or hydrolysis has been observed in samples stored in plastic containers for over three years.

CoF_2 is manufactured commercially by the action of aqueous or anhydrous hydrogen fluoride on cobalt carbonate (see COBALT COMPOUNDS) in a plastic, ie, polyethylene/polypropylene, Teflon, Kynar, rubber, or graphite-lined container to avoid metallic impurities. The partially hydrated mass is lavender pink in color. It is dried at 150−200°C and then pulverized to obtain the anhydrous salt. A very high (99.9%) purity CoF_2 having less than 0.05% moisture content has also been prepared by reaction of $CoCO_3$ and liquid hydrogen fluoride. This is a convenient synthetic route giving quantitative yields of the pure product. The reaction of $CoCl_2$ and anhydrous HF is no longer commercially practical because of environmental considerations. The various hydrates, eg, the cobalt(II) fluoride dihydrate [13455-27-1], $CoF_2 \cdot 2H_2O$, cobalt(II) fluoride trihydrate [13762-15-7], $CoF_2 \cdot 3H_2O$, and cobalt(II) fluoride tetrahydrate [13817-37-3], $CoF_2 \cdot 4H_2O$, have been obtained by the reaction of freshly prepared oxide, hydroxide, or carbonate of cobalt(II) and aqueous hydrogen fluoride (9).

Cobalt difluoride, used primarily for the manufacture of cobalt trifluoride, CoF_3.

Cobalt Trifluoride. Cobalt(III) fluoride [10026-18-3] or cobalt trifluoride, CoF_3, is one of the most important fluorinating reagents. Physical properties may be found in Table 1. It is classified as a hard fluorinating reagent (10) and has been employed in a wide variety of organic and inorganic fluorination reactions. CoF_3, a light brown, very hygroscopic compound, is a powerful oxidizing agent and reacts violently with water evolving oxygen. It should be handled in a dry box or in a chemical hood and stored away from combustibles, moisture, and heat. The material should not be stored in plastic containers for more than two years. The crystals possess a hexagonal structure.

Cobalt trifluoride is readily prepared by reaction of fluorine (qv) and $CoCl_2$ at 250°C or CoF_2 at 150−180°C. Direct fluorination of CoF_2 leads to quantitative yields of 99.9% pure CoF_3 (11).

CoF_3 is used for the replacement of hydrogen with fluorine in halocarbons (12); for fluorination of xylylalkanes, used in vapor-phase soldering fluxes (13); formation of dibutyl decalins (14); fluorination of alkynes (15); synthesis of unsaturated or partially fluorinated compounds (16–18); and conversion of aromatic compounds to perfluorocyclic compounds (see FLUORINE COMPOUNDS, ORGANIC). CoF_3 rarely causes polymerization of hydrocarbons. CoF_3 is also used for the conversion of metal oxides to higher valency metal fluorides, eg, in the assay of uranium ore (19). It is also used in the manufacture of nitrogen fluoride, NF_3, from ammonia (20).

2.3. Cobalt Oxides. Cobalt(II) oxide [1307-96-6], CoO, is an olive green, cubic crystalline material. The product of commerce is usually dark gray and contains 75–78 wt% cobalt. The simple oxide is most often produced by oxidation of the metal at temperatures above 900°C. The product must be cooled in the absence of oxygen to prevent formation of Co_3O_4. Cobalt(II) oxide is insoluble in water, ammonia solutions, and organic solvents, but dissolves in strong mineral acids. It is used in glass (qv) decorating and coloring and is a precursor for the production of cobalt chemicals.

Cobalt(II) dicobalt(III) tetroxide [1308-06-1], Co_3O_4, is a black cubic crystalline material containing about 72% cobalt. It is prepared by oxidation of cobalt metal at temperatures below 900°C or by pyrolysis in air of cobalt salts, usually the nitrate or chloride. The mixed valence oxide is insoluble in water and organic solvents and only partially soluble in mineral acids. Complete solubility can be effected by dissolution in acids under reducing conditions. It is used in enamels, semiconductors, and grinding wheels. Both oxides adsorb molecular oxygen at room temperatures.

2.4. Cobalt Carbonyls. Dicobalt octacarbonyl [15226-74-1], $Co_2(CO)_8$, is an orange-red solid that decomposes in air. It is prepared by heating cobalt metal to 300°C under 20–30,000 kPa (3–4000 psi) of carbon monoxide, by reduction of cobalt(II) carbonate with hydrogen under pressure at high temperatures, or by heating a mixture of cobalt(II) acetate and cyclohexane to 160°C in the presence of carbon monoxide and hydrogen at 30,000 kPa (4000 psi) pressure. The octa-carbonyl is reduced with sodium amalgam and acidified to yield tetracarbonylhy-dridocobalt [16842-03-8], $HCo(CO)_4$, a yellow liquid that is an active oxo catalyst (see CARBONYLS; OXO PROCESS).

3. Economic Aspects

Approximately 51% of U.S. cobalt use was in superalloys, 8% was in cemented carbides, 19% was in various other metallic uses, and the remaining 22% was in a variety of chemical uses (1) (see Table 2). Tables 3 and 4 give U.S imports for consumption of cobalt and U.S. exports of cobalt materials (21).

4. Analytical Methods

Typical analyses of selected cobalt compounds are given in Table 5.

4.1. Separation. 1-Nitroso-2-naphthol [131-91-9], $C_{10}H_7NO_2$, can be used for the preliminary separation of cobalt from other metals by extraction

Table 2. **U.S. Reported Consumption of Cobalt, by End Use, t Contained Cobalt**[a,b]

End use	2001	2002
steel	624	543
superalloys	4,850	3,970
magnetic alloys	472	374
other alloys[c]	661	W
cemented carbides[d]	720	747
chemical and ceramic uses[e]	2,100	1,860
miscellaneous and unspecified	63	300
Total	*9,490*	*7,790*

[a] Ref. 21; W = Withheld to avoid disclosing company proprietary data; included with "Miscellaneous and unspecified."
[b] Data are rounded to no more than three significant digits; may not add to totals shown.
[c] Includes nonferrous alloys, welding materials, and wear-resistant alloys.
[d] Includes diamond tool matrices, cemented and sintered carbides, and cast carbide dies or parts.
[e] Includes catalysts, driers in paints or related usage, feed or nutritive additive, glass decolorizer, ground coat frit, pigments, and other uses.

into chloroform (22,23). Cobalt can be separated from cadmium, lead, and zinc by extraction using dithizone [60-10-6], $C_{13}H_{12}N_4S$, at pH 6–10 followed by hydrolysis in dilute HCl. The more stable cobalt complex remains in the organic extract. The formation of stable anionic halide complexes allow for the separation from nickel. Extraction of the complexes is effected by amines such as triisooctylamine, trioctyl-methylammonium salts, or strongly basic anionic resins. Nickel and chromium do not form anionic chloride complexes and are not extracted under conditions of the experiment. Copper, zinc, and iron can be eluted from basic anionic resins using 0.01 *M* HCl whereas cobalt is eluted with 4 *M* HCl. Cobalt can also be separated from nickel as the sulfate salt by extraction with bis(2,4,4-trimethylpentyl)phosphinic acid. The blue thiocyanate complex of cobalt can be extracted into a mixture of ether and amyl alcohol to bring about separation from nickel and iron(III) in the presence of citrate ion (24). Manganese can be separated from cobalt by chlorination at a pH of 2.0. Cobalt sulfate is separated from a variety of metals using a chelating ion-exchange (qv) resin (25).

Cobalt(II) can be separated from cobalt(III) as the acetylacetonate (acac) compounds by extraction of the benzene soluble cobalt(III) salt (26). Magnesium hydroxide has been used to selectively adsorb cobalt(II) from an ammonia solution containing cobalt(II) and cobalt(III) (27).

4.2. Determination. Pure cobalt compounds can be assayed by EDTA titration at 40°C using hexamine [100-97-0], $C_6H_{12}N_4$, buffer (pH = 6) to a xylenol orange endpoint. Cobalt and nickel can be determined by cyanometry (28) or potentiometric titration using ferricyanide (29) can be used in the presence of large amounts of nickel, zinc, or copper. Colorimetry can be used to determine large amounts of cobalt by formation of the blue thiocyanate complex,

Table 3. **U.S. Imports for Consumption of Cobalt, by Country**[a,b]

Period and country of origin	Metals[c]		Oxides and hydroxides		Salts and compounds[d]		Cobalt content, year to date[f]
	Quantity, kg	Value, $[e]	Quantity, kg	Value, $[e]	Quantity, kg	Value, $[e]	
Australia	2,970	42,200					162,000
Belgium	43,300	686,000	31,000	396,000			804,000
Brazil	49,000	860,000					269,000
Canada	56,000	926,000					818,000
China			596	17,900			40,500
Congo (Kinshasa)							271,000
Finland	62,200	1,070,000	33,500	370,000	182,000	554,000	1,840,000
France	2,910	150,000	4,060	84,600			55,200
Germany							45,800
Japan					4,000	37,400	22,800
Korea, Republic of	54	3,440					669
Morocco							56,000
Netherlands							54,400
Norway	51,000	782,000					1,590,000
Philippines					9,070	65,300	33,700
Russia	17,900	252,000					952,000
South Africa	20,000	274,000	1,360	21,300			230,000
Sweden	1,330	46,200					26,900
Switzerland							3
Uganda							44,000
United Kingdom			6,480	148,000			148,000
Zambia							278,000
Total	*307,000*	*5,090,000*	*77,000*	*1,040,000*	*195,000*	*657,000*	*7,740,000*

[a] Ref. 21.

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

[c] Unwrought cobalt, excluding alloys; includes cobalt cathode and cobalt metal powder.

[d] Includes cobalt acetates, cobalt carbonates, cobalt chlorides, and cobalt sulfates.

[e] Customs value.

[f] Oct. 2002.

Source: U.S. Census Bureau, with adjustments by the U.S. Geological Survey.

$Co(SCN)^{2-}$;$_4$. An excellent discussion of interferences and their elimination is available (30). Colorimetric methods using nitroso-naphthols (31,32) or nitroso-R salt [525-05-3], $C_{10}H_5NNa_2O_8S_2$ (33,34) are quite specific for cobalt, but not particularly sensitive. 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) is a very sensitive reagent for certain metals and methods for cobalt have been developed (35). Nitroso-naphthol is an effective precipitant for cobalt(III) and is used in its gravimetric determination (36,37). Atomic absorption spectroscopy (38,39), x-ray fluorescence, polarography, and atomic emission spectroscopy are specific and sensitive methods for trace level cobalt analysis (see Spectroscopy, Optical; Trace and Residue analysis).

Table 4. **U.S. Exports of Cobalt Materials**[a]

Period	Unwrought cobalt, powders, matte, waste and scrap[b]		Oxides and hydroxides		Salts and compounds[c]		Total cobalt content for the month[e,f]	Cobalt content, year to date[c,f]
	Quantity, kg	Value, \$[d]	Quantity, kg	Value, \$[d]	Quantity, kg	Value, \$[d]		
2001:								
November	306,000	4,520,000	41,600	581,000	7,770	34,300	338,000	3,000,000
December	182,000	3,220,000	32,500	701,000	9,110	77,100	207,000	3,210,000
January–December	2,240,000	7,300,000	1,260,000	10,200,000	254,000	1,980,000	3,210,000	XXg
2002:								
January	127,000	2,870,000	25,600	379,000	14,100	98,500	149,000	149,000
April	161,000	3,690,000	35,500	483,000	19,000	97,200	191,000	662,000
July	69,700	1,680,000	62,800	1,150,000	12,200	52,700	118,000	1,200,000
November	173,000	3,520,000	47,000	741,000	61,700	233,000	221,000	1,92,0000

[a] Ref. 21; data are rounded to no more than three significant digits; may not add to totals shown.

[b] May include other intermediate products of cobalt metallurgy and unwrought cobalt alloys.

[c] Cobalt acetates and cobalt chlorides.

[d] Free alongside ship (f.a.s.) value.

[e] Estimated from gross weights.

[f] Year to date may include revisions to prior months.

[g] XX, not applicable.

Source: U.S. Census Bureau, with adjustments by the U.S. Geological Survey.

Table 5. **Analysis of Cobalt Compounds**[a]

Assay, wt%	Acetate tetrahydrate	Carbonate	Chloride hexahydrate	Hydroxide	Nitrate	Mixed oxide[b]	Sulfate hexahydrate	Sulfate feed grade
Co	23.5	46.0	24.8	61.0	20.3	71.0	21.0	21.0
Ni	0.04–0.10	0.1–0.3	0.07–0.1	0.1–0.2	0.03–0.10	0.15–0.35	0.05	0.10
Fe	0.005–0.015	0.1–0.6	0.005	0.01–0.10	0.001–0.002	0.05–0.20	0.001–0.002	0.01
Cu	0.0005		0.002	0.01	0.004	0.008–0.02	0.001–0.004	0.005
Mn	0.001–0.01	0.006		0.015	0.005	0.03–0.3	0.002	0.005
Pb		0.01	0.002	0.005	0.001	0.02	0.001	0.001
HCl insols[c]				0.02		0.01		
H_2O insols[c]	0.007–0.015				0.01		0.05	0.10
ABD[d], kg/m^3	940	660	1000	350	950	1500	1000	1000

[a] All materials are technical-grade cobalt(II) compounds unless indicated.

[b] Material is Co_3O_4.

[c] Insols = insoluable material.

[d] ABD = apparent bulk density.

5. Health and Safety Factors

Cobalt is one of twenty-seven known elements essential to humans (40) (see MINERAL NUTRIENTS). It is an integral part of the cyanocobalamin [68-19-9] molecule, ie, vitamin B_{12}, the only documented biochemically active cobalt component in humans (41,42) (see VITAMINS, VITAMIN B_{12}). Vitamin B_{12} is not synthesized by animals or higher plants, rather the primary source is bacterial flora in the digestive system of sheep and cattle (43). Except for humans, nonruminants do not appear to require cobalt. Humans have between 2 and 5 mg of vitamin B_{12}, and deficiency results in the development of pernicious anemia. The wasting disease in sheep and cattle is known as bush sickness in New Zealand, salt sickness in Florida, pine sickness in Scotland, and coast disease in Australia. These are essentially the same symptomatically, and are caused by cobalt deficiency. Symptoms include initial lack of appetite followed by scaliness of skin, lack of coordination, loss of flesh, pale mucous membranes, and retarded growth. The total laboratory synthesis of vitamin B_{12} was completed in 65–70 steps over a period of eleven years (44). The complex structure was reported by Dorothy Crowfoot-Hodgkin in 1961 (45) for which she was awarded a Nobel prize in 1964.

Cobalt compounds can be classified as relatively nontoxic (46). There have been few health problems associated with workplace exposure to cobalt. The primary workplace problems from cobalt exposure are fibrosis, also known as hard metal disease (47,48), asthma, and dermatitis (49). Finely powdered cobalt can cause silicosis. There is little evidence to suggest that cobalt is a carcinogen in animals and no epidemiological evidence of carcinogenesis in humans. The LD_{50} (rat) for cobalt powder is 1500 mg/kg. The oral LD_{50} (rat) for cobalt(II) acetate, chloride, nitrate, oxide, and sulfate are 194, 133, 198, 1700, 5000, and 279 mg/kg, respectively; the intraperitoneal LD_{50} (rat) for cobalt(III) oxide is 5000 mg/kg (50).

Several nonoccupational health problems have been traced to cobalt compounds. Cobalt compounds were used as foam stabilizers in many breweries throughout the world in the mid to late 1960s, and over 100 cases of cardiomyopathy, several followed by death, occurred in heavy beer drinkers (51,52). Those affected consumed as much as 6 L/d of beer (qv) and chronic alcoholism and poor diet may well have contributed to this disease. Some patients treated with cobalt(II) chloride for anemia have developed goiters and polycythemia (53). The impact of cobalt on the thyroid gland and blood has been observed (54).

For cobalt fluorides , ACGIH TLV, NIOSH TWA are both 2.5 mg (F)/m^3 (55).

The ACGIH TLV for cobalt metal, dust, and fumes is 0.02 mg (Co)/mg^3, the OSHA PEL is 0.05 mg/m^3 (55).

6. Uses

The uses of cobalt compounds are summarized in Table 6.

6.1. Cobalt in Catalysis.

About 80% of cobalt catalysts are employed in three areas: (*1*) hydrotreating/desulfurization in combination with molybdenum for the oil and gas industry (see SULFUR REMOVAL AND RECOVERY); (*2*) homogeneous catalysts used in the production of terphthalic acid or dimethylterphthalate (see

Table 6. **Uses of Cobalt Compounds**[a]

Compound	CAS Registry number	Molecular formula	Molecular weight	Uses
cobalt(III) acetate	[917-69-1]	$Co(C_2H_3O_2)_3$	235.9	catalyst, powder
cobalt(II) acetate tetrahydrate	[71-48-7]	$Co(C_2H_3O_2)_2 \cdot 4H_2O$	248.9	drier for lacquers and varnishes, sympathetic inks, catalyst, pigment for oil cloth, mineral supplement, anodizing agent
cobalt(II) acetylacetonate	[14024-48-7]	$Co(C_5H_7O_2)_3$	355.9	vapor plating of cobalt, catalyst synthesis enamels
cobalt(II) aminobenzoate		$Co(C_7H_6NO_2)_2$	194.9	tire cord adhesion
cobalt(II) ammonium sulfate	[13586-38-4]	$CoSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	394.9	catalyst, plating solutions
cobalt(II) bromide	[7789-43-7]	$CoBr_2$	218.7	catalyst, hydrometers
cobalt(II) carbonate	[513-79-1]	$CoCO_3 \cdot Co(OH)_2$	118.9	pigment, ceramics, feed supplement, catalyst, fodder fat stabilizer
cobalt(II) carbonate (basic)	[7542-09-8]	$2CoCO_3 \cdot Co(OH)_2 \cdot H_2O$	348.7	chemicals
dicobalt octacarbonyl	[15226-74-1]	$Co_2(CO)_8$	341.8	catalyst, powder
cobalt(II) chloride	[7791-13-1]	$CoCl_2 \cdot 6H_2O$	237.9	chemicals, sympathetic inks, hydrometers, plating baths, metal refining, pigment, catalyst, dyestuffs, magnetic recording materials, moisture indicators
cobalt(II) citrate	[18727-04-3]	$Co_3(C_6H_5O_7)_2 \cdot 2H_2O$	590.7	therapeutic agents, vitamin preparations, plating baths
cobalt(II) fluoride	[10026-17-2]	CoF_2	96.7	fluorinating agent
cobalt(II) fluoride tetrahydrate	[13817-37-3]	$CoF_2 \cdot 4H_2O$	168.7	catalyst
cobalt(III) fluoride	[10026-18-3]	CoF_3	115.6	fluorinating agent

Table 6 (*Continued*)

Compound	CAS Registry number	Molecular formula	Molecular weight	Uses
cobalt(II) fluorosilicate hexahydrate	[15415-49-3]	$CoSiF_6 \cdot 6H_2O$	308.3	ceramics
cobalt(II) formate	[6424-20-0]	$Co(CHO_2)_2 \cdot 2H_2O$	184.9	catalyst
cobalt(II) hydroxide	[1307-86-4]	$Co(OH)_2$	92.9	paints, chemicals, catalysts, printing inks, battery materials, powder
cobalt(II) iodide	[15238-00-3]	CoI_2	312.7	moisture indicator
cobalt(II) linoleate	[14666-96-7]	$Co(C_{18}H_{31}O_2)_2$	616.9	paint and varnish drier
cobalt(II) naphthenate		$Co(C_{11}H_{10}O_2)_2$	406.9	catalyst, paint and varnish drier, tire cord adhesive, antistatic adhesive
cobalt(II) nitrate hexahydrate	[10026-22-9]	$Co(NO_3)_2 \cdot 6H_2O$	290.9	pigments, chemicals, ceramics, feed supplements, catalysts, battery materials
cobalt(II) 2-ethyl-hexanoate	[136-52-7]	$Co(C_{18}H_{15}O_2)_2$	344.9	paint and varnish drier, adhesion additive
cobalt(II) oleate	[14666-94-5]	$Co(C_{18}H_{33}O_2)_2$	620.9	paint and varnish drier, antistatic adhesive
cobalt(II) oxalate	[814-89-1]	CoC_2O_4	146.9	catalysts, cobalt powders
cobalt phthalocyanine		Co(pc)	572.9	coating, conducting polymer
cobalt(II) potassium nitrite	[17120-39-7]	$K_3Co(NO_2)_6 \cdot 1.5H_2O$	478.9	pigment
cobalt(II) resinate		$Co(C_{44}H_{62}O_4)_2$	1366.9	paint and varnish drier, catalyst
cobalt Schiff-base complexes				oxygen-sensing and oxygen-indicating agents
cobalt(II) stearate	[13586-84-0]	$Co(C_{18}H_{35}O_2)_2$	624.9	paint and varnish drier, tire cord adhesive
cobalt(II) succinate trihydrate	[3267-76-3]	$Co(C_4H_4O_4) \cdot 3H_2O$	228.9	therapeutic agents, vitamin preparations

Table 6 (*Continued*)

Compound	CAS Registry number	Molecular formula	Molecular weight	Uses
cobalt(II) sulfamate		$Co(NH_2SO_3) \cdot 3H_2O$	208.9	plating baths
cobalt(II) sulfate	[10026-24-1]	$CoSO_4 \cdot xH_2O$	154.9	chemicals, ceramics, pigments, plating baths, dyestuffs, magnetic recording materials, anodizing agents, corrosion protection agent
cobalt(II) sulfide	[1317-42-6]	CoS	90.0	catalysts
cobalt(II) thiocyanate	[3017-60-5]	$Co(CNS)_2 \cdot 3H_2O$	174.9	humidity indicator, drug testing
cobalt(II) aluminate	[13820-62-7]	$CoAl_2O_4$	176.7	pigment, catalysts, grain refining
cobalt(II) arsenate	[24719-19-5]	$Co_3(AsO_4)_2 \cdot 8H_2O$	598.5	pigment for paint, glass, and porcelain, vapor plating
cobalt(II) chromate	[24613-38-5]	$CoCrO_4$	174.8	pigment
cobalt(II) ferrate	[12052-28-7]	$CoFe_2O_4$	234.5	catalyst, pigment
cobalt(II) manganate	[12139-69-4]	$CoMn_2O_4$	232.7	catalyst, electrocatalyst
cobalt(II) oxide	[1307-96-6]	CoO	74.9	chemicals, catalysts, pigments, ceramic gas sensors, thermistors
cobalt oxide	[1308-06-1]	Co_3O_4	240.7	enamels, semiconductors, solar collectors pigments, magnetic recording materials
cobalt dilanthanum tetroxide	[39449-41-7]	La_2CoO_4	400.7	anode, catalyst
tricobalt tetralanthanum decaoxide	[60241-06-7]	$La_4Co_3O_{10}$	892.3	catalyst
lithium cobalt dioxide	[12190-79-3]	$LiCoO_2$	97.8	battery electrode
sodium cobalt dioxide	[37216-69-6]	$NaCoO_2$	113.8	battery electrode
dicobalt manganese tetroxide	[12139-92-3]	$MnCo_2O_4$	236.7	catalyst

Table 6 (*Continued*)

Compound	CAS Registry number	Molecular formula	Molecular weight	Uses
dicobalt nickel tetroxide	[12017-35-5]	$NiCo_2O_4$	240.5	anode, catalyst
lanthanum cobalt trioxide	[12016-86-3]	$LaCoO_3$	245.8	oxygen electrode
cobalt(II) phosphate	[10294-50-5]	$Co_3(PO_4)_2 \cdot 8H_2O$	510.9	glazes, enamels, pigments, steel pretreatment
cobalt(II) tungstate	[12640-47-0]	$CoWO_4$	305.7	paint and varnish drier

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PHTHALIC ACID AND OTHER BENZENE POLYCARBOXYLIC ACIDS); and (*3*) the high pressure oxo process for the production of aldehydes (qv) and alcohols (see ALCOHOLS, HIGHER ALIPHATIC; ALCOHOLS, POLYHYDRIC). There are also several smaller scale uses of cobalt as oxidation and polymerization catalysts (57–59).

Cobalt's ability to actively catalyze reactions comes from one or more of the following properties (56): (*1*) the facile redox properties of the element, the ability to form stable species in multiple oxidation states, and the ease of electron transfer between the oxidation states via unstable intermediates or free radicals; (*2*) the ability to form complexes with suitable donor groups and the relative stabilities of those complexes; (*3*) the ability of cobalt to form complexes of varying coordination number and to exist in equilibrium in more than one stereochemical form; (*4*) the ability to undergo equilibrium decomposition reactions such as $Co(RCOO)_2 \rightleftharpoons Co^{2+} + 2\,RCOO^-$ in polymerization systems. The decomposition products may take part in the catalysis; (*5*) cobalt complexes are able to undergo ligand exchange reactions which can be important in assisting catalysis. This is an example of vitamin B_{12}'s activity as a catalyst; and (*6*) cobalt oxides and sulfides, because of lattice vacancies, bond energies, or electronic effects, are active heterogenous catalysts.

The breadth of reactions catalyzed by cobalt compounds is large. Some types of reactions are hydrotreating petroleum (qv), hydrogenation, dehydrogenation, hydrodenitrification, hydrodesulfurization, selective oxidations, ammonoxidations, complete oxidations, hydroformylations, polymerizations, selective decompositions, ammonia (qv) synthesis, and fluorocarbon synthesis.

Hydrotreating Catalysts. A preliminary step in refining of crude oil feedstocks is the removal of metals, significant reduction of the organic sulfur and nitrogen constituents, and reduction of the molecular weight of the high molecular-weight fraction. This step is called hydrotreating and it typically employs a catalyst of cobalt and molybdenum on a high surface area alumina or silica support. Hydrotreating of a nominal 4000 cubic meters (25,000 barrel) per day operation produces 200 tons per day of sulfur and deposits ca 450 kg of metal, primarily vanadium and nickel, on the catalyst (60) which must be sulfur tolerant.

The primary reactions occurring during hydrotreating are (56) desulfurization of sulfides, polysulfides, mercaptans, and thiophene as exemplified by

$$R—S—R' + 2\,H_2 \longrightarrow RH + R'H + H_2S$$

denitrification of pyridine and pyrrole resulting in the corresponding alkane and ammonia; deoxygenation of phenol; hydrogenation of alkenes and aromatics, eg, of butadiene and benzene; and hydrocracking of alkanes such as n-decane

$$C_{10}H_{22} + H_2 \longrightarrow 2\,C_5H_{12}$$

Hydrodesulfurization, by far the most common hydrotreating reaction, usually occurs in the presence of a cobalt–molybdenum catalyst support on alumina. Hydrodesulfurization constitutes the largest single use of cobalt in catalysis (qv). These catalysts are not easily poisoned, are regenerable numerous times, and usable for several years. The catalysts are prepared by precipitation of cobalt and molybdate solutions in the presence of an alumina support, by mixing the dried components in powder form, by precipitation of the three components, or by impregnation of the support with solutions of cobalt salts and molybdic acid or ammonium molybdate. The material is calcined at about 600°C to produce oxides of the cobalt–molybdenum–alumina followed by activation by reduction–sulfidation to yield the cobalt–molybdenum sulfide catalyst. The activity of the catalyst depends on several factors: type of support, ratio of cobalt to molybdenum, content of cobalt and molybdenum, impregnation procedure, calcination conditions, and reduction–sulfidation (61,62). The cobalt content is commonly between 2.5 and 3.7 wt%.

Homogeneous Oxidation Catalysts. Cobalt(II) carboxylates, such as the oleate, acetate, and naphthenate, are used in the liquid-phase oxidations of p-xylene to terephthalic acid, cyclohexane to adipic acid, acetaldehyde (qv) to acetic acid, and cumene (qv) to cumene hydroperoxide. These reactions each involve a free-radical mechanism that for the cyclohexane oxidation can be written as

initiation $$C_6H_{12} + R\cdot \longrightarrow C_6H_{11} + RH$$

chain $$C_6H_{11} + O_2 \longrightarrow C_6H_{11}OO\cdot$$

$$C_6H_{11}OO\cdot + C_6H_{12} \longrightarrow C_6H_{11}OOH + C_6H_{11}$$

decomposition $$C_6H_{11}OOH \longrightarrow C_6H_{10}O + H_2O$$

$$Co^{2+} + C_6H_{11}OOH \longrightarrow Co^{3+} + C_6H_{11}O\cdot + OH^- \longrightarrow C_6H_{12}$$

$$Co^{3+} + C_6H_{11}OOH \longrightarrow Co^{2+} + C_6H_{11}OO\cdot + H^+ \longrightarrow \text{chain}$$

Cobalt-catalyzed oxidations form the largest group of homogeneous liquid-phase oxidations in the chemical industry.

Oxo or Hydroformylation and Hydroesterification. Reactions of alkenes with hydrogen and formyl groups are catalyzed by $HCo(CO)_4$

$$HCo(CO)_4 + RCH{=\!=}CH_2 \longrightarrow RCH_2CH_2Co(CO)_4$$

$$RCH_2CH_2Co(CO)_4 + CO \longrightarrow RCH_2CH_2COCo(CO)_4$$

$$RCH_2CH_2COCo(CO)_4 + H_2 \longrightarrow RCH_2CH_2COH + HCo(CO)_4$$

and hydroesterification occurs according to

$$R{-\!-}CH{=\!=}CH_2 + R'OH + CO \longrightarrow RCH_2CH_2COOR'$$

The oxo reactions occur under 10,000–30,000 kPa (1450–4000 psi) of synthesis gas at temperatures of 75–200°C. Oxo syntheses account for the third largest use of cobalt in catalysis.

Cobalt compounds are used as catalysts in several processes of lesser industrial importance. Fischer-Tropsch catalysts produced from cobalt salts produce less methane than the corresponding iron catalysts. The chemistry of carboxylation reactions catalyzed in the presence of cobalt is also rich (63). Cobalt cyanide can be used to hydrogenate a broad range of organic and inorganic materials. Exhaust gas purification including oxidation of carbon monoxide and nitrogen monoxide is effected in the presence of Co_3O_4 (see EXHAUST CONTROL, INDUSTRIAL). The oxide is also effective in the production of nitric acid (qv) from ammonia. Cobalt carboxylates are used in the adhesive industry as cross-linking and polymerization catalysts (see ADHESIVES).

Cobalt in Driers for Paints, Inks, and Varnishes. The cobalt soaps, eg, the oleate, naphthenate, resinate, linoleate, ethylhexanoate, synthetic tertiary neodecanoate, and tall oils, are used to accelerate the natural drying process of unsaturated oils such as linseed oil and soybean oil. These oils are esters of unsaturated fatty acids and contain acids such as oleic, linoleic, and eleostearic. On exposure to air for several days a film of the acids convert from liquid to solid form by oxidative polymerization. The incorporation of oil-soluble cobalt salts effects this drying process in hours instead of days. Soaps of manganese, lead, cerium, and vanadium are also used as driers, but none are as effective as cobalt (see DRYING).

A film of drying oils undergoes a series of reactions, but the primary reaction is autooxidation polymerization where oxygen attacks a carbon adjacent to a double bond forming a hydroperoxide. Once peroxide formation begins, dissociation into free radicals occurs giving polymers having carbon–carbon, carbon–oxygen–carbon, alcohol, ketone, aldehyde, and carboxylic acid linkages (56). The reactions depend on drying conditions and properties of the dried film may change.

The concentration of drier also effects the rate and physical characteristics of the dried film. In dryer combinations cobalt is considered a surface oxidation catalyst, whereas driers such as lead are considered a through drier or polymerization catalyst. Lead, cerium, manganese, and iron soaps are often used in combination with cobalt to slow down the rate of drying. Zinc and calcium soaps are not active as driers, but can also be used as cobalt diluents to slow down the drying rate. The mixture of metal soaps determines the rate of drying as well as the properties of the final dried film. Coordination driers such as aluminum and zirconium soaps aid the cross-linking polymerization process and are always used along with an oxidative polymerization catalyst.

For water-based alkyd paints, greater (0.2% cobalt on a resin basis) concentrations of drier are required than for other systems because the reaction of the drier with water decreases the activity of the catalyst. The cobalt content of oil-based paint formulations is usually 0.01–0.05% cobalt. Although the concentration of cobalt in the formulations is small, the large volume of paints, inks, and varnishes constitute a significant use for cobalt chemicals.

6.2. Cobalt as a Colorant in Ceramics, Glasses, and Paints.

Cobalt(II) ion displays a variety of colors in solid form or solution ranging from pinks and reds to blues or greens. It has been used for hundreds of years to impart color to glasses and ceramics (qv) or as a pigment in paints and inks (see COLORANTS FOR CERAMICS). The pink or red colors are generally associated with cobalt(II) ion in an octahedral environment and the chromophore is typically $Co{-}O_6$. The tetrahedral cobalt ion, $Co{-}O_4$ chromophore, is sometimes green, but usually blue in color.

Cobalt pigments are usually produced by mixing salts or oxides and calcining at temperatures of 1100–1300°C. The calcined product is then milled to a fine powder. In ceramics, the final color of the pigment may be quite different after the clay is fired. The materials used for the production of ceramic pigments are

Color	Ingredients
purple	$Co_3O_4{-}Al_2O_3{-}MgO$
blues	$Co_3O_4{-}SiO_2{-}CaO$
Thenard blue	$Co_3O_4{-}Al_2O_3$
blue-greens	$Co_3O_4{-}Cr_2O_3{-}Al_2O_3$
blue-black	$Co_3O_4{-}Fe_2O_3{-}Cr_2O_3$
black	$Co_3O_4{-}Cr_2O_3{-}Fe_2O_3{-}MnO_2{-}Ni_2O_3$

Paint pigments do not change colors on application. Other common colors are violet from cobalt(II) phosphate [18475-47-3], pink from cobalt and magnesium oxides, aureolin yellow from potassiuim cobalt(III) nitrite [13782-01-9], $KCo(NO_2)_4$, and cerulean blue from cobalt stannate [6546-12-5]. Large quantities of cobalt are used at levels of a few ppm to decolorize or whiten glass and ceramics. Iron oxide or titanium dioxide often impart a yellow tint to various domestic ware. The cobalt blue tends to neutralize the effect of the yellow.

Cobalt is used in ceramic pigments and designated as underglaze stains, glaze stains, body stains, overglaze colors, and ceramic colors. The underglaze is applied to the surface of the article prior to glazing. The glaze stain uses cobalt colorants in the glaze. A body stain is mixed throughout the body of the ceramic. Overglaze colors are applied to the surface and fired at low temperatures. Ceramic colors are pigments used in a fusible glass or enamel and are one of the more common sources of the blue coloration in ceramics, china, and enamel ware.

Cobalt oxides are used in the glass (qv) industry to color or decolorize. Usually the cobalt is tetrahedrally coordinated and the color that it imparts to the glass is blue. Some special low temperature glasses contain pink, octahedrally, coordinated cobalt. These pink glasses turn blue on heating. The blue color from cobalt is very stable and its intensity easily controlled by doping rates. A discernable tint can be noticed for glass containing only a few parts per million of cobalt ion. The more typical blue cobalt glass usually contains closer to 200 ppm cobalt.

Cobalt is used as a blue phosphor in cathode ray tubes for television, in the coloration of polymers and leather goods, and as a pigment for oil and watercolor paints. Organic cobalt compounds that are used as colorants usually contain the azo (64) or formazon (65) chromophores.

6.3. Miscellaneous Uses. *Adhesives in the Tire Industry.* Cobalt salts are used to improve the adhesion of rubber to steel. The steel cord must be coated with a layer of brass. During the vulcanization of the rubber, sulfur species react with the copper and zinc in the brass and the process of copper sulfide formation helps to bond the steel to the rubber. This adhesion may be further improved by the incorporation of cobalt soaps into the rubber prior to vulcanization (66,67) (see TIRE CORDS).

Adhesion of Enamel to Steel. Cobalt compounds are used both to color and to enhance adhesion of enamels to steel (68). Cobalt oxide is often incorporated into the ground frit at rates of 0.5–0.6 wt%, although levels from 0.2 to 3 wt% have been used. The frit is fired for ten minutes at 850°C to give a blue enamel that is later coated with a white cover coat.

Agriculture and Nutrition. Cobalt salts, soluble in water or stomach acid, are added to soils and animal feeds to correct cobalt deficiencies. In soil application the cobalt is readily assimilated into the plants and subsequently made available to the animals (69). Plants do not seem to be affected by the cobalt uptake from the soil. Cobalt salts are also added to salt blocks or pellets (see FEEDS AND FEED ADDITIVES).

Electroplating. Cobalt is plated from chloride, sulfate, fluoborate, sulfamate, and mixed anionic baths (70). Cobalt alloyed with nickel, tungsten, iron, molybdenum, chromium, zinc, and precious metals are plated from mixed metal baths (71,72). A cobalt phosphorus alloy is commonly plated from electroless baths. Cobalt tungsten and cobalt molybdenum alloys are produced for their excellent high temperature hardness. Magnetic recording materials are produced by electroplating cobalt from sulfamate baths (73) and phosphorus-containing baths or by electroless plating of cobalt from baths containing sodium hypophosphite as the reducing agent. Cobalt is added to nickel electroplating baths to enhance hardness and brightness or for the production of record and compact discs (74).

Electronic Devices. Small quantities of cobalt compounds are used in the production of electronic devices such as thermistors, varistors, piezoelectrics (qv), and solar collectors. Cobalt salts are useful indicators for humidity. The blue anhydrous form becomes pink (hydrated) on exposure to high humidity. Cobalt pyridine thiocyanate is a useful temperature indicating salt. A conductive paste for painting on ceramics and glass is composed of cobalt oxide (75).

Batteries and Fuel Cells. Cobalt salts are used as activators for catalysts, fuel cells (qv), and batteries. Thermal decomposition of cobalt oxalate is used in the production of cobalt powder. Cobalt compounds have been used as selective absorbers for oxygen, in electrostatographic toners, as fluoridating agents, and in molecular sieves.

Cure Accelerator. Cobalt ethylhexanoate and cobalt naphthenate are used as accelerators with methyl ethyl ketone peroxide for the room temperature cure of polyester resins.

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