NICKEL COMPOUNDS

1. Introduction

Nickel [7440-02-0], Ni, recognized as an element as early as 1754 (1), was not isolated until 1820 (2). It was mined from arsenic sulfide mineral deposits (3) and first used in an alloy called German Silver (4). Soon after, nickel was used as an anode in solutions of nickel sulfate [7786-81-4], $NiSO_4$, and nickel chloride [7718-54-9], $NiCl_2$, to electroplate jewelry. Nickel carbonyl [13463-39-3], $Ni(CO_2)_4$, was discovered in 1890 (see METAL CARBONYLS). This material, distilled as a liquid, decomposes into carbon monoxide and pure nickel powder, a method used in nickel refining (5) (see NICKEL AND NICKEL ALLOYS).

Nickel has a [Ar] $3d^84s^2$ electronic configuration and forms compounds in which the nickel atom has oxidation states of -1 through $+4$. Whereas reagents yield an array of compounds in a variety of nickel oxidation states (6-8), Ni(II) represents the bulk of all known compounds. More than 237,000 (9) compounds of nickel have been reported. The primary uses for nickel compounds, aside from nickel refining and electroplating (10), are in steel (qv) making, catalysis (qv), storage batteries (qv), specialty chemicals, and specialty ceramics (qv).

Simple nickel salts form ammine and other coordination complexes (see COORDINATION COMPOUNDS). The octahedral configuration, in which nickel has a coordination number (CN) of 6, is the most common structural form. The square-planar and tetrahedral configurations (11), in which nickel has a coordination number of 4, are less common. Generally, the latter group tends to be reddish brown. The 5-coordinate square pyramid configuration is also quite common. These materials tend to be darker in color and mostly green (12).

Examples of stable crystalline derivatives of Ni(III) and Ni(IV) are the hexafluoride anions [32698-29-6], NiF_6^{3-} and [23712-86-9], NiF_6^{2-} (13,14). A review of dicarbamates stabilizing Ni(III) and Ni(IV) is available (15). Examples of the binuclear and diamagnetic species of Ni(I) are the cyanonicklates $K_4[Ni_2(CN)_6]$ [40810-33-1] and $K_6[Ni_2(CN)_8]$ (16,17). Dihydrohexacarbonyldinickel($-$I) [12549-35-8], $H_2Ni_2(CO)_6$, an example of nickel in the -1 oxidation state, decomposes above -33°C (18). Many Ni(0) compounds have been prepared. Nickel carbonyl, $Ni(CO)_4$, is the most common (19). Other types of Ni(0) compounds are nickel dicyclooctadiene [33221-58-8], $(C_8H_{12})_2Ni$ (20), $(C_6H_5NC)_4Ni$ [23411-45-2] (21), $Ni(P(OCH_3)_3)_4$ [14881-35-7] (22); $((C_5H_4N)_2)_2Ni$ [15186-68-2] known as $Ni(bipy)_2$ (23); and the anion $[Ni(CN)_4]^{4-}$ [15453-80-2] (24).

2. Inorganic Compounds

2.1. Nickel Oxides.

Properties. Nickel oxide [1313-99-1], NiO, is a green cubic crystalline compound, mp 2090°C, density 7.45 g/cm^3, the properties of which are related to its method of preparation. Green nickel oxide is prepared by firing a mixture of water and pure nickel powder in air at 1000°C or by firing a mixture of high purity nickel powder, nickel oxide, and water in air (25,26). Whereas this temperature is required for full development of the crystal, the temperature is high enough that an equilibrium leading to dissociation back to the elements is established. Consequently, it is virtually impossible to obtain green nickel oxide made by high temperature firing that does not have traces of nickel metal. Single whiskers of green nickel oxide have been made by the closed-tube transport method from oxide powder formed by the decomposition of nickel sulfate using HCl as the transport gas (27). Green nickel oxide, free of nickel metal, also is formed by thermal decomposition of nickel carbonate [3333-67-3], $NiCO_3$, or nickel nitrate [13138-45-9], $Ni(NO_3)_2$. Green nickel oxide is a refractory material that is inert in most aqueous systems. At high temperatures it reacts with other ceramic materials in the presence of various fluxes (28).

Black nickel oxide, NiO, a microcrystalline form, results from calcination of the carbonate or nitrate at 600°C. This incompletely annealed product typically has more oxygen than its formula indicates, ie, 76–77 wt% nickel compared to the green form which has 78.5% nickel content. This results from chemisorption of oxygen on the surface of the crystal defects. Black nickel oxide compositions are chemically reactive and form simple nickel(II) salts when heated with mineral acids. Both black and green nickel oxide can be converted to the metal by heating with carbon, carbon monoxide, or hydrogen. Both green and black nickel oxide fuse with potassium hydroxide at 700°C to form potassium nickelate [50811-97-7], K_2NiO_2 (27). Other nickel oxides, eg, Ni_2O_3 [1314-06-3], density 4.84 g/cm^3, NiO_2 [12035-36-8], and Ni_3O_4 [12137-09-6], have been reported. Although detailed characterization evidence is lacking, many claims have been made for the electrochemical and photochemical properties (29).

Manufacture. Several nickel oxides are manufactured commercially. A sintered form of green nickel oxide is made by smelting a purified nickel matte at 1000°C (30); a powder form is made by the desulfurization of nickel matte. Black nickel oxide is made by the calcination of nickel carbonate at 600°C (31). The carbonate results from an extraction process whereby pure nickel metal powder is oxidized with air in the presence of ammonia (qv) and carbon dioxide (qv) to hexaamminenickel(II) carbonate [67806-76-2], $[Ni(NH_3)_6]CO_3$ (32). Nickel oxides also are made by the calcination of nickel carbonate or nickel nitrate that were made from a pure form of nickel. A high purity, green nickel oxide is made by firing a mixture of nickel powder and water in air (25).

Uses. The sinter oxide form is used as charge nickel in the manufacture of alloy steels and stainless steels (see STEEL). The oxide furnishes oxygen to the melt for decarburization and slagging. Nickel oxide sinter is charged as a granular material to an electric furnace with steel scrap and ferrochrome; the mixture is melted and blown with air to remove carbon as CO_2. The melt is slagged, poured into a ladle, the composition is adjusted, and the melt is cast into appropriate shapes. A modification of the use of sinter oxide is its injection directly into the molten metal (33).

Green nickel oxide powder, used in the refining of nickel, is agglomerated to a particular shape and then reduced to metal in a furnace. Green and black nickel oxides are used in the ceramic industry for making frit, ferrites (qv), and inorganic colors (see CERAMICS, OVERVIEW; COLORANTS FOR CERAMICS). Black nickel oxide is used for the manufacture of nickel salts and specialty ceramics. Nickel dioxide [12035-36-8], NiO_2, also known as Nickel Black, has been reported to have a solar absorbance coefficient of >0.92 (29). Green and black nickel oxides are used for nickel catalyst manufacture by admixing, usually when wet, with a powdered ceramic support material. The mixture is formed into a suitable shape and then reduced with hydrogen to form the finished catalyst. Green nickel oxide displays a negative temperature coefficient (NTC) and is used in the formation of thermisters, heat-sensitive electric switches that are extremely sensitive to changes in temperature and are used in process control (qv) in chemical manufacturing. NTC devices are also used in computer circuitry, in air conditioners, and fire detection equipment (34). Green nickel oxide is used in a mixture with other high purity metal oxides in varistors or voltage surge arrestors in lightning strike devices or as in-line varistors in electronics (35). The equilibrium of nickel oxide with its elements is important commercially: nickel oxide is used along with aluminum azide as the propellent for automotive air bags. The mixture is rapidly heated by resistance wire to 1400°C and the reaction of dissociated oxygen and aluminum azide to release nitrogen gas to fill the bag is complete in microseconds (36).

Nickel oxide is used commercially to make nickel fibers in a process whereby a water slurry containing nickel oxide and a cellulose (qv) type binder is forced through tiny orifices to form green fibers. Subsequent steps include drying and reduction with hydrogen. The resulting nickel fibers are matted together and used for the filtration (qv) of gases (37,38).

2.2. Nickel Sulfate. *Properties.* Nickel sulfate hexahydrate [10101-97-0], $NiSo_4 \cdot 6H_2O$ is a monoclinic emerald-green crystalline salt that dissolves easily in water and in ethanol. When heated, it loses water and above 800°C decomposes into nickel oxide and SO_3. Its density is 2.03 g/cm^3.

Manufacture. The preferred method for making nickel sulfate is adding nickel powder to hot dilute sulfuric acid. Adding sulfuric acid to nickel powder in hot water enhances the formation of H_2S. Hydrogen sulfide always forms as a by-product upon reaction of metallic nickel and sulfuric acid. The liberated hydrogen is absorbed by the metal and then reduces the sulfate anion to H_2S.

Nickel sulfate also is made by the reaction of black nickel oxide and hot dilute sulfuric acid, or of dilute sulfuric acid and nickel carbonate. The reaction of nickel oxide and sulfuric acid has been studied and a reaction induction temperature of 49°C determined (39). High purity nickel sulfate is made from the reaction of nickel carbonyl, sulfur dioxide, and oxygen in the gas phase at 100°C (40). Another method for the continuous manufacture of nickel sulfate is the gas-phase reaction of nickel carbonyl and nitric acid, recovering the solid product in sulfuric acid, and continuously removing the solid nickel sulfate from the acid mixture (41). In this last method, nickel carbonyl and sulfuric acid are fed into a closed-loop reactor. Nickel sulfate and carbon monoxide are produced; the CO is thus recycled to form nickel carbonyl.

Uses. The principal use for nickel sulfate is as an electrolyte for the metal-finishing application of nickel electroplating (qv). Nickel sulfate also is used as the electrolyte for nickel electrorefining. High purity nickel sulfate is used in electroless plating (qv) (42), where nickel sulfate and a reducing agent, eg, sodium hypophosphite, are brought together in hot water in the presence of the workpiece to be plated (43). Another application for nickel sulfate is as a nickel strike solution, which is used for replacement coatings (qv) or nickel flashing on steel that is to be porcelain-enameled (see ENAMELS, PORCELAIN OR VITREOUS). Nickel sulfate is also used as an intermediate in the manufacture of other nickel chemicals and as a catalyst intermediate.

2.3. Nickel Nitrate. *Properties and Preparation.* Nickel nitrate hexahydrate [13478-00-7], $Ni(NO_3)_2 \cdot 6H_2O$, is a green monoclinic deliquescent crystal, mp 56°C, density 2.05 g/cm^3, that is extremely soluble in water. Nickel nitrate hexahydrate loses water on heating and eventually decomposes, forming nickel oxide. The loss of the individual waters of hydration upon heating the hexahydrate has been studied, and the existence of the anhydrous covalent compound ($Ni(NO_3)_2$ [13138-45-9], before it decomposes, can be observed using thermal analysis techniques. The latter compound is prepared by the addition of methyl glyme to nickel nitrate hexahydrate followed by vacuum distillation and drying (44). Nickel nitrate hexahydrate can be prepared by the reaction of dilute nitric acid and nickel carbonate.

Manufacture. Nickel nitrate is made commercially by several methods. Nickel metal reacts vigorously with nitric acid and, if the reaction is not closely controlled, excess heating occurs and causes breakdown of the nitric acid. Nickel ammonium nitrate [22026-79-5], $H_3N \cdot xHNO_3 \cdot xNi$, also forms in the commercial methods that use nitric acid and metallic nickel because nickel absorbs the released hydrogen and catalytically reduces the nitrate anion to ammonia. The methods vary as to the amount of ammonia formed and the relative concentrations of acid and metal control the ammonia formation. The use of solid nickel such as electrolytic nickel or nickel briquettes enhances ammonia formation. Nickel powder, added slowly to a stirred mixture of nitric acid and water, yields nickel nitrate containing the least ammonia. Adding nitric acid to nickel powder in water results in the formation of considerable quantities of ammonium nitrate. A method to eliminate the ammonia formation employs the addition of nitric acid to a mixture of black nickel oxide powder and hot water. The reaction is controlled by using a cooling coil or cold water condenser because the reaction is highly exothermic (39).

Uses. Nickel nitrate is an intermediate in the manufacture of nickel catalysts, especially those that are sensitive to sulfur and therefore preclude the use of the less expensive nickel sulfate. Nickel nitrate also is an intermediate in loading active mass in nickel–alkaline batteries of the sintered plate type (see BATTERIES ALKALINE SECONDARY CELLS). Typically, hot nickel nitrate syrup is impregnated in the porous sintered nickel positive plates. Subsequently, the plates are soaked in potassium hydroxide solution, whereupon nickel hydroxide [12054-48-7] precipitates within the pores of the plate.

2.4. Nickel Halides. *Properties.* Nickel forms anhydrous as well as hydrated halides. The properties of the anhydrous salts are given in Table 1.

Nickel chloride hexahydrate [7791-20-0] is formed by the reaction of nickel powder or nickel oxide with a hot mixture of water and HCl. Nickel bromide [18721-96-5], $NiBr_2 \cdot 6H_2O$, is made by the reaction of black nickel oxide and HBr. The reaction of hydriodic acid with nickel carbonate yields nickel iodide [7790-34-3], $NiI_2 \cdot 6H_2O$.

Nickel fluoride tetrahydrate [13940-83-5], $NiF_2 \cdot 4H_2O$, and its anhydrous counterpart, nickel fluoride [10028-18-9], NiF_2, are the only known stable binary compounds of nickel and fluorine. The former is a greenish light yellow crystal or powder prepared by the addition of nickel carbonate to 30–50% aqueous HF solution. The nickel fluoride formed first goes into solution and then precipitates out as the tetrahydrate as the concentration of nickel fluoride increases and that of

HF decreases. When the addition of nickel is complete, the solution and the precipitates are dried at 75–100°C until all the water is expelled. The tetrahydrate has high solubility in aqueous HF, eg, 13.3 wt% in 30% HF. It is slightly soluble in water and insoluble in alcohol and ether.

Anhydrous nickel fluoride, a light yellow colored powder, is prepared by the action of anhydrous HF on anhydrous $NiCl_2$, or nickel fluoride tetrahydrate at 300°C. It is also prepared by heating a mixture of NH_4HF_2 and $NiF_2 \cdot 4H_2O$. The other methods include the fluorination of metal salts using excess SF_4 (47) or using ClF_3 (48) at elevated temperatures, or the reaction of $NiCO_3$ and anhydrous HF at 250°C (49).

Uses. Nickel chloride hexahydrate is an important material in nickel electroplating. It is used with nickel sulfate in the conventional Watts plating bath (50). Nickel chloride is an intermediate in the manufacture of certain nickel catalysts, and it is used to absorb ammonia in industrial gas masks. Anhydrous nickel chloride [7718-54-9] is formed from a mixture of nickel powder and sodium chloride at the anode during recharging of sodium nickel chloride batteries, which have possible use as the power source in electric vehicles (51). Nickel bromide has limited use in nickel electroplating. The reaction of nickel chloride or nickel bromide with dimethoxyethane yields ether-soluble $NiX_2 \cdot 2C_2H_4(OCH_3)_2$ compounds which are useful as nickel-containing reagents for a variety of reactions used to form coordination compounds of nickel (52). Nickel fluoride is used for cold sealing of anodic coatings on aluminum (53,54).

It is also used in marking ink compositions (see INKS), for fluorescent lamps (55) as a catalyst in transhalogenation of fluoroolefins (56), in the manufacture of varistors (57), as a catalyst for hydrofluorination (58), in the synthesis of XeF_6 (59), and in the preparation of high purity elemental fluorine for research (60) and for chemical (qv) (61).

2.5. Nickel Carbonate. Nickel carbonate [3333-67-3], $NiCO_3$, is a light-green, rhombic crystalline salt, density 2.6 g/cm^3, that is very slightly soluble in water. The addition of sodium carbonate to a solution of a nickel salt precipitates an impure basic nickel carbonate. The commercial material is the basic salt $2NiCo_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$ [29863-10-3]. Nickel carbonate is prepared best by the oxidation of nickel powder in ammonia and CO_2. Boiling away the ammonia causes precipitation of pure nickel carbonate (32).

Nickel carbonate is used in the manufacture of catalysts, in the preparation of colored glass (qv), in the manufacture of certain nickel pigments, and as a neutralizing compound in nickel electroplating solutions. It also is used in the preparation of many specialty nickel compounds.

2.6. Nickel Hydroxides. Nickel hydroxide [12054-48-7], $Ni(OH)_2$, is a light-green, microcrystalline powder, density 4.15 g/cm^3. It decomposes into nickel oxide and water when heated at 230°C, and is extremely insoluble in water. A solution of nickel sulfate which is treated with sodium hydroxide yields the gelatinous nickel hydroxide which, when neutralized, forms a fine precipitate that can be filtered. Another industrial route for the manufacture of nickel hydroxide is by electrodeposition at an inert cathode using metallic nickel as the anode and nickel nitrate as the electrolyte. High purity crystalline nickel hydroxide can be made from nickel nitrate solution and potassium hydroxide by subsequently extracting the gelatinous precipitate with hot alcohol. Nickel hydroxide is an intermediate in the manufacture of nickel catalysts. The principal use for nickel hydroxide is in the manufacture of nickel–cadmium batteries. Product morphology, particle size, and method of synthesis all bear important roles in the utility of nickel hydroxide in nickel alkaline storage batteries (62). Nickel hydroxide can be formed electrochemically within the sintered positive-electrode plaque if the porous plaque is used as the cathode (63). A variation of this method involves two porous electrodes and a d-c pole-reversing technique (64).

When nickel hydroxide is oxidized at the nickel electrode in alkaline storage batteries the black trivalent gelatinous nickel hydroxide oxide [12026-04-9], Ni(OH)O, is formed. In nickel battery technology, nickel hydroxide oxide is known as the nickel active mass (see BATTERIES, ALKALINE SECONDARY CELLS). Nickel hydroxide nitrate [56171-41-6], $Ni(OH)NO_3$, and nickel chloride hydroxide [25965-88-2], NiCl(OH), are frequently mentioned as intermediates for the production of nickel powder in aqueous solution. The binding energies for these compounds have been studied (65).

2.7. Nickel Fluoroborate. Fluoroboric acid and nickel carbonate form nickel fluoroborate [14708-14-6], $Ni(BF_4)_2 \cdot 6H_2O$. Upon crystallization, the high purity product is obtained (50). Nickel fluoroborate is used as the electrolyte in specialty high speed nickel plating. It is available commercially as a concentrated solution.

Nickel Fluoride Complexes. The complex hexafluoronickelates, M_2NiF_6 (M = Na [21958-95-2], K [17218-47-2], Rb [17218-48-3], Cs [17218-49-4]) and M_3NiF_6 (M = Na [22707-99-9], K [14881-07-3], Rb [72151-96-3], and Cs [72138-72-8]), are prepared by reaction of elemental fluorine, chlorine trifluoride, or xenon difluoride and a mixture of nickel fluoride and alkali metal fluorides or other metal halides (66,67). If the fluorination is carried out using mixed fluorides, a lower temperature can be used, yields are quantitative, and the final products are of high purity. Bis(tetrafluoroammonium) hexafluoronickelate[63105-40-8], $(NF_4)_2NiF_6$, prepared from Cs_2NiF_6 and NF_4SbF_6 by a metathesis in anhydrous HF, is also known.

These hexafluoronickelates can be used as fluorinating reagents (68), as a source of high purity elemental fluorine (60,61), and as high energy solid propellant oxidizers (see EXPLOSIVES AND PROPELLANTS).

2.8. Nickel Cyanide. Nickel cyanide tetrahydrate [20427-77-4], $Ni(CN)_2 \cdot 4H_2O$, forms apple-green plates which are, like other metal cyanides, highly poisonous. When the tetrahydrate is heated to 200°C, anhydrous nickel cyanide [557-19-7], $Ni(CN)_2$, forms. Further heating causes decomposition. Nickel cyanide is made by the reaction of potassium cyanide and nickel sulfate. Nickel cyanide, highly insoluble in water, precipitates from the reaction medium. Nickel cyanide is soluble in aqueous alkali cyanides as well as in other bases, including ammonium hydroxide and alkali metal hydroxides. The latter yield the stable, water-soluble orange tetracyanonickelate(II). An aqueous solution of $K_2[Ni(CN)_4]$ [14220-17-8] does not yield a nickel sulfide precipitate in the presence of hydrogen sulfide. Nickel cyanide has been used in the Reppe process for the conversion of acetylene to butadiene (qv) and other products (69) (see ACETYLENE-DERIVED CHEMICALS; CYANIDES).

2.9. Nickel Sulfamate. Nickel sulfamate [13770-89-3], $Ni(SO_3NH_2)_2 \cdot 4H_2O$, commonly is used as an electrolyte in nickel electroforming systems, where low stress deposits are required. As a crystalline entity for commercial purposes, nickel sulfamate never is isolated from its reaction mixture. It is prepared by the reaction of fine nickel powder or black nickel oxide with sulfamic acid in hot water solution. Care must be exercised in its preparation, and the reaction should be completed rapidly because sulfamic acid hydrolyzes readily to form sulfuric acid (70).

2.10. Nickel Sulfide. Nickel, like iron and cobalt, forms monosulfides which may show considerable deviation from stoichiometry without exhibiting heterogeneity. Nickel sulfide [1314-04-1], NiS, occurs naturally as the mineral millerite, and has a trigonal crystalline form and a yellow metallic luster; density 5.65 g/m^3, mp 797°C. It is insoluble in water. Nickel sulfides often are thought of as binary alloys of sulfur and nickel because the metallic appearance of the sulfides resembles alloys more than chemical compounds. Other nickel sulfides include two subsulfides, Ni_2S [12137-08-5] and Ni_3S_2 [12035-72-2]. The latter is found as the mineral heazlewoodite. Another naturally occurring sulfide is polydymite [12137-12-1], Ni_3S_4 (4).

Nickel sulfide, NiS, can be prepared by the fusion of nickel powder with molten sulfur or by precipitation using hydrogen sulfide treatment of a buffered solution of a nickel(II) salt. The behavior of nickel sulfides in the pure state and in mixtures with other sulfides is of interest in the recovery of nickel from ores, in the high temperature sulfide corrosion of nickel alloys, and in the behavior of nickel-containing catalysts.

2.11. Other Nickel Salts. *Nickel Arsenate.* Nickel arsenate [7784-48-7], $Ni_3(AsO_4)_2 \cdot 8H_2O$, is a yellowish green powder, density 4.98 g/cm^3. It is highly insoluble in water but is soluble in acids, and decomposes on heating to form As_2O_5 and nickel oxide. Nickel arsenate is formed by the reaction of a water solution of arsenic anhydride and nickel carbonate. Nickel arsenate is a selective hydrogenation catalyst for inedible fats and oils (71).

Nickel Phosphate. Trinickel orthophosphate [14396-43-1], $Ni_3(PO_4)_2 \cdot 7H_2O$, exists as apple-green plates which decompose upon heating. It is prepared by the reaction of nickel carbonate and hot dilute phosphoric acid. Nickel phosphate is an additive to control the crystal size of zinc phosphate in conversion coatings which are applied to steel prior to its being painted (see METAL SURFACE TREATMENTS, CASE HARDENING).

Nickel Double Salts. Nickel ammonium chloride [16122-03-5], $NiCl_2 \cdot NH_4Cl \cdot 6H_2O$, nickel ammonium sulfate [15699-18-0], $NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, and nickel potassium sulfate [10294-65-2], $NiSO_4 \cdot K_2SO_4 \cdot 6H_2O$, are prepared by crystallizing the individual salts from a water solution. These have limited use as dye mordants and are used in metal-finishing compositions (71).

2.12. Nickel Amine Complexes. The thermal stability of the hexaamminenickel(II) halides increases with the size of the halide (7). Decomposition temperatures at 13 kPa (100 mm Hg) for $Ni(NH_3)_6Cl_2$ [10534-88-0], $Ni(NH_3)_6Br_2$ [13601-55-3], and $Ni(NH_3)_6I_2$ [13859-68-2] are 398, 433, and 450°C, respectively. The thermal decomposition of tetrakispyridinenickel(II) dichloride [14076-99-4] (72) and the bidendate ethylenediamine (en) complex $[Ni(en)_3]Cl_2$ [13408-70-3] (73) have also been studied.

3. Organic Compounds

Nickel plays a role in the Reppe polymerization of acetylene where nickel salts act as catalysts to form cyclooctatetraene (74); the reduction of nickel halides by sodium cyclopentadienide to form nickelocene [1271-28-9] (75); the synthesis of cyclododecatrienenickel [39330-67-1] (76); and formation from elemental nickel powder and other reagents of nickel(0) complexes that serve as catalysts for oligomerization and hydrocyanation reactions (77).

3.1. Nickel Carbonyl.

Properties. Nickel carbonyl, $Ni(CO)_4$, is a colorless liquid having a high vapor pressure. The vapor density is ca four times that of air. As a liquid it is miscible in all proportions with most organic solvents and is practically insoluble in water. Nickel carbonyl reacts slowly with hydrochloric or sulfuric acid but reacts vigorously with nitric acid or the halogens, forming the corresponding nickel salts upon the liberation of CO. Bromine water is a useful reagent for the controlled decomposition of nickel carbonyl and for destroying residual amounts of it in a chemical apparatus. The properties of nickel carbonyl are given in Table 2 (see also METAL CARBONYLS).

Thermodynamic properties (83,84), force constants (85), and infrared absorption characteristics (86) are documented. The coordinatively unsaturated species, $Ni(CO)_3$ and $Ni(CO)_2$, also exist and the bonding and geometry data have been subjected to molecular orbital treatments (87,88).

Manufacture. Nickel carbonyl can be prepared by the direct combination of carbon monoxide and metallic nickel (89). The presence of sulfur, the surface area, and the surface activity of the nickel affect the formation of nickel carbonyl (90). The thermodynamics of formation and reaction are documented (91). Two commercial processes are used for large-scale production (92). An atmospheric method, whereby carbon monoxide is passed over nickel sulfide and freshly reduced nickel metal, is used in the United Kingdom to produce pure nickel carbonyl (93). The second method, used in Canada, involves high pressure CO in the formation of iron and nickel carbonyls; the two are separated by distillation (93). Very high pressure CO is required for the formation of cobalt carbonyl and a method has been described where the mixed carbonyls are scrubbed with ammonia or an amine and the cobalt is extracted as the ammine carbonyl (94). A discontinued commercial process in the United States involved the reaction of carbon monoxide with nickel sulfate solution.

3.2. Substituted Nickel Carbonyl Complexes.

The reaction of trimethyl phosphite and nickel carbonyl yields the monosubstituted colorless oil, $(CO)_3NiP(OCH_3)_3$ [17099-58-0], the disubstituted colorless oil, $(CO)_2Ni[P(OCH_3)_3]_2$ [16787-28-3], and the trisubstituted white crystalline solid, $(CO)Ni[P(OCH_3)_3]_3$ [17084-87-6] (mp 98°C). Liquid complexes result from the reaction of trifluorophosphine with nickel carbonyl yielding $(CO)_3Ni(PF_3)$ [14264-32-5], $(CO)_2Ni(PF_3)_2$ [13859-78-4], and $(CO)Ni(PF_3)_3$ [14219-40-0]. A bidendate substituted nickel carbonyl, $(CO)_2Ni(o\text{-}C_6H_4[P(CH_3)_2]_2)$ [76404-14-3], a white crystalline compound (mp 123°C), is known. Substituted arsine complexes and a substituted stibine derivative have been isolated. Reviews of N-, P-, As-, and Sb- donor nickel carbonyl complexes are available (95,96). The electrochemical reduction of bisbipryridinenickel(II) with CO_2 in DMF solvent gives the nickel zero complex, (2,2′-bipyridine-*N,N,*′)-dicarbonylnickel(0) [14917-14-7] (T-4) (97). An example of the C-ylide nickel carbene complex is (1,3-diethyl-2-imidazolidene-ylidene)-nickel(0) tricarbonyl (98).

3.3. π-Cyclopentadienyl Nickel Complexes. Nickel bromide dimethoxyethane [29823-39-9] forms bis(cyclopentadienyl)nickel [1271-28-9] upon reaction with sodium cyclopentadienide (75). This complex, known as nickelocene, π-$(C_5H_5)_2Ni$, is an emerald-green crystalline sandwich compound, mp 173°C, density 1.47 g/cm^3. It is paramagnetic and slowly oxidizes in air. A number of derivatives of nickelocene are known, eg, methylnickelocene [1292-95-4], which is green and has mp 37°C, and bis(π-indenyl)nickel [52409-46-8], which is red, mp 150°C (99,100).

Substituted derivatives of nickelocene, where one ring has been replaced, include the complex cyclopentadienyl nitrosyl nickel [12071-73-7], (π-C_5H_5) NiNO, a red liquid, mp −41°C. A review of nitrosyl complexes with nickel is available (101). The dimer complex di-μ-carbonyl-bis(η^5-cyclopentadienyldinickel) [12170-92-2], (π-$C_5H_5NiCO)_2$, is made in reversible reaction from nickel carbonyl and nickelocene (75). The complex is a red-violet solid and is diamagnetic, and spectroscopic studies show the presence only of bridging carbonyl groups.

3.4. Tetrakisligand Nickel(0) Complexes. Tetrakisligand nickel(0) complexes are made by several methods. One procedure is the substitution of CO in nickel carbonyl. Tetrakistrichlorophosphinenickel(0) [36421-86-0], $Ni(PCl_3)_4$, yellow, mp 120°C (dec) is a product of CO substitution synthesis (22). Another method of preparation involves substitution of more powerful donor ligands, such as triphenylphosphine, in other tetrakisligand nickel(0) complexes. The red solid tetrakistriphenylphosphinenickel(0) [15133-82-1], mp 125°C, and the yellow solid tetrakistrimethylphosphinenickel(0) [28069-69-4], mp 185°C (dec), are examples of the ligand-substitution method of preparation (102). A third method of preparation involves the direct reaction of nickel powder and ligands where halogens are on the donor atom. Examples of complexes prepared by this method are $Ni(PF_3)_4$ [13858-65-9] and $Ni(CH_3PCl_2)_4$ [76404-15-4] (103). A fourth method of preparation of NiL_4 complexes involves reaction of nickel halides and ligands in the presence of a reducing agent, eg, zinc metal powder (104). The mixed ligand complex Ni(P(*o*-$CH_3C_6H_4)_3)_3$ $(NCCH(CH_3)CHCH_2)$ [41686-95-7] has been prepared from anhydrous nickel chloride [7718-54-9], 3-pentenenitrile, and tri-*o*-tolylphosphine (105).

Tetrakisligand nickel(0) complexes have tetrahedral structures. Electronic structures have been studied and conformational analysis performed. Quantitative equilibria measurements of the ligands in these complexes imply a dominant role for ligand steric effects when the complexes are employed as catalysts (106).

Tetrakisligand nickel(0) complexes catalyze the reaction of ethylene and butadiene to give 1,4-hexadiene (107), the isomerization of 1-butene to 2-butene (108), and hydrocyanation of butadiene to form adiponitrile (109,110). The thermal decomposition of tetrakis(triorganophosphite)nickel(0) complexes in high boiling solvents is a method for depositing a high purity coating of nickel on steel (111).

3.5. Other Complexes. Several other classes of organonickel complexes are known. Allyl bromide and nickel carbonyl react to give a member of the π-allyl system [12012-90-7], $[\pi\text{-}C_3H_5NiBr]_2$ (112). Tris(η^2-ethene)nickel [50696-82-7] reacts with acetylene and 1,2-bis(diisopropylphosphino)ethane to form the ethyne complex (η^2-ethyne)(1,2-bis(diisopropylphosphino)ethane)nickel and related species (113). A review of nickel η-bonded complexes containing unsaturated organic molecules is available (114).

1,2,3,4-Tetramethylcyclobutadiene dichloride [76404-16-5] can be prepared by reaction of nickel carbonyl and 3,4-dichlorotetramethylcyclobutene (CBD) in polar solvents (115). The complex is black-violet, mp 185°C (dec).

The reaction of a mixture of 1,5,9-cyclododecatriene (CDT), nickel acetylacetonate [3264-82-2], and diethylethoxyaluminum in ether gives red, air-sensitive, needle crystals of (CDT)Ni [12126-69-1] (78). Crystallographic studies indicate that the nickel atom is located in the center of the 12-membered ring of (CDT)Ni (116). The latter reacts readily with 1,5-cyclooctadiene (COD) to yield bis(COD) nickel [1295-35-8] which has yellow crystals and is fairly air stable, mp 142°C (dec) (20). Bis(COD)nickel also can be prepared by the reaction of 1,5-COD, triethylaluminum, and nickel acetylacetonate.

In another class of compounds a nickel complex serves as anion. Two examples are [5964-71-6], $((C_2H_5)_4N)_2[NiCl_4]$ (117), and tetraethylammonium triphenylphosphinetribromonickelate [41828-60-8], $[(C_2H_5)_4N][(C_6H_5)_3PNiBr_3]$ (118).

Nickel salts form coordination compounds with many ligands. Dibromobis(tri-*n*-butylphosphine)nickel(II) [15242-92-9], $[(n\text{-}C_4H_9)_3P]_2NiBr_2$, dicyanoammineaquanickel(II), $Ni(NH_3)(H_2O)(CN)_2$, and bromonitrosobis(triphenylphosphine)nickel(II) [14586-72-2], are complexes used for syntheses in preparative organonickel chemistry.

Reduction of compounds of the type $LNiX_2$ and L_2NiX_2 where L is a ligand yields hydride complexes, ie, LNiHX and L_2NiHX (see HYDRIDES). The LNiHX are generally stable only at low temperatures; the L_2NiHX are more stable. A high degree of stability can result when bulky ligands are employed, eg, chlorohydridobis(tricyclohexylphosphine)nickel [25703-57-5], $HNi(P(cyclo\text{-}C_6H_{11})_3)_2Cl$, has mp 150°C (dec) (119).

The presence of strongly electron-donating ligands has a large effect on the synthesis of alkyl and aryl nickel compounds. Whereas dimethylnickel [54836-89-4], $Ni(CH_3)_2$, cannot be isolated, even at −130°C, bis(tricyclohexylphosphine)-dimethylnickel [36427-03-9] $[(cyclo\text{-}C_6H_{11})_3P)_2Ni(CH_3)_2$, is stable at ambient temperature (120). Bis(triphenylmethyl)nickel [7544-48-1], $[(C_6H_5)_3C]_2Ni$, has violet crystals and mp 120°C (dec). This compound, considered to be a ligand-free nickel aryl complex (121), can be prepared by the reduction of nickel salts in the presence of hexaphenylethane. Chlorobis(triphenylphosphine)phenylnickel [38415-93-3], $[(C_6H_5)_3P]_2NiC_6H_5Cl$, mp 122°C, is a bisligand aryl nickel halide (122). The complex $((CH_3)_3P)_2Ni(CH_3)_2$ [60802-48-4] reacts further to yield the orange-red solid, mp 49–51°C $((CH_3)_3P)_3Ni(CH_3)_2$ [42725-08-4], containing three phosphines (123).

π-Complexes of alkylnickel and arylnickel also have been prepared. The stronger electronic donating compounds impart greater stability. Methyl Grignard reagent and π-allylnickel [12077-85-9] yield the dimer of π-allylmethylnickel, a complex which cannot be isolated above −78°C. However, tricyclohexylphosphine π-allylmethylnickel [76422-11-2], $\pi\text{-}CH_2CHCH_2NiCH_3$ $(P(cyclo\text{-}C_6H_{11})_3)$, is a stable yellow solid, mp 50°C (dec) (124). Tri-*n*-butylphosphine-π-cyclopentadienylmethylnickel [7298-70-0], $P(C_4H_9)_3(\pi\text{-}C_5H_5)NiCH_3$, can be prepared by the reaction of a cyclopentadienyl ligand nickel halide and methyl Grignard reagent. It is a greenish brown solid, mp 29–30°C (125).

Nickel(0) compounds containing CO_2 ligands are of interest for environmental studies. When dry CO_2 is bubbled into $Ni(PR_3)_4$ solutions, red-orange diamagnetic complexes, $[Ni(PR_3)_2CO_2]$, form (126). Nickel complexes also form with macroligands such as tetraazamacrocycles (127). Macro ligand complexes of nickel have been studied in the redox process of CO_2 in water–CH_3CN solutions (128,129). Cationic nickel ligand complexes $[Ni(C_6Cl_5)L(PR_3)]^+$ have been reported (130). There is much interest in this field because of possible biochemical implications.

3.6. Nickel Salts and Chelates. Nickel salts of simple organic acids can be prepared by reaction of the organic acid and nickel carbonate of nickel hydroxide; reaction of the acid and a water solution of a simple nickel salt; and, in some cases, reaction of the acid and fine nickel powder or black nickel oxide.

Nickel acetate tetrahydrate [6018-89-9], $Ni(C_2H_3O_2) \cdot 4H_2O$, is a green powder which has an acetic acid odor, density 1.74 g/cm^3. When heated, it loses its water of crystallization and then decomposes to form nickel oxide. Nickel acetate is used as a catalyst intermediate, as an intermediate in the formation of other nickel compounds, as a dye mordant, as a sealer for anodized aluminum, and in nickel electroplating (71).

Nickel formate dihydrate [15694-70-9], $Ni(HCOO)_2 \cdot 2H_2O$, is a green monoclinic crystalline compound which melts with decomposition to nickel oxide at 180°C; density 2.15 g/cm^3. Nickel formate is used in the preparation of fat-hardening nickel hydrogenation catalysts (131).

Other simple nickel salts of organic acids include the oxalate [20543-06-0], oleate [68538-38-5], and stearate [2223-95-2]. The latter two have been used as oil-soluble nickel forms in the dyeing of synthetic polyolefin fibers (see DRIERS AND METALLIC SOAPS). Nickel oxalate has been used as a catalyst intermediate (71).

Nickel acetylacetonate [3264-82-2], $Ni(C_5H_7O_2)_2$, is a green powder which can be made by the aqueous reaction of a soluble nickel salt with 2,4-pentanedione. It is the simplest of the bidentate coordination compounds of nickel. Its use is primarily in preparative organonickel chemistry. Nickel acetylacetonate complexes with aluminoxanes have been reported to be active copolymerization catalysts for styrene and 2-norbornene (132). Other well-known chelates include ethylenediaminebisacetylacetonatenickel(II) [42948-35-6], nickel phthalocyanine [14045-02-8], and nickel dimethylglyoxime [13478-93-8] (133,134). The last two compounds have been studied as pigments. A review of polydentate nickel complexes is available (135). Nickel also forms derivatives with organic sulfur compounds, eg, trithiocarbonato triamminenickel [39282-88-7], $(NH_3)_3NiCS_3$, dimethyldithiocarbamatenickel [15521-65-0], $Ni[(CH_3)_2NCS_2]_2$, and nickel ethyl xanthate [52139-56-7], $Ni(C_2H_5OCS_2)_2$ (136).

4. Economic Aspects

Estimated 2002 U.S. usage of nickel and nickel compounds Table 3.

5. Analytical Methods

Analytical determination of nickel in solution is usually made by atomic absorption spectrophotometry and, often, by x-ray fluorescence spectroscopy.

Nitric acid can be used for the dissolution of nickel from many inorganic substances. In some cases perchloric acid is used in combination with nitric acid. Simple organic forms of nickel also can be dissolved in nitric acid. In the case of complicated structural organic forms of nickel, oxidation calorimetry must be used to decompose the substances.

Nickel also is determined by a volumetric method employing ethylenediaminetetraacetic acid as a titrant. Inductively coupled plasma (ICP) is preferred to determine very low nickel values (see TRACE AND RESIDUE ANALYSIS). The classical gravimetric method employing dimethylglyoxime to precipitate nickel as a red complex is used as a precise analytical technique (134). A colorimetric method employing dimethylglyoxime also is available. The classical method of electrodeposition is a commonly employed technique to separate nickel in the presence of other metals, notably copper (qv). It is also used to establish calibration criteria for the spectrophotometric methods. X-ray diffraction often is used to identify nickel in crystalline form.

6. Health and Safety Factors

6.1. Eye and Skin Contact. Some nickel salts and aqueous solutions of these salts, eg, the sulfate and chloride, may cause a primary irritant reaction of the eye and skin. The most common effect of dermal exposure to nickel is allergic contact dermatitis. Nickel dermatitis may occur in sensitized individuals following close and prolonged contact with nickel-containing solutions or metallic objects such as jewelry, particularly pierced earrings. It is estimated that 8–15% of the female human population and 0.2–2% of the male human population is nickel-sensitized (138).

Although most nickel sensitization results from nonoccupational exposures, nickel dermatitis was historically a problem in workplaces where there was a high risk of continuous contact with soluble nickel, eg, in electroplating (qv) shops. Improved personal and industrial hygiene has largely eliminated this problem. However, there are a few occupations involving wet nickel work, particularly where detergents facilitate the penetration of skin by nickel, where hand eczema may occur (139).

Protective equipment and clothing such as face shields and gloves should be worn and safety showers should be available wherever there is a possibility of being splashed or otherwise contacted by nickel-containing solutions. If dermatitis should occur, the possibility that it is nickel-related should be brought to the attention of a physician.

6.2. Inhalation. *Nickel Carbonyl.* Nickel carbonyl is an extremely toxic gas. The permissible exposure limit (PEL) in the United States is 0.001 ppm (Ni) (140). The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit value (TLV) for an 8-h, time-weighted average concentration is

0.05 mg (Ni)/m^3 (140). Nickel carbonyl may form wherever carbon monoxide and finely divided nickel are brought together. Its occurrence has been suspected but never demonstrated in some industrial operations, eg, welding of nickel alloys.

Concentrations of nickel carbonyl as low as 30 ppm in air for 30 min may be lethal for humans. Individuals exposed to these high concentrations show immediate symptoms of dizziness, headache, shortness of breath, and vomiting. These early symptoms generally disappear in fresh air, but delayed symptoms may develop 12–36 h later. These latter symptoms include shortness of breath, cyanosis, chest pain, chills, and fever. In severe exposure cases, death results from pneumonitis.

Nickel carbonyl should be used in totally enclosed systems or under good local exhaust. Plants and laboratories where nickel carbonyl is used should make use of air-monitoring devices, alarms should be present in case of accidental leakage, and appropriate personal respiratory protective devices should be readily available for emergency uses. Monitoring of urinary nickel levels is useful to help determine the severity of exposure and identify appropriate treatment measures. Some large-scale users of nickel carbonyl maintain a supply of sodium diethyldithiocarbamate, or Antabuse, a therapeutic agent, on hand for use in case of overexposure.

Other Nickel Compounds. With the exception of nickel carbonyl, nickel compounds are not known to be acutely toxic by inhalation. The potential chronic toxicity of nickel compounds is likely to be of greater concern. In particular, the incidence of cancer of the nose and lungs has been found to be significantly increased in a number of obsolete nickel refinery workers. Based on epidemiological and experimental results, the International Agency for Research on Cancer (IARC) (141) has concluded that all nickel compounds are Category 1, ie, known human carcinogens. There has generally been a lack of epidemiological evidence of a carcinogenic risk associated with exposure to metallic nickel and nickel alloys (142–144). The IARC has classified metallic nickel as a Category 2B carcinogen, ie, possibly carcinogenic to humans. Cancer risk in nickel refineries has been related primarily to exposure to soluble nickel at concentrations >10 mg/m^3 and to less soluble forms of nickel, principally nickel subsulfide and nickel oxides, at concentrations >10 mg/m^3 (143).

Epidemiological studies of nickel-producing and nickel-using workers seldom indicate excess mortality from nonmalignant respiratory disease. Evidence for such effects exists mainly as a few reports of isolated incidents of asthma, pulmonary fibrosis, chronic bronchitis, and emphysema in nickel workers. Nickel may or may not play a causal role in these incidents (143).

Some nonmalignant respiratory effects have been observed in experimental animals during acute or subchronic exposures. Soluble and moderately soluble compounds were more toxic than were insoluble compounds and produced different effects. Sulfate and subsulfide produced fibrosis whereas nickel oxide did not.

It is good practice to keep concentrations of airborne nickel in any chemical form as low as possible and certainly below the relevant standard. Local exhaust ventilation is the preferred method, particularly for powders, but personal respirator protection may be employed where necessary. In the United States, the Occupational Safety and Health Administration (OSHA) personal exposure limit (PEL) for all forms of nickel except nickel carbonyl is 1 mg/m^3. The

ACGIH TLVs are respectively 1 mg/m^3 for Ni metal, insoluble compounds, and fume and dust from nickel sulfide roasting, and 0.1 mg/m^3 for soluble nickel compounds. The ACGIH is considering whether to lower the TLVs for all forms of nickel to 0.05 mg/m^3, based on nonmalignant respiratory effects in experimental animals.

7. Environmental Concerns

The obvious destination for nickel waste is in the manufacture of stainless steel, which consumes 65% of new refined nickel production. Stainless steel is produced in a series of roasting and smelting operations. These can be hospitable to the various forms of nickel chemical waste. Quantities are expected to increase dramatically as development of the technology of waste recycle collection improves.

Recovery from waste begins with pulverization of brittle forms, shredding of storage batteries and mixing with other powdery forms such as spent catalysts, and using spent nickel plating and other nickel-containing chemical pickle solutions to form a slurry. The slurry is then dehydrated into pellet form and charged into reverbatory furnaces where it meets up with scrap and other alloy-forming ingredients in the molten state for smelting. The finished premelt product is cast into metal pigs and shipped to the steel industry. There it is used with other forms of feed to produce finished stainless steel products.

8. Uses

8.1. Catalysts.

Nickel is an important hydrogenation catalyst because of its ability to chemisorb hydrogen. One important nickel catalyst is Raney nickel. Raney nickel catalyst is used widely in laboratory and industrial hydrogenation processes. It is the most active, least specific of the nickel catalysts. Raney nickel catalyst has been used in a continuous hydrogenation process by filling a tube with chunks of the nickel–aluminum alloy and activating the surface by passing a solution of caustic over it, thereby removing some of the surface aluminum. Periodic flushes with caustic enable the catalyst to be reactivated in place. A review is available (145).

A number of variations of the nickel–aluminum catalyst have been developed. One involves rolling nickel and aluminum foil at 630°C followed by leaching with caustic (146). Nickel–aluminum alloy has been flame-sprayed on the inside of steel tubes, followed by leaching (147), and has been suggested for use as a continuous reactor for the conversion of synthesis gas to methane (148) (see FUELS, SYNTHETIC, GASEOUS FUELS). Another method is the electroplating of nickel on the inside wall of stainless steel tubing, followed by aluminizing the nickel surface and activating with a caustic leach (149). Other alloying compositions include a nickel–iron–aluminum alloy which, upon caustic activation, is used as a catalyst for the selective hydrogenation of organic nitro compounds (see AMINES BY REDUCTION) (150). A composition of nickel and silicon yields the nickel silicides [12035-57-3], NiSi, and [12201-89-7], $NiSi_2$, which, upon caustic leaching, activate a nickel surface (151). Nickel–boron alloy [12007-00-0], when activated with caustic, has been claimed to be a more reactive hydrogenation catalyst than the nickel–aluminum catalyst (152).

Supported nickel catalysts of the precipitated and impregnated types are used for methanation, steam-hydrocarbon reforming, petrochemical hydrogenation, and fat hardening (see SUPPORTED CATALYSTS, SUPPORTED). The nickel compound and the ceramic carrier in a dry reduction technique are heated in a stream of inert gas to decompose the nickel compound to nickel oxide, which then is reduced with hydrogen to nickel metal. Precipitated catalysts generally are made from nickel carbonate and nickel hydroxide. Nickel nitrate, nickel chloride, hexammine nickel carbonate, and nickel acetate solutions are used for impregnation (153). Supported catalysts of nickel on alumina or nickel on zirconia have been suggested as a heterogeneous methanation system for the hydrogenation of CO. The latter catalyst has been reported to be quite active in the presence of H_2S (154).

Nickel is used with other elements for special types of hydrogenation catalysts. Nickel sulfide and nickel tungsten sulfide catalysts are used when high concentrations of sulfur compounds are present in the hydrogenation of petroleum distillates. Nickel–molybdenum catalysts are used to denitrogenate petroleum fractions that are high in nitrogen-containing components.

Black nickel oxide is used as an oxygen donor in three-way catalysts containing rhodium, platinum, and palladium (155). Three-way catalysts, used in automobiles, oxidize hydrocarbons and CO, and reduce NO_x. The donor quality, ie, the ability to provide oxygen for the oxidation, results from the capability of nickel oxide to chemisorb oxygen (see EMISSION CONTROL, AUTOMOTIVE).

Nickel and other transition metals function as solvent-catalysts for the transformation of carbon species into the diamond allotrope. At temperatures high enough to melt the metal or metal–carbon mixture and at pressures high enough for diamond to be stable, diamond forms by what is probably an electronic mechanism.

Important organic chemical intermediates are manufactured using nickel organometallic compounds as catalysts. One example is Shell's Higher Olefins Process (SHOP), a commercial method for the oligerimerization of ethylene (qv) to detergent-range alpha-olefins. The catalyst is a ligand-stabilized nickel chelate dissolved in a polar solvent, into which ethylene is pressurized. The resulting alpha-olefins are insoluble in the solvent and thus easily separated from the reaction mixture (156–159).

Another example is the DuPont process for the production of adiponitrile. Tetrakisarylphosphitenickel(0) compounds are used to affect the hydrocyanation of butadiene. A multistage reaction results in the synthesis of dinitrile, which is ultimately used in the commercial manufacture of nylon-6,6 (156–161).

Nickel Carbonyl. Nickel carbonyl serves as an intermediate in nickel refining. High purity nickel pellets for melting and dissolving are a product of the carbonyl-refining process. The nickel powders useful in nickel chemical synthesis and for making nickel alkaline-battery electrodes and powder metallurgical parts are derived from the carbonyl-refining process (162–176). Nickel carbonyl also is used in a carbonylation reaction in the synthesis of acrylic and methacrylic esters from acetylene and alcohols (168) (see ACRYLIC ACID AND

DERIVATIVES; METHACRYLIC ACID AND DERIVATIVES). Nickel carbonyl has been proposed as a catalyst of as an addition agent for a variety of organic reactions including catalysis, polymerization, and other carbonylation reactions.

The surface of the decomposition of nickel carbonyl is important in numerous commercial applications. Graphite, always present in the nickel powder formed from nickel carbonyl, results from the disproportionation of CO. The quantity of graphite formed can be related to a few ppm of iron carbonyl present in the nickel carbonyl gas. A smooth coating of nickel forms when graphite powder is used as a substrate for nickel carbonyl decomposition. An autocatalytic process involving graphite may thus occur during nickel carbonyl decomposition. The facile decomposition of nickel carbonyl on the surfaces of aluminum and alumina powders leads to smoothly nickel-coated substrate particles (169–171). For most metallic and oxide particles in the presence of nickel carbonyl, the primary nucleation species reverts to the newly formed graphite interface. Scanning electron micrographs particles show the growth of nickel warts, suggesting that the population of nucleating species on these substrates is very low.

Nickel-coated powder products are used as conductive pigments for application in surface coatings (qv), adhesives (qv), injection molding powders, and for sealants (172). Nickel-coated aluminum powder is also used in plasma spray applications for hard-facing metals (see PLASMA TECHNOLOGY). Nickel-coated alumina is useful in grinding-wheel applications (173) and as an interface material for the cementation of nickel to alumina in electronic applications. Nickel carbonyl gas is used commercially to coat graphite fiber tows which are useful in lightning-strike devices, eletromagnetic interference (EMI) shielding in plastic parts, and a variety of epoxy composites requiring conductivity (174,175). The polyacrylonitrile (PAN) graphite fiber, however, does not form a nucleation surface for nickel carbonyl decomposition. A promotor such as a Lewis acid must be added to the gas stream and the nickel film rapidly forms on the heated graphite fiber surface. The nickel, however, is not bonded to the fiber as it is to the powder substrates.

8.2. Electroplating. The second-largest application for nickel chemicals is as electrolytes in nickel electroplating (qv). In ordinary plating systems, nickel present in the electrolyte never forms on the finished workpiece; the latter results from dissolution and transfer from nickel anodes. Decorative nickel plating is used for automobile bumpers and trim, appliances, wire products, flatware, jewelry, and many other consumer items. A comprehensive review of nickel electroplating has been compiled (176).

8.3. Specialty Ceramics. Black or green nickel oxide and nickel carbonate are used extensively in the ceramic industry (see CERAMICS, OVERIEW). Nickel oxide is added to glass frit compositions which are used for porcelain-enameling of steel. Nickel enhances the adhesion of glass (qv) to steel through the formation of spinel structures of the mixed silicates of iron and nickel at the interface (177). Nickel oxides also are used in the manufacture of the magnetic nickel–zinc ferrite powders, which are made into parts for use in electric motors, antennas, and cathode ray tube (CRT) yokes (see FERRITES). They are also used for shielding and filtering electromagnetic radiation interference (EMI) in electronics equipment (178–180).

The nickel silicides, ie, Ni_3Si [12059-22-2], Ni_5Si_2 [12059-27-7], Ni_2Si [12059-14-2], and NiSi [39467-10-2], are electroconductive materials that are useful in resistors and resistance heating elements (181). Nickel silicides are also used to discharge static electricity from glass in automobile windshields. Nickel boride [12007-00-0], NiB, made from the exothermic reaction of boron with molten nickel, is used as a getter for the removal of oxygen from the nickel film that is manufactured for use as the screen backing in mercury-vapor displays.

Nickel niobium [59913-35-8], NiNb, is a glassy-type compound formed by reaction of niobium oxide and nickel powder. Adding nickel niobium to molten nickel–iron alloys is an important and convenient way of introducing this refractory metal, niobium, to the structure and therefore reducing the oxidation potential for corrosion. Nickel aluminide [12003-81-5], Ni_3Al, an intermetallic compound formed by the reaction of molten aluminum and nickel pellets, is a high strength, light, ductile material. It can be used in powder form to make compacted products that can be sintered to high strength, such as gears (182).

Nickel phosphorus compounds also have been studied for their electroconductive nature (see ELECTROLESS PLATIING ELECTROLESS PLATING). Nickel selenite [15060-62-5], nickel phosphate, nickel tungstate [14177-51-6], nickel chromite [12018-18-7], potassium nickel molybdate [59228-72-7], nickel oxide, and nickel nitrate have been used as glass colorants (see COLORANTS FOR CERAMICS). Nickel oxide also is employed as a colorant in ceramic body stains used in ceramic tile, dishes, pottery, and sanitary ware. Nickel oxide imparts avocado green and gray colors in ceramic glazes. When fired, nickel oxide, antimony oxide, and titanium dioxide produce the yellow chalking pigment, nickel (antimony) titanate [11118-07-3]. This pigment is used extensively in exterior house paint and in vinyl house siding because of its good weatherability. Nickel titanate has been recommended as a replacement for heavy-metal pigments, such as lead chromate and cadmium yellow (183). Nickel cobalt aluminate is a useful fade-resistant blue pigment for exterior paint application (184) (see PIGMENTS, INORGANIC).

8.4. Plastics Additives. Many claims have been made for the use of nickel chemicals as additives to various resin systems. By far the most important application is as uv-quenchers in polyolefins (185,186). Among the useful nickel complexes in these systems are dibutyldithiocarbamate nickel [13927-77-0], nickel thiobisphenolates, and nickel amide complexes of bisphenol sulfides (187). The nickel complex of *O*,*O*-dimethylcyclohexyldithiophosphate increases the uv-stability of high density polyethylene (HDPE) (188). Several classes of nickel compounds are effective as light stabilizers in poly(vinyl chloride) (PVC), although none have become commercially important, because of objectionable coloring of the plastic. Nickel aminothiobisphenolates have been claimed as light stabilizers in ABS graft copolymers (189). Nickel dialkylhydroxyphenylalkylphosphonate imparts light stability to ABS terpolymers and polyurethanes (190) (see ANTIOXIDANTS, POLYMERS; UV STABILIZERS).

Nickel dialkyldithiocarbamates stabilize vulcanizates of epichlorhydrinethylene oxide against heat aging (190). Nickel dibutyldithiocarbamate [56377-13-0] is used as an oxidation inhibitor in synthetic elastomers. Nickel chelates of substituted acetylacetonates are flame retardants for epoxy resins (191).

Nickel dicycloalkyldithiophosphinates have been proposed as flame-retardant additives for polystyrene (192–194) (see FLAME RETARDANTS: AN OVERIEW; HEAT STABILIZERS).

8.5. Organic Dyes and Pigments. A number of nickel pigments have been reported, eg, the nickel disazomethine complex [61312-95-6] which is prepared from 2-hydroxy-1-naphthaldehyde (195), the water-soluble nickel azo–azomethine complex (196), and nickel chelates of azines and disazines (197). Nickel Azo Yellow [51931-46-5] is a commercially important pigment with excellent lightfastness and good heat stability and bleed resistance (198,199). Other nickel azo pigments which have had some success include Nickel Azo Gold and Nickel Azo Red (200) (see DYES, AZO). The lightfastness in other pigment systems, eg, the quinacridones and iron blue, have been improved by the addition of 1–2-wt% nickel in soluble salt form.

Nickel also has been used as a dye site in polyolefin polymers, particularly fibers. When a nickel compound, eg, the stearate or bis(*p*-alkylphenol) monosulfide, is incorporated in the polyolefin melt which is subsequently extruded and processed as a fiber, it complexes with certain dyes upon solution treatment to yield bright fast-colored fibers which are useful in carpeting and other applications (201). Nickel stearate complexing of disperse mordant dyes has been studied (202).

8.6. Agricultural Chemicals. Many claims exist for the use of nickel chemicals as nematocides, miticides, and other pesticides (qv) (203). However, extensive testing of many classes of nickel complexes in insecticide, fungicide, nematocide, and herbicide programs leaves little doubt that, except in the case of a few selected fungus organisms, nickel chemicals afford little more efficacy than the nonnickel-containing derivatives (see HERBICIDES; INSECTICIDES). The application of nickel ion, particularly the halides, as a commercial fungicide to control blister blight of tea (qv) was formerly practiced in the Far East (204). Tea is one of a few botanical species that naturally contains nickel (205), and in India the nickel content of certain plants grown in lateritic soils has been found to be up to 100 ppm (206). Nickel sulfate is used to control rust in bluegrass seed crops in the northwestern United States (207). The use of nickel sulfate has been thoroughly explored for the control of cereal rusts, but no commercial application has resulted (208). Nickel sulfate has been proposed as an additive to wood (qv) chips against fungus attack in long-term chip storage piles (209). Evidence exists for the possible requirement of nickel ion in chicks, rats, and pigs (210), and studies show that nickel ion activates certain enzymes and may have a metabolic role (see FEEDS AD FEED ADDITIVES, NONRUMINANT FEEDS; MINERAL NUTRIENTS).

8.7. Other Specialty Chemicals. In fuel-cell technology, nickel oxide cathodes have been demonstrated for the conversion of synthesis gas and the generation of electricity (211) (see FUEL CELLS). Nickel salts have been proposed as additions to water-flood tertiary crude-oil recovery systems (see ENHANCED OIL RECOVERY). The salt forms nickel sulfide, which is an oxidation catalyst for H_2S, and provides corrosion protection for downwell equipment. Sulfur-containing nickel complexes have been used to limit the oxidative deterioration of solvent-refined mineral oils (212).

Nickel salts and soaps have been used in electrosensitive copy paper for image development. Nickel bis-(3,5 di-*tert*-butylsalicylate) [68569-24-4] has been studied in pressure-sensitive color developer sheets (213). It has also been used for color stabilization of color copy paper (see ELECTROPLATING).

Nickel phosphate complexes with ammonia have been used for high speed photographic image amplification (214), and nickel chelated quenching compounds, which stabilize image dyes in photographic film, also have been used (see PHOTOGRAPHY)(215). Nickel (2-hydroxy-4-methoxybenzophenone-5-sulfonate) [130543-71-4] reduces ultraviolet photofading of the dyes Rose Crystal Violet and Erioglaucine (216).

A nickel-boron coating having lubricant properties has been reported (217).

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Table 1. **Properties of Anhydrous Nickel Halides**[a]

Compound	CAS Registry number	Mp, °C	Density, g/cm^3	Color	Solubility, 0°C, g/100 mL H_2O
nickel difluoride	[10028-18-9]	1000[b]	4.63	light green	4
nickel dichloride	[7718-54-9]	1001	3.56	yellow	64
nickel dibromide	[13462-88-9]	963	5.10	orange	113
nickel diiodide	[13462-90-3]	797	5.83	black	124

[a] Refs. 45 and 46.

[b] Sublimes.

Table 2. **Physical Properties of Nickel Carbonyl**[a]

Property	Value
melting point, °C	−17
crystallization point, °C	−25
density at 20.0°C, g/mL	1.3103
electronic absorption, nm	240[b]
molecular rotation at 578 nm, μ_{rad}	2.768
bond distances, pm	
Ni−C	183.8
C−O	114.1
vapor pressure data, kPa[c]	
at 0°C	17.1
16.1°C	36.2
21.1°C	44.3
28.5°C	60.0
35.1°C	77.7
42.2°C	101
critical temperature, °C	200

[a] Refs. 78–82.

[b] Intense.

[c] To convert kPa to psi, multiply by 0.145.

Table 3. **U.S. Consumption of Nickel in 2002, t of Contained Nickel by Use**[a,b]

								Grand total	
Use	Metal	Ferro-nickel	Oxide and oxide sinter	Chemicals	Other forms	Total primary	Secondary (scrap)	2002	2001
cast irons	132	W			40	172	359	531	886
chemicals and chemical uses	25		W	342		367		367	1,630
electric, magnet, expansion alloys	130					130	W	130	273
electroplating, sales to platers	12,300			37	W	12,300	W	12,300	12,500
nickel-copper and copper-nickel alloys	2,750		W		15	2,770	2,960	5,720	7,190
other nickel and nickel alloys	11,800	W	W		57	11,900	2,020	13,900	17,900
steel:									
stainless and heat resistant	25,300	12,500	1,620	W	503	39,900	89,600	129,000	121,000
alloys, excludes stainless	3,170	60			W	3,230	745	3,980	7,590
superalloys	11,200		W	W	393	11,600	534	12,100	18,400
other[c]	4,440	5	88	361	105	5,000	3,570	8,570	12,200
Total	71,200	12,500	1,710	740	1,110	87,300	99,800	187,000	200,000
Total all companies, apparent	XX	XX	XX	XX	XX	121,000	69,800	191,000	188,000

[a] Ref. 137.

[b] W Withheld to avoid disclosing company proprietary data; included with "Other." XX Not applicable.

[c] Includes batteries, catalysts, ceramics, coinage, other alloys containing nickel, and data indicated by the symbol "W."