ZINC COMPOUNDS

1. Introduction

Zinc usually occurs as the sulfide, but significant quantities of the oxide, carbonate, silicate [14374-77-7], and basic compounds of the latter two are also mined (see ZINC AND ZINC ALLOYS).

2. Properties

Zinc is in Group 12 (IIB) of the Periodic Table and exhibits a valence of +2 in all its compounds. Being high on the electromotive series, zinc forms quite stable compounds and, as such, resembles magnesium. Bonding in zinc compounds tends to be covalent, as in the sulfide and oxide. With strongly electropositive elements, eg, chlorine, the bond is more ionic. Zinc also tends to form stable covalent complex ions, eg, with ammonia $[Zn(NH_3)_2]^{2+}$, cyanide $[Zn(CN)_4]^{2-}$, and hydroxyl $[Zn(OH)_4]^{2-}$. The coordination number is usually 4, to a lesser degree 6, and in some cases 5. A good review of zinc compounds is given in Ref. 1.

Zinc forms salts with acids, but since it is amphoteric, it also forms zincates, eg, $[Zn(OH)_3 \cdot H_2O]^-$ and $[Zn(OH)_4]^{2-}$. The tendency of zinc to form stable hydroxy complexes is also important because some basic zinc salts are only slightly soluble in water. Examples are $3\,Zn(OH)_2{\cdot}ZnSO_4$ [12027-98-4] and $4\,Zn(OH)_2 \cdot ZnCl_2$ [11073-22-6], which may precipitate upon neutralization of acidic solutions of the salts.

Properties of zinc salts of inorganic and organic salts are listed in Table 1 with other commercially important zinc chemicals. In the dithiocarbamates, 2-mercaptobenzothiazole and formaldehyde sulfoxylate, zinc is covalently bound to sulfur. In compounds, such as the oxide, borate, and silicate, the covalent bonds with oxygen are very stable. Zinc–carbon bonds occur in diorganozinc compounds, eg, diethylzinc [557-20-0]. Such compounds were used much more in organic synthesis prior to the development of the more convenient Grignard route (see GRIGNARD REACTION).

The water solubility of zinc compounds varies greatly, as shown in Table 1. Water-soluble compounds not listed are zinc formate [557-41-5] chlorate [10361-95-2], fluorosilicate [16871-71-9], and thiocyanate [557-42-6]. Also, the water-soluble amino and cyanide complexes have many uses.

Zinc compounds are generally colorless unless the other component, eg, chromate, is colored. The lack of color of most zinc compounds in visible light is a great advantage in that they do not color paint films, plastics, rubber, cosmetics, etc. However, when excited by various types of radiation and at various temperatures, zinc oxide, sulfide, selenide [1315-09-9], and related compounds exhibit luminescence, ie, they emit colored light (see LUMINESCENT MATERIALS). Zinc-based phosphors can be produced in many colors, depending on the added dopants. They are used in television tubes, luminescent glasses, and various specialty products.

Table 1. **Properties, Prices, and Uses of Zinc Compounds**

Zinc compound	Formula, synonym	CAS Registry No.	Sp gr	mp,^{a} °C	Solubility^a, g/100 g solvent water			Price^b, \$/kg (Aug. 1981)	
								Other	Uses
acetate	$Zn(C_2H_3O_2)\cdot 2\,H_2O$	[5970-45-6]	1.735	237	$40^{25°C}$	$67^{100°C}$	$3^{25°C}$ alcohol	3.53	wood preservative, mor-dant antiseptics, cata-lyst, waterproofing
ammonium chloride	$ZnCl_2\cdot 2NH_4Cl$	[52628-25-8]	1.88	150 dec	$66^{0°C}$	$69^{30°C}$		0.71	galvanizing, solder flux, adhesives
diborate	$ZnO\cdot B_2O_3\cdot 2\,H_2O$	[27043-84-1]	3.64		$0.007^{25°C}$		sl sol HCl	1.21	fireproofing, ceramics, fungicide
dodecaborate	$2\,ZnO\cdot 3\,B_2O_3\cdot 3.5\,H_2O$	[12513-27-8]	4.22	980	insol			1.54	fire retardant
bromide	$ZnBr_2$	[13550-22-6]	4.21	394	$471^{25°C}$	$675^{100°C}$	sol alcohol, ether	62.00^c	photographic paper, catalyst, batteries
carbonate	$ZnCO_3$	[3486-35-9]	4.40	$-CO_2$ at 300	$0.001^{15°C}$		insol alcohol	45.40^c	ceramics, rubber, astringent (lotions)
chloride	$ZnCl_2$	[7646-85-7]	2.91	275	$432^{25°C}$	$614^{100°C}$	sol ether	0.41	textiles, adhesives, flux, wood preservative, antiseptic, astringent
cyanide	$Zn(CN)_2$	[557-21-1]	1.85	800 dec	$0.005^{20°C}$		sol alkali, CN^-	3.63	electroplating, gold extraction
dithiocarbamates									
dibutyl	 $Zn\left[S\overset{\overset{S}{\|}}{C}N(C_4H_9)_2\right]_2$	[136-23-2]	1.21	106	insol		sol C_6H_6, CS_2, $CHCl_3$	3.17	vulcanization accel-erator, lube oil

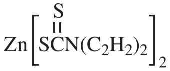
diethyl	 $Zn\left[S\overset{S}{\overset{\|}{C}}N(C_2H_2)_2\right]_2$	[14324-55-1]	1.48	176	insol		sol C_6H_6, CS_2, $CHCl_3$	3.32	vulcanization accelerator
ethylenebis	 $Zn\left[S\overset{S}{\overset{\|}{C}}NHCH_2\right]_2$ zineb	[12122-67-7]			insol		sol C_6H_6, CS_2, $CHCl_3$	5.50	fungicide, insecticide
dimethyl	 $Zn\left[S\overset{S}{\overset{\|}{C}}N(CH_3)_2\right]_2$ ziram	[137-30-4]	1.71	249	$0.0065^{25°C}$		sol CS_2, ace-tone, alkali	3.06	vulcanization accel-erator, fungicide
2-ethylhexanoate	$Zn(C_8H_{16}O_2)_2$	[136-53-8]	0.90		insol		sol hydro-carbon	1.87	paint drier, silicone rubber cure
fluoroborate	$Zn(BF_4)_2 \cdot 6H_2O$	[13826-88-5]		$-H_2O$ at 60°C	$>100^{25°C}$		sol alcohol	0.60	plating, bonderizing, textile resin cure
fluoride	ZnF_2	[7783-49-5]	4.95	872	$1.6^{18°C}$		sol hot acid, NH_4OH	100.00^c	ceramics, impregnating wood, galvanizing
formaldehyde sulfoxylate	$Zn(HSO_2 \cdot CH_2O)_2$	[24887-06-7]		90 dec	$60^{25°C}$		insol alcohol	2.31	reducing agent, drying, polymerization
hydrosulfite	$ZnS_2O_4 \cdot 2\,H_2O$	[7779-86-4]		200 dec	$40^{20°C}$			2.25	bleach, especially textile, paper, reducing agent
iodide	ZnI_2	[10139-47-6]	4.70	446	$432^{18°C}$	$510^{100°C}$	sol alcohol	182	medicine, photography
2-mercaptobenzo-thiazole	$Zn(SC_6H_4NCS)_2$	[155-04-4]	1.70	300 dec	insol	insol	sol C_6H_6, CS_2, $CHCl_3$	3.17	vulcanization accelera-tor for latex
naphthenate	$Zn[(C_2H)_5CHCOO]_2$	[12001-85-3]			insol	insol	sol hydrocar-bon, acid	1.17	paint film improver, rot proofer
nitrate	$Zn(NO_3)_2 \cdot 6\,H_2O$	[10196-18-6]	2.065	−18	93	$900^{70°C}$	sol alcohol	0.75	textiles as resin cata-lyst, mordant latex coagulant

Table 1. (*Continued*)

Zinc compound	Formula, synonym	CAS Registry No.	Sp gr	mp,[a] °C	Solubility[a], g/100 g solvent water			Price[b], $/kg (Aug. 1981)	
								Other	Uses
oxide	ZnO	[1314-13-2]	5.47, 5.61	1800 sublimes	$0.00042^{18°C}$		sol acid, alkali, NH_4OH	1.05–1.12	vulcanization accelera-tor, mildewstat, pig-ment, supplement in feed and fertilizer, catalyst, ceramics, intermediate
peroxide	ZnO_2	[1314-22-3]	1.57	212 explodes	insol		sol acid	5.50	cosmetic powders as antiseptic
phosphate	$Zn_3(PO_4)_2$	[7779-90-0]	4.00	900	$2.6^{25°C}$	insol	sol NH_4OH, insol alcohol	1.85	metal coatings, dental cement
potassium chromate	$4\,ZnO{\cdot}K_2O{\cdot}4\,CrO_3{\cdot}3\,H_2O$, zinc yellow	[37300-23-5]	3.36–3.46		$0.24^{25°C}$			2.47	rust-inhibiting pigment
resinate	$Zn(C_{20}H_{30}O_2)_2$	[9010-69-9]	1.24	205	insol	insol	sol hydro-carbon	0.99	inks, paint drier
selenide	ZnSe	[1315-09-9]	5.42	1100	insol		sol acid	330.0	phosphor
silicofluoride	$ZnSiF_6{\cdot}6\,H_2O$	[18433-42-6]	2.10	100 dec	$77^{10°C}$	$93^{60°C}$		0.37	laundry sour, wood preservative, plaster additive
stearate	$Zn(C_{17}H_{35}COO)_2$	[557-05-1]	1.09	120	insol	insol	sol hydro-carbon	1.90	lubricant, mold release, vinyl stabilizer, anti-cake, water repellant

sulfate	$ZnSO_4$	[7733-02-0]	3.54	680 dec	$41.9^{0°C}$	$91^{70°C}$	sol glycerol	0.77	rayon bath, agriculture, zinc plating, interme-diate, flotation, mordant
sulfate	$ZnSO_4{\cdot}H_2O$	[7446-19-7]	3.28	238 dec	$101^{70°C}$	$87^{105°C}$		0.58	rayon bath, agriculture, zinc plating, interme-diate, flotation, mordant
sulfide	ZnS	[1314-98-3]	3.98, 4.10	1185 sublimes	$0.0007^{18°C}$	insol	sol acid	1.76[d]	phosphor, white pig-ment, dental materials
tetroxychromate	$4Zn(OH)_2{\cdot}ZnCrO_4$	[13530-65-9]	3.87–3.97		$0.01^{25°C}$			2.57	wash primer
undecylenate	$Zn[CH_2CH(CH_2)_8{\cdot}COO]_2$	[557-08-4]		115	insol	insol	sol hydro-carbon	9.70	dermal fungicide

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[a] Insol = insoluble, v sol = very soluble, dec = decompose.

[b] Ref. 2.

[c] Reagent price.

[d] Pigment price.

3. Zinc Oxide

3.1. Physical Properties. Some of the physical properties of zinc oxide are listed in Table 2. Of great importance is the fact that it completely absorbs ultraviolet (uv) light < 366 nm and, thus, is unique among white pigments (15). Its high refractive indexes make it a good white pigment where its mean diameter for maximum light scattering is 0.25 µm. The crystal structure of zinc oxide is likely to stabilize defects, eg, zinc excess or deficiency and inclusion of foreign ions, and therefore has useful semiconductor properties. Variously doped oxides are used for photocopying, catalysts, and phosphors (16,17) (see Repography; Catalysts; Semiconductor).

3.2. Chemical Properties. Zinc oxide, as an amphoteric material, reacts with acids to form zinc salts and with strong alkalies to form zincates. In the vulcanization of rubber, the chemical role of zinc oxide is complex and the free oxide is required, probably as an activator (see Rubber chemical). Zinc soaps result from the oxide's interaction with organic acids and their interaction with the accelerator. The oxide is used alone as an accelerator in certain elastomers, eg, neoprene and thiokols, which contain chlorine and sulfur in the polymer molecules. Zinc oxide reacts with carbon dioxide in moist air to form oxycarbonate. Acidic gases, eg, hydrogen sulfide, sulfur dioxide, and chlorine, react with zinc oxide, and carbon monoxide or hydrogen reduce it to the metal. At high temperatures, zinc oxide replaces sodium oxide in silicate glasses. An important biochemical property of the oxide is its fungicidal/moldewstatic action (see Fungicides) (18). It is also soluble in body fluids and soils (19).

Table 2. **Selected Physical Properties of Zinc Oxide**

Property	Value	Reference
mp, °C	~ 1975 (subl)	3
color	white in finely divided form	
refractive index, 0.5 µm	2.015, 2.068	4
specific gravity	5.68	
water solubility, minimum at pH	9.7	5
K_{sp} $Zn(OH)_2$	4.5×10^{-17}	
heat capacity (at 25°C), J/(mol °C)[a]	40.26	3
$\Delta H_{formation}$ (at 419.5–907°C), kJ/mol[a]	−356.1	6
$\Delta F_{formation}$ (at 419.5°C), kJ/mol[a]	−281.6	6
$\Delta F_{formation}$ (at 907°C), kJ/mol[a]	−229.0	
S formation (at 25°C), J/mol[a]	43.65	7
coefficient of expansion, $\times 10^{-6}$/°C	4.0	8
conductivity, W/(m·K)	25.2	9
crystal structure	hexagonal, wurtzite	
conductivity (n-type), S/cm	10^{-7}–10^{3}	10
piezoelectricity (lithium-doped)	~ 4 × that of quartz	11
magnetic susceptibility (at 196°C), $\times 10^{-6}$ Hz units	0.20	12
pyroelectric current density, MA/(m^2·s·K)	6.8	13
$E°$ of $Zn + ½O_2 = ZnO$ (at 25°C), V	1.649	

[a] To convert J to cal, divide by 4.184.

3.3. Production and Processing. Primary zinc oxide is manufactured by oxidizing zinc vapor in burners wherein the concentration of zinc vapor and the flow of air is controlled so as to develop the desired particle size and shape. The hot gases and particulate oxide or fume pass through tubular coolers, and then the ZnO is separated in a baghouse. The purity of the zinc oxide depends on the source of the zinc vapor. Zinc oxide of great purity is required for pharmaceutical, photoconductive, and certain other grades, and these are made by the indirect (French) process, which accounted for 60% of world zinc production in 2003. Zinc vapor from previously purified zinc metal is burned (20,21). Less-pure zinc oxide is manufactured by the direct (American) process, by which impure zinc oxide is reduced to zinc vapor that is then burned (20). The American process accounted for 40% of world zinc oxide production in 2003. Certain impurities in the original crude ore and carbonaceous reductant are inseparable from the product oxide. Nevertheless, the uses dictate that certain impurities be at low levels. For example, cadmium, lead, iron, sulfur, copper, and manganese can be deleterious in rubber if they exceed certain concentrations (22,23). Some scrap zinc materials undergo both French and American processes; other processes are used to produce secondary zinc oxide from zinc scrap, zinc-containing sludges, and metallurgical slags. Worldwide sources for zinc oxide production in 2003 were from galvanizers scrap (40%), primary zinc (40%), and old roofing, die castings, etc (20%).

Direct (American) Process. Grate Furnaces. In the eastern Wetherhill furnace, four or more firebrick furnaces (called a block) having common walls are charged in cyclic fashion. Coal that is hot from the previous charge is first spread on the grate and, after ignition, a damp, well-blended mixture of zinciferous material and coal is added. The bed is maintained in a reducing condition with carbon monoxide to produce zinc and lead, if present. Metal vapors are drawn into a chamber above the furnace, where combustion air oxidizes them to pigment. The hot pigment–gas stream enters a cooling duct common to the whole block and, in this way, the product becomes a uniform blend. The raw material contains 15–75 wt% zinc, but usually > 60 wt%, and the coal is adjusted accordingly. For best results, anthracite or coke is used (see COAL). Calcium, iron, and silica influence the nature of the clinker and the elimination of zinc and must, therefore, be minimized.

The western Wetherill furnace is like the eastern furnace except that a block of 12 or more furnaces has a common combustion chamber. This results in improved control and uniformity of product. Clinker usually contains 8–15 wt% zinc, which is often recovered in a Waelz kiln (24).

The traveling-grate furnace requires less labor, increases the output per unit of grate area, and produces more uniform product than the Wetherill furnaces. The traveling grate is an endless chain of cast-iron bars, driven by sprockets, which traverses a firebrick chamber. Anthracite briquettes are fed to a depth of ~ 15 cm. After ignition by the previous charge, the coal briquettes are covered by 15–16.5 cm of ore/coal briquettes. The latter are dried with waste heat from the furnace. Zinc vapor evolves and burns in a combustion chamber and the spent clinker falls into containers for removal (24,25).

Rotary Kilns. The pigment-grade oxide kiln, because of its high temperature, produces pigment-quality zinc oxide and makes possible higher recovery as compared to the grate furnaces. The kilns, which are 2.4-m diameter and 12.1–15.2-m long, are fed in the firing end with a mixture of 65 wt% sinter and 35 wt% anthracite. Very slow rotation and small slope give sufficient retention time for good zinc elimination. The atmosphere in the kiln is reducing. Air is then control-fed into a firebrick combustion chamber, where the zinc is burned to the desired size and shape. The exiting solid residue is water quenched.

The Waelz process is used to beneficiate many metals, including zinc, and produces a relatively impure oxide (26). This is true because the loose feed is charged at the end of the kiln where metal vapors are exiting and because the feed materials are usually quite impure. Where the process is used to make crude zinc oxide, feeds include oxidized and sulfide zinc ores, residues, zinc-bearing iron ores and flue dusts, lead furnace slags, mill slimes, electrolytic-zinc leach residues, and ores of various other metals, eg, tin and gold (27). The metallurgy of the process is similar to the preceding processes, but it is complicated by the presence of other materials in the feed, eg, sulfates, sulfides, carbonates, and silicates. Conditioners, eg, silica, lime, and iron oxide, are often added to control the fluidity of the charge (28). Also, lime can be used to fix sulfur as calcium sulfide, so that materials containing up to 20 wt% sulfur can be introduced into the kiln. Any sulfur dioxide formed tends, because of the high temperature and long retention time, to be oxidized to trioxide and reacts with metallic oxides to form sulfate.

The charge, which contains ~25 wt% carbon, progresses through the 11–30-m long kiln, countercurrent to the hot gases from the fuel burner and the burning carbon in the bed. Lifters give the bed a considerable mixing action, as the kiln rotates at 1–1.5 rpm. The particles are reduced when submerged in the bed and are oxidized on the surface. Conditions are adjusted so that the products in the exiting gas are zinc and cadmium vapors, stannous oxide, germanium monoxide, carbon monoxide, and often further oxidized states of these compounds. They are fully oxidized in the combustion chamber, which may also serve as a settling chamber for fly ash from the kiln. Settled material is recycled to the kiln. The fume is cooled and collected in a baghouse. Very often, the crude ZnO is sintered to remove cadmium, sulfur, and lead and used for the production of zinc oxide or zinc metal.

Electrothermic Process. Electrothermic zinc smelting is described in Ref. 29. The oxide furnaces in the one U.S. plant are 11-m high, three are 1.75-m in diameter, and the fourth is 2.44-m in diameter with eight graphite electrodes at each of two levels. The electrical resistance path through the descending charge of 70 wt% sinter and 30 wt% coke is 9-m long, and it supplies the energy for smelting. The zinc vapor and carbon monoxide pass through exit ports at four levels between the upper and lower electrodes into manifolds where pigment forms by oxidation with added air. After cooling and passing through a cleaning cyclone, the oxide is collected in a baghouse (30).

Indirect (French) Process. Zinc metal vapor for burning is produced in several ways. Because all the vapor is burned in a combustion chamber, the purity of the oxide depends on that of the zinc feed. Oxide of the highest purity requires special high grade zinc and less-pure products are made by blending in Prime Western and even scrap zinc.

Another method involves an electric-arc vaporizer that is $> 2000°C$ before burning (25,31). One of the features of the process is a rapid quench of the hot gas flow to yield very fine oxide particles ($\leq 0.15\,nm$). This product is quite reactive and imparts accelerated cure rates to rubber. Internally fired rotary kilns are used extensively in Canada and Europe and, to a limited extent, in the United States (24). The burning occurs in the kiln and the heat is sufficient to melt and vaporize the zinc. Because of the lower temperatures, the particles are coarser than those produced in the other processes. In a fourth process, zinc metal that is purified in a vertical refining column is burned. In essence, the purification is a distillation and impure zinc can be used to make extremely pure oxide. Also, a wide range of particle sizes is possible (32).

Secondary Zinc Oxide. Secondary oxide is that made from scrap, eg, galvanizer's dross, trimmings, automotive zinc scrap, and is largely used by rubber and ceramics manufacturers. About one-fifth of the oxide produced in the United States is from secondary material, although some of it is made by primary producers. Most secondary oxide is of the French type in that the starting zinc is metallic. The zinc is usually vaporized in upright retorts in such a way that the higher boiling impurities, eg, lead, do not vaporize and relatively pure oxide is produced (33). Another procedure for manufacturing secondary oxide is precipitation of zinc carbonate from waste zinc solution, followed by drying, calcining, and grinding to a coarse oxide suited for ceramics. A similar product results from the calcination of zinc hydrosulfite [7779-86-4] sludge. Such sludges are by-products of the use of zinc hydrosulfite as a bleaching agent.

Leaded Zinc Oxide. Oxides containing $> 5\,wt\%$ basic lead sulfate are classified as leaded and are made in the American process from high lead materials, usually lead sulfide mineral, or by blending zinc oxide and basic lead sulfate. There is only one manufacturer in the United States and the product contains 20–28 wt% basic lead sulfate. Leaded oxides are used only in rubber in the United States.

Slag-Fuming Process. Three plants in the United States, two in Canada, and one in Mexico process slag from blast furnaces (usually lead) and residues to make zinc oxide fume. The oxide is impure and most is sent to zinc smelters for conversion into metal; however, a small amount is sold as pigment. The process consists of blowing powdered coal into a bath of molten slag via multiple double-inlet tuyeres (34). Zinc is eliminated from the 10–18 wt% zinc charge in $\sim 2\,h$, and the coal is the fuel and the reductant, ie, carbon monoxide, source. The direct method of introduction of the coal combines drying and grinding with the feeding of coal into the furnace feed lines. Indirect feeding uses previously dried and ground coal from a bin. In either case, the coal–air mixture must be carefully controlled to minimize excess coal yet avoid too low a temperature. The slag temperature is maintained at 1150–1200°C. Recovery is $\sim 90\%$ or better for both lead and zinc, and results in fume of $\sim 70\,wt\%$ zinc oxide and 7–10 wt% lead.

Zinc Oxide Treatments. There are a number of treatment procedures in addition to the customary screening and pulverizing. Various chemical materials are added to improve ease of incorporation and dispersibility of the oxide in rubber and paint (see PAINT). Commonly, these are fatty acids, eg, propionic and stearic, and oils (35,36). Phosphoric acid is added to reduce chemical activity and trialkyl phosphates to combat dusting (37,38). American-process zinc oxide may contain acidity in the form of oxysulfur compounds; this can be removed by washing with solutions of ammonia or ammonium salts (39). However, improved American-process oxides, which do not need washing, are being produced. Unless recalcined, zinc oxide tends to be bulky, dusty, and have poor dry flow. These characteristics are especially objectionable to those who use the oxide in ceramics and rubber. Therefore, some grades are pelleted in rotating drums or densified by passing through rolls.

3.4. Economic Aspects.

Tires and rubber have dominated zinc oxide consumption for many years, with some regional variations. In the United States, the rubber industry is the major market for zinc oxide and accounts for $\sim 60\%$ of usage, while in Europe $\sim 40\%$ of zinc oxide is used in rubber production. For Japan, the proportion is $\sim 50\%$. Zinc oxide is important in rubber processing because of its effectiveness as an activator in the vulcanization process. In its raw state, rubber consists of long randomly linked hydrocarbon chains that can slide past each other. Vulcanization chemically links the rubber chains together by cross-links, forming a three-dimensional (3D) network. Vulcanization has remained the key process in rubber production for over a century and during this time zinc oxide has been the most cost efficient vulcanization process activator (Table 3).

Zinc oxide also protects rubber from thermal effects caused by internal friction and acts as a heat sink that accepts frictional energy without large increases in internal temperature. It also improves the performance of uncured rubber during processing by decreasing shrinkage of molded rubber products and maintaining cleanliness of the molds. Tire wear, abrasion, performance and degradation by ultraviolet radiation are also moderated by zinc oxide additions.

Zinc oxide prices are listed in Table 4.

3.5. Health and Safety Factors.

Zinc oxide is considered nontoxic, but inhalation of freshly formed fume can cause zinc chills also known as brass-founder's ague. The symptoms are fever and cough followed by chills after $\sim 4-8$ h (41). No aftereffects have been noted and workers who are continually exposed quickly develop a resistance (42). So-called chronic zinc poisoning is caused by toxic impurities, eg, lead, cadmium, arsenic, and antimony, which commonly contaminate zinc ores (43). The U.S. Occupational Safety and Health Administration (OSHA) has set a maximum concentration limit for zinc oxide fumes in workplace air of 5 mg of zinc/m^3 of air for an 8-h workday over a 40-h work week (29).

Table 3. **World Zinc Oxide Consumption, 2003**

Product	Amount, metric tons
tires	30,000
rubber	210,000
chemicals	160,000
ceramics/glass	130,000
agriculture	70,000
paints	60,000
others	40,000

Table 4. **Year-End U.S. Prices of Zinc Oxide**[a,b]

Grade	1975	1978	1979	1980	1996
American process, lead-free	0.89	0.90	0.98	0.97	
French process, lead-free					
lead-free	0.91	0.93	1.01	1.01	1.87
high purity	0.95	0.97	1.04	1.05	1.96
electrophotographic	0.97	0.99	1.07	1.05	2.53
leaded[c]					
12 wt% lead	0.78	0.82	0.87	0.87	
18 wt% lead					
35 wt% lead					

[a] In $/kg.
[b] Ref. 40.
[c] As basic lead sulfate.

3.6. Uses. The uses of zinc oxide can be divided into two groups based on the chemical and physical properties of the compound (44). The largest user, the rubber industry, uses it chemically as a vulcanization activator and accelerator and to slow rubber aging by neutralizing sulfur and organic acids formed by oxidation. Fine oxides are used for fast cures and coarse, sulfated grades for slow cures. Physically, it is a reinforcing agent, a heat conductor, a white pigment, and an absorber of ultraviolet (uv) light.

In paints, zinc oxide serves as a mildewstat and acid buffer as well as a pigment. In exterior house paints, zinc oxide additions allow absorption of uv rays of the sun. For many years, paint was the second largest market for zinc oxide, but the introduction of latex coatings into exterior house paints reduced market share. Latex paints were sensitive to mold growth and originally carried mercury compounds as fungicides, which were zinc oxide free. Because of the elimination of mercury compounds during the 1970s, the paint industry has since developed zinc oxide containing exterior latex paints, accounting for much of current usage. Its chemical action in cosmetics (qv) and drugs is varied and complex but, based upon its fungicidal activity, it promotes wound healing. It is also essential in nutrition. Zinc oxide is used to prepare dental cements in combination with eugenol and phosphoric and poly(acrylic acid)s (45) (see DENTAL MATERIALS). Because of zinc oxide's uv radiation absorption capabilities, it is an active ingredient in many sun tan lotions. Recently, use of nanometer-sized zinc oxide has allowed transparent sun protection formulations to be developed rather than the traditional white colored sun preparations made with larger sized zinc oxide particles. Zinc oxide is present in dietary supplements and vitamin tablets as a source of the essential micronutrient zinc for the human body. The oxide also is a starting material for many zinc chemicals. The oxide supplies zinc in animal feeds and is a fertilizer supplement used in zinc-deficient soils.

Zinc oxide functions in ceramics in several ways. Added to glasses, it imparts low thermal expansion, low melting, and increased chemical resistivity. Low melting point zinc oxide containing glasses are used for metal-to-glass seals and in the electronics industry. The semiconducting property of a great variety of glasses and ceramics is based on their zinc oxide content. Zinc oxide varisters are used to protect against low voltage surges in electronics applications, such as computers, and also for high voltage surges in lightening arrestors. Zinc ferrites are basically zinc–ferrite oxide spinels, which are highly magnetic. Usually they also contain other oxides, eg, nickel and manganese oxides, (qv) are used in many electrical and electronic devices. The oxide is used as a catalyst in alkylation, oxidation, hydrogenation, and dehydrogenation. The oxide is also used in coated photocopy paper (see ELECTROPHOTOGRAPHY). For many years zinc oxide has been used in amounts up to 2–3 wt% in transparent raw glazes for art ware or dinnerware and in larger amounts in semitransparent glazes for stoneware. Zinc oxide is also widely used in tile glazes and its content in certain glaze types may exceed 10%. The higher percentages are used for the development of a matte finish.

Miscellaneous applications of zinc oxide include zinc dialkyldithiophosphate (ZDTP), which is a major additive in the production of lubricant for engines where it helps reduce oxidation and engine corrosion and wear. In plastics, zinc oxide imparts fire resistance and helps degradation caused by uv light, such as in lawn furniture and other outdoor applications.

Nutrition. Zinc is essential to the proper functioning of plants and animals and, as zinc sulfate and oxide, it is used as a feed supplement (46–48) (see MINERAL NUTRENTS; FEED AND FEED ADDITIVES). Most crops use less than a kilogram of zinc per 1000 m^2/year, so that zinc salts added at 1.3–4.5 kg/ha gradually build up the zinc reserve (49). Animals, including humans, store relatively little available zinc and, thus, require a constant supply in the diet. For example, beef cattle require 10–30 mg/kg dry feed, dairy cattle 40 mg/kg, and breeding hens 65 mg/kg. Zinc from plants is considered less available to monogastric aminals than zinc from animal protein.

Zinc is second only to iron as a trace metal in humans. A 70-kg human body has $\sim$4.0 g iron, 2.0 g zinc, 0.2 g manganese, 0.1 g copper, and $<$ 0.1 g of all other elements combined (50). The recommended dietary allowance of zinc is 15 mg/day for adults and 25 mg/day for lactating females (51). Supplemental zinc is administered in the form of sulfate, chloride, acetate, gluconate [4468-02-4], stearate, or oxide but the anion is not involved in the processes of utilization. Supplementary zinc is prescribed for zinc deficiency and certain disorders. Deficiency is thought to be more widespread in the United States than previously assumed (52). Although excessive zinc produces toxic symptoms, such symptoms rarely occur. Large doses or continued ingestion of zinc may cause gastrointestinal distress; eg, 2 g of zinc sulfate is recommended as an emetic. However, 18 patients given 660 mg zinc daily for 16–26 weeks showed no ill effects, but a 16-year-old boy who ingested 12 g of elemental zinc in 2 days did develop noticeable ill effects (53).

Insufficient zinc results in slowed growth, delayed wound healing, poor appetite, mental lethargy, and sexual immaturity and it interferes with the immune response. The main function of zinc in metabolism is enzymatic and there is evidence of other physiologic roles, eg, in stabilization of membrane structure (54).

4. Zinc Chloride

Zinc chloride melts at 275°C, boils at 720°C, and is stable in the vapor phase up to 900°C. It is very hygroscopic, extremely water soluble, and soluble in organic liquids, eg, alcohols, esters, ketones, ethers, amides, and nitrides. Hydrates with 1, 1.5, 2.5, 3, and 4 molecules of water have been identified and great care must be exercised to avoid hydration of the anhydrous form. Aqueous solutions of zinc chloride are acidic ($pH = 1.0$ for $6\,M$) and, when partially neutralized, can form slightly soluble basic chlorides, eg, $ZnCl_2 \cdot 4\,Zn(OH)_2$ [11073-22-6] and Zn(OH)Cl [14031-59-5]. Many other basic chlorides have been reported (55).

Anhydrous zinc chloride can be made from the reaction of the metal with chlorine or hydrogen chloride. It is usually made commercially by the reaction of aqueous hydrochloric acid with scrap zinc materials or roasted ore, ie, crude zinc oxide. The solution is purified in various ways depending on the impurities present. For example, iron and manganese precipitate after partial neutralization with zinc oxide or other alkali and oxidation with chlorine or sodium hypochlorite. Heavy metals are removed with zinc powder. The solution is concentrated by boiling, and hydrochloric acid is added to prevent the formation of basic chlorides. Zinc chloride is usually sold as a 47.4 wt % (sp gr 1.53) solution, but is also produced in solid form by further evaporation until, upon cooling, an almost anhydrous salt crystallizes. The solid is sometimes sold in fused form.

The fumes of zinc chloride are highly toxic and can damage mucous membranes and cause pale gray cyanation. It can also ulcerate the skin of workers using it as a soldering flux or those handling wood impregnated with it (56). OSHA has set a maximum concentration limit for zinc chloride fumes in workplace air of 1 mg of zinc per cubic meter of air for an 8-h day over a 40-h work week (29).

The largest use of zinc chloride in the United States is in wood preservation, fluxes, and batteries (qv). Zinc chloride solution dissolves vegetable fiber and is widely used in mercerizing (qv), swelling fibers, as a mordant in dyeing, parchmentizing paper, etc. It dissolves metal oxides and is used as a flux, especially in galvanizing. Zinc electroplating is often done with a chloride bath. In medicine, it is used in antiseptics, deodorants, dental cements, and (qv). Zinc chloride solutions preserve wood and textiles and are used in (qv) and embalming fluids. Other uses are in organic synthesis, eg, in the preparation of methyl chloride and diethylzinc, as a dehydrant, in rubber vulcanization, and in oil refining. The consumption of zinc chloride is declining, as shown in Table 5.

5. Zinc Sulfate

Anhydrous zinc sulfate forms when its hydrates are heated $>238°C$. At $\sim 680°C$, sulfur trioxide separates from the compound, forming $3\,ZnO \cdot 2\,SO_3$ [12037-14-8] and $>930°C$ the compound is decomposed to zinc oxide. The three stable hydrates are $ZnSO_4 \cdot H_2O$ [7446-19-7], $ZnSO_4 \cdot 6H_2O$ [13986-24-8], and $ZnSO_4 \cdot 7\,H_2O$ (orthorhombic) [7446-20-0]. The latter heptahydrate occurs in a few small deposits as the mineral goslarite [7446-20-0]. Three unstable hydrates are $ZnSO_4 \cdot 4H_2O$ [33309-49-8], $ZnSO_4 \cdot 2\,H_2O$ [80867-26-1], and $ZnSO_4 \cdot 7\,H_2O$ (monoclinic).

The solubility of zinc sulfate increases almost linearly with temperature from 27.6 wt% (as $ZnSO_4$) at $-7°C$ to 41.4 wt% at 39°C. In this range, the

Table 5. **U.S. Production and Importation of Zinc Oxide, Sulfate, and Chloride, Metric Tons**[a]

	1970		1975		1980		1992		1996	
Zinc compound	Production	Import	Production	Import	Production	Import	Production	Import	Production	Import
zinc oxide	202,059	10,952	150,050	11,963	145,509	29,843	103,037	38,997	128,000	56,300
zinc sulfate	48,236	5,713	21,223	2,895	35,159	3,871	27,763	3,828	29,200	5,230
zinc chloride[b]	20,139	1,044	NA[c]	696	11,676	1,008	6,309	3,096	2,770	1,470

[a] Ref. 57.

[b] Includes zinc chloride in zinc ammonium chloride and chromated zinc chloride.

[c] NA = not available.

heptahydrate is the solid phase. As the temperature rises, the solid phase becomes the hexahydrate and its solubility increases to a maximum of 47.7 wt% at 70°C. Above this temperature, the solid phase is the monohydrate and solubility declines with temperature to 44.0 wt% at the boiling point (105°C). Many basic zinc sulfates have been reported but probably the only true compounds are hydrates of $3Zn(OH)_2 \cdot ZnSO_4$ [12027-98-4] (58).

Zinc sulfate is usually made from secondary materials (93%) and from roasted ore, ie, zinc oxide (7%). The zinciferous material reacts with sulfuric acid to form a solution, which is purified. After filtration, the solution is heated to evaporation and heptahydrate crystals are separated. It is sometimes sold in this form but usually as the monohydrate [7446-19-7], which is made by dehydration at ~ 100°C. Very pure zinc sulfate solution is made in the manufacture of the pigment lithopone [1345-05-7], $ZnS \cdot BaSO_4$, and of zinc by electrowinning.

Zinc sulfate is used in (qv), sprays, and animal feeds in which it serves as a valuable trace element and disease-control agent. In the manufacture of rayon, it is a crenulating agent in the precipitation bath. It is also the starting material for the manufacture of many zinc chemicals and is used in textile dyeing and printing, (qv) reagents, electrogalvanizing, paper bleaching, and glue. In 1950, rayon accounted for 46% of zinc sulfate consumption, in 1960 55%, and in 1966 39%. Statistics for rayon are not available beyond 1966, but the use in agriculture grew from 39% in 1966 to 49% in 1977, to 72% in 1979, and to 78% in 1980. The actual tonnage used in agriculture also has increased steadily.

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