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Review

Zinc oxide particles: Synthesis, properties and applications

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ABSTRACT

Zinc oxide powder has traditionally been used as a white pigment and as an additive to rubber. While it has largely been displaced as a pigment in paints, its usage in rubber remains very important. However, the myriad of other practical uses of ZnO are sometimes overlooked, and reviews in the recent scientific literature tend to emphasize high technology applications that do not yet have any commercial reality. Similarly, while some of the low-volume processes used to manufacture ZnO nanostructures have been well covered in the literature, there has been far less reported on the tonnage chemical engineering processes by which most ZnO is actually made. The multiplicity of processes by which ZnO can be produced is a potential source of confusion, however, the process used has a large influence on the properties of the oxide, and hence on its suitability for various applications. Here we provide a contemporary review and analysis of the manufacture of ZnO, and its properties, applications, and future prospects.

1. Introduction

Zinc oxide has been used in diverse applications for thousands of years [1] and could reasonably be considered to be a mature engineering material [2] with annual production now approaching one and a half million tons [3]. Nevertheless, there has been a steep rise in the number of scientific publications addressing this material in the last decade indicating significant new interest. In the present review we analyze this phenomenon, and show that it is driven by the prospect of many exciting new technological functionalities for ZnO. While recent reviews describing aspects of the condensed matter physics, surface chemistry, synthesis techniques and semiconducting applications of ZnO are available [4–12], these have generally neglected the more practical aspects of the subject, including the extensive patent literature on ZnO. In our opinion the latter contains a considerable amount of accumulated insight and information. Therefore, we provide a contemporary review of the literature – both scientific and patent – that is oriented towards larger scale industrial production methods and commercial applications of ZnO. Discussion of intermediate products such as ZnO-bearing slags or fumes or "metallurgical grade" ZnO is largely excluded from the review as these non-standard materials require further processing before they become suitable for end-use.

Zinc oxide has been in use since at least 2000 B.C. as a constituent of medicinal ointments for the treatment of boils and carbuncles [1,13]. Somewhat later, ZnO ore was exploited as a source of zinc for brass, a discovery usually attributed to the Romans [14] but which may have come from India a century or so earlier [15]. Brass could be produced by smelting a mixture of the powdered zinc ore, charcoal and granules of copper, but a by-product was the ZnO that collected on the walls and flues of the brass smelting furnaces. The latter was known to the Romans as *cadmia fornacis* (furnace accretions) and was purified for use in ointments. Use of ZnO in skin lotions has continued up to the present day in the form of a slurry of zinc and iron oxide known in many English-speaking countries as "*calamine lotion*" [1]. There is also a rich tradition of ZnO manufacture from about 1100 A.D. onwards in Iran [14,16] and India [15]. There was significant production of zinc metal in China from about 1600 onwards [14].

The deliberate manufacture of ZnO powder by oxidation of Zn metal was pioneered in Germany in the 1700s and white pigment was produced in France by these means from 1781 onwards [17]. The new pigment (known also as zinc white or Chinese white) competed with "white lead" (basic lead carbonate) because it did not darken in the presence of sulfurous gases and had better hiding power [17,18], Fig. 1. In the Nineteenth Century two large-scale processes, the indirect ("French") process and the direct ("American") process were developed to produce ZnO. These are still in use today and are discussed in detail below.

A major development during the second half of the nineteenth century was the use of ZnO in rubber to reduce vulcanization process times. Zinc oxide had been used as a reinforcing agent in rubber until 1912, when it was replaced by carbon black. With the discovery of the first organic accelerator for vulcanization by Oenslager in 1906, zinc white found a new application as an activator in these materials [17,19]. Today, the rubber industry consumes a significant proportion of the ZnO produced (see below).

Zinc oxide is produced mainly by three distinct processes: directly oxidizing zinc metal, or reduction of an ore to zinc metal followed by controlled re-oxidation or, to a far lesser extent,

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Fig. 1. Advertisement label for zinc oxide, 1868 (USA Library of Congress. http://www.loc.gov/pictures/item/2006679062/Reproduction Number: LC-USZ62-51233).

precipitation of the oxide or a carbonate from an aqueous solution followed by calcination. Not surprisingly, there is a close industrial and commercial relationship between zinc metal and ZnO. Zinc is the fourth most widely used metal in the world after iron, aluminum and copper. The most common zinc production process is from sulfidic ores using the hydrometallurgical roast-leach-electrowin method [14]. This is quite energy-intensive with an energy consumption of $\sim$15 GJ per ton of zinc, 80% of which is used during electrolysis [20]. Obviously, these costs carry over to any ZnO that is produced from metallic zinc. Therefore, the price of the oxide is sometimes reckoned as the LME (London Metal Exchange) price of the metal plus some additional sum to account for the cost of manufacturing the oxide. Global annual zinc production in 2009 was more than 11 million metric tons [21].

The end uses of zinc at present are summarized in Fig. 2. Between 50% and 60% of the ZnO is used in the rubber industry [3,17,22] where it is normally added at between 3 and 5 parts per hundred (phr) rubber [23,24]. Global annual rubber output was $\sim$25 million tons in 2010 [25], about half of which is consumed by the tire industry [3]. A typical tire contains of the order of 100 g of ZnO.

It is important to note the intertwined relationship between the ZnO and Zn industries: besides the close relationship in price, the raw materials also cross over. For example between 5 and 15% of the zinc metal charged to galvanizing baths is collected again as zinc ash or dross, and this is an important feedstock for the production of ZnO [26]. Other industries that generate zinc-containing wastes are casting, smelting, and scrap recycling, and electric arc manufacture of steel from scrap. These wastes may contain from 10 to 96% total zinc in the form of metallic zinc, zinc hydroxy-chloride (such as simonkolleite) and ZnO. It is estimated that more than 80% of available recyclable zinc-containing wastes are recycled, usually by hydrometallurgical or pyrometallurgical processes [27–30].

2. Synthesis

2.1. Background

There is a very large variety of zinc-containing materials available as feedstock and therefore, correspondingly, a large number of possible processing technologies. From an economic perspective, the synthetic processes for ZnO may be divided into two groups: low cost bulk industrial methods and high cost laboratory or pilot-plant scale methods. The main technological differences between the various production methods involve the zinc precursors and the process temperatures, the unit operations used and, of course, the scale at which they are carried out. In addition, an extremely wide range of laboratory or pilot-scale techniques have been reported but very few of these are of actual commercial interest, and we will mention only those that appear to offer some advantages for specialized applications.

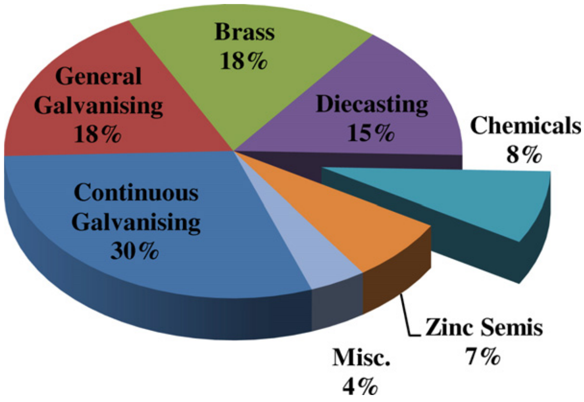

Fig. 2. Chart showing the various uses of zinc metal. Zinc oxide is the main chemical produced from zinc metal. Compiled using data from diverse sources.

2.2. Industrial production methods

Industrially, most ZnO is produced by pyrometallurgical methods (e.g. the indirect process, the direct process, or spray pyrolysis) or by hydrometallurgical methods. Zinc oxide can also be produced as a by-product of some chemical reactions such as in the production of sodium dithionite. Generally, the selection of the production process is based on the zinc-containing raw material to be consumed. Each process produces grades of ZnO with relatively different properties and hence different applications.

The largest proportion of ZnO is produced by the indirect (French) process. The direct (American) process accounts for the next greatest share followed by the hydrometallurgical processes, which generally exploit zinc-containing wastes [17]. Each of these methods is discussed below. The formal specifications of the major types of ZnO available industrially are listed in Table 1. The different grades of ZnO powder are also commonly referred to in the trade using somewhat vaguely defined terms such as “gold seal”, “white seal”, “green seal” and “red seal”, with purity decreasing in the order listed (see Section 3.4).

2.2.1. Pyrometallurgical synthesis

2.2.1.1. The indirect (French) process. The indirect, so-called “French process”, was developed between 1840 and 1850 to meet a demand for ZnO for use in paints. The first US patent was registered in 1850 to Leclaire and Barruel of France, Fig. 3 [17,32]. Zinc metal is the starting material in this process. A heated crucible containing zinc is covered with a lid to channel the zinc vapor through a central orifice. In the temperature range of 1230–1270 °C, zinc vapor has a pressure of 0.2–1.1 MPa (zinc melts at 420 °C and boils at 907 °C). When the orifice cover (if used) is removed, zinc vapor streams into the atmosphere with a calculated nozzle speed of 8–12 m s^{-1} resulting in rapid oxidation and a greenish-white flame with a length of $\sim$30 cm and temperature of 1000–1400 °C, Fig. 4. A temperature drop from the combustion temperature to between 500 and 800 °C within $\sim$5 s between the crucible and suction hood is the main cause of non-uniform growth conditions [33].

In a typical plant, the ZnO powder formed by combustion then enters a cooling duct of between 50 and 300 m long [34] before it is collected in the bag-house at a temperature below 100 °C by a system of vertical fabric bags. After collection the powder is fractionated according to particle size using vibrating hopper sieves [23]. The French process is widely considered to be the fastest and

Table 1
Typical properties of different grades of zinc oxide according to ASTM D4295-89 [31].

Property	ASTM Method	American (direct) type	French (indirect) type			Secondary types		
			Class 1	Class 2	Class 3	Chemical	Metallurgical	
							Class 1	Class 2
Zinc oxide (%)	D3280	99.0	99.5	99.5	99.5	95.0	99.0	99.0
Lead (%)	D4075	0.10	0.002	0.002	0.002	0.10	0.10	0.10
Cadmium (%)	D4075	0.05	0.005	0.005	0.005	0.05	0.05	0.05
Sulfur (%)	D3280	0.15	0.02	0.02	0.02	0.15	0.02	0.02
Heat loss at 105 °C (%)	D280	0.25	0.03	0.25	0.25	0.50	0.25	0.25
Sieve residue, 45 μm (%)	D4315	0.10	0.05	0.05	0.05	0.10	0.10	0.10
Surface area ($m^2 g^{-1}$)	D3037	3.5	9.0	5.0	3.5	40.0	5.0	3.5
Manufacturing process	–	Pyrometallurgical reduction of ZnO	Combustion of pure Zn			Wet chemical reactions	Combustion of Zn dross and scrap	

Reproduced with permission, from ASTM D4295-89 (2005) Standard Classification for Rubber Compounding Materials-Zinc Oxide, copyright ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

most productive industrial method to produce ZnO [34] but, as we will see, the product it makes is not optimum for all applications.

The quality of the ZnO depends on the precursors used. For instance, for the production of “gold seal” or pharmaceutical grade ZnO, SHG (special high grade, 99.99% Zn) zinc metal is used whereas ordinary HG zinc (99.95%) may be adequate to produce the ZnO used in the rubber industry. Other zinc-containing feed materials such as galvanizer’s dross, die-casting alloys or zinc ash may also be used for less demanding applications and are becoming increasingly popular due to their lower cost. However, if metal residues are to be used then various liquid or vapor-phase separation techniques may need to be applied first to eliminate Cd, Pb, Fe, and Al before the Zn is oxidized. Theoretically, the maximum yield of ZnO in the French process is 1.245 tons per ton of zinc used; but in practice ZnO recovery of around 1.2 tons is obtained when using SHG zinc as the raw material and even less if zinc dross (85–95% zinc content) is used as feedstock. Zinc ash can contain up to 30% metallic zinc with the balance composed of ZnO and zinc hydroxy-chloride, however, the metallic content must first be separated from the ash by physical separation processes such as rotary mills and sieving before it can be used in the French process.

Zinc oxide produced by the French process can have high purity (>99%) if high purity zinc is used a feedstock. However, the product may contain traces of zinc metal, the amount of which is inversely proportional to particle size and which may render it unsuitable for some applications [31,35,36].

The particles are nodular in shape [31,36] and the individual primary ZnO crystallites are 30–2000 nm in size. Scanning electron microscope images of typical French process ZnO are shown in Fig. 5. The surface area of French process ZnO is generally 3–5 $m^2 g^{-1}$ but can reach 12 $m^2 g^{-1}$ by carefully controlling combustion conditions such as air flow and flame turbulence [3,17] or the distance between the suction hood and nozzle (which affects the air velocity). If the flame temperature increases, the specific surface area will drop. By increasing the excess of reactant air (oxygen) by making a better circulation of air or forced flow of compressed air in the combustion zone, ZnO quenching becomes faster and finer particles can be achieved, resulting in higher specific surface area.

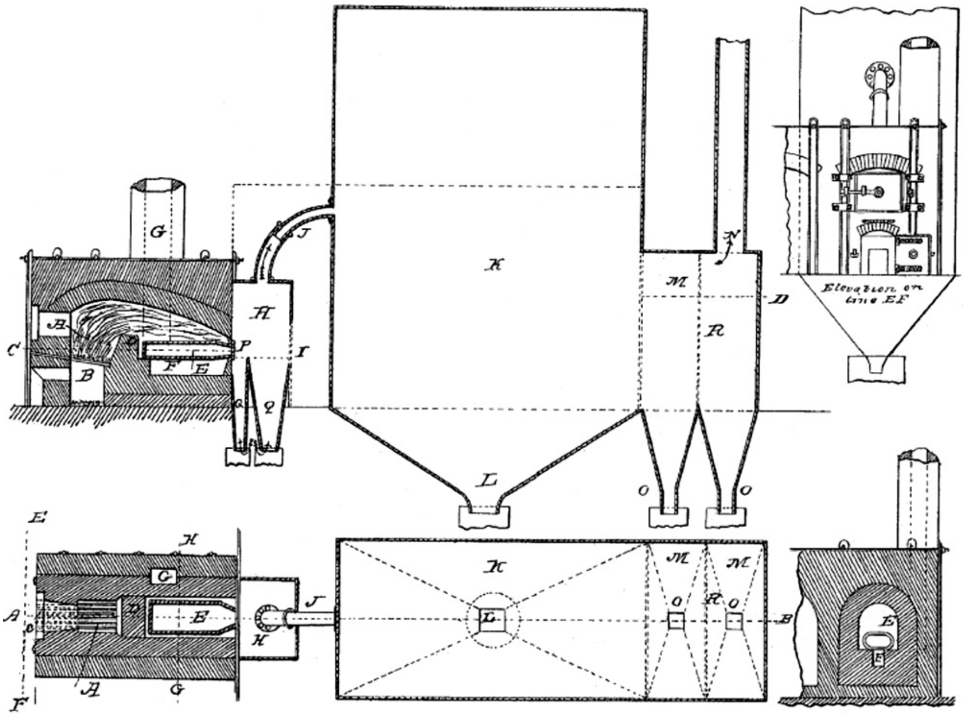

Fig. 3. Schematic of the indirect process to produce ZnO reproduced from the 1850 US patent of Leclaire and Barruel [32].

Fig. 4. Photograph of a French process drum in operation, by permission from PT. Indo Lysaght, Indonesia.

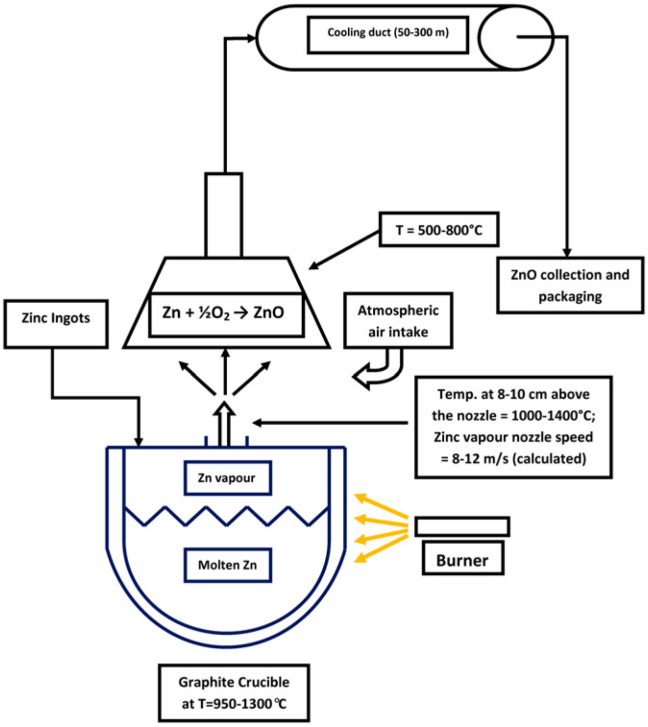

Fig. 6. Process flow diagram (PFD) of the French process.

Superheating the zinc vapor also results in finer ZnO particles. The purity of the ZnO product is solely a function of the composition of the zinc vapor.

Some relevant standards for ZnO produced by this route include ASTM D4295-89, a standard for rubber compounding [31], which also indicates the classifications of ZnO by type, and ASTM D79-86 for pigments [36].

There are various implementations of the French process. Older technology principally uses a batch process that takes place in a crucible with a long cooling duct, most of which is horizontal. Newer technologies use a semi-continuous process with a vertically-designed cooling duct to save space. A batch is recharged with zinc ingots at approximately four hour intervals whereas in the semi-continuous process a zinc ingot (often 25 kg) is added to the furnace every 6 min. The productivity of the semi-continuous process is often higher than that of the batch process. The semi-continuous system is rarely shut down unless for an overhaul and it is generally very compact. The process flow diagram (PFD) of a basic French process furnace is depicted in Fig. 6.

There are several other variations to the process, the selection of which depends on the feedstock material and local conditions. Graphite or silicon carbide muffle furnaces or retorts are utilized in the most common design which uses Zn ingots or dross as feed material. The solid ingots may be fed into the furnace either batch-wise or pre-melted and fed continuously as a liquid. The retort is generally heated from the outside using a natural gas or oil burner, although electric heating elements (silicon carbide) are in use in some plants. In the case of using dross from smelting or casting, Fe, Pb or Al-containing residues build up in the crucible and must be removed periodically [17]. Production capacity is generally in the range of 70–500 kg h^{-1} depending on design [37,38].

In another design, a fractional distillation system (invented in Norway in 1960 [39]) is implemented for refining the Zn prior to

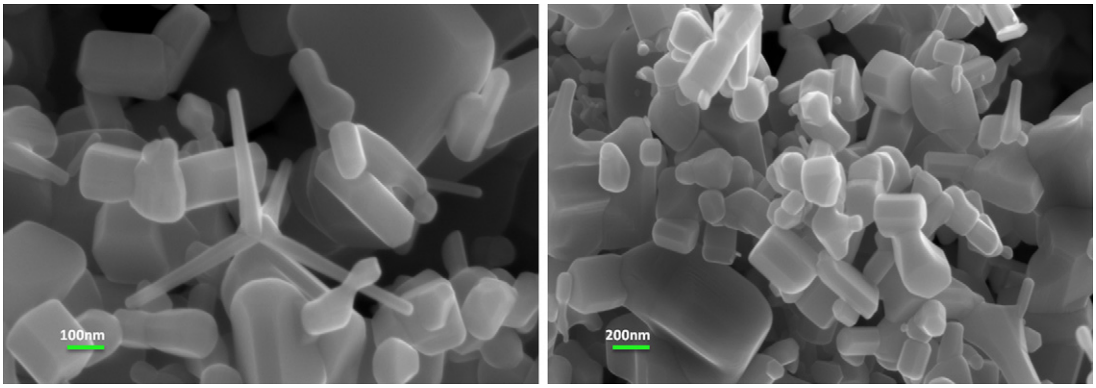

Fig. 5. SEM images of the French process ZnO.
Samples from PT. Indo Lysaght, Indonesia; photos by Dr R. Wuhrer, University of Technology Sydney.

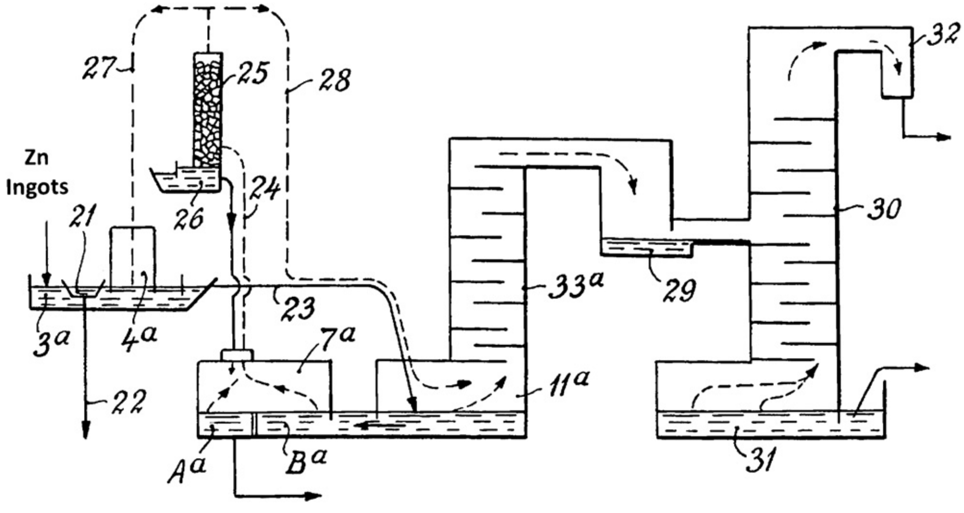

Fig. 7. Schematic of the Larvik process designed by Lundevall [39].

its combustion to make ZnO. This technique is now referred to as the Larvik distillation technology and is in use by industrial producers of zinc/ZnO such as the multinational Umicore Group [40]. The purification process as depicted in the patent is shown in Fig. 7 and includes a furnace with two separate chambers and a distillation column. Impurities such as Fe, Pb and Cd remain behind (Fig. 7, 33a) and are periodically removed [39].

The process works because the relatively large differences in boiling point between Cd, Pb, Zn and Fe allow the Zn fraction to be separated by distillation. Oxidation of the distilled zinc results in high quality ZnO [17]. Lead can be a problematic element: its melting point is only 327 °C but its boiling point of 1749 °C is well above that of zinc. At temperatures above the boiling point of zinc, lead exists in the molten form. Therefore along with zinc vapor, lead mist can enter the vapor phase and must be condensed in a lead trap (e.g. splash condenser) before the zinc vapor is oxidized [39,41].

2.2.1.2. The direct (American) process. The direct, so-called “American” process [42,43], makes use of a feedstock containing a mixture of oxidized zinc-containing raw materials and carbonaceous reducing agents. Zinc metal is produced from the charge by reduction at elevated temperature and is vaporized. In the case of ZnO production, the vapor moves into a combustion chamber where it is re-oxidized in a similar manner to that used in the indirect process. Finally, the oxide is collected in a bag-house [17,23].

Four interdependent reactions (1)–(4) are important in the formation of the zinc vapor:

$$ZnO_{(s)} + C_{(s)} \rightarrow Zn_{(g)} + CO_{(g)} \tag{1}$$

$$ZnO_{(s)} + CO_{(g} \rightarrow Zn_{(g)} + CO_{2(g)} \tag{2}$$

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \tag{3}$$

$$CO_{2(g)} + C_{(s)} \rightleftharpoons 2CO_{(g)} \tag{4}$$

Zinc oxide is reduced in Reactions (1) and (2). The resultant CO_2 is reduced by carbon to form CO again according to the Boudouard Reaction (4), providing more reductant for the reaction with ZnO [44].

Under standard state conditions, ΔG for Reaction (1) becomes negative for $T > 940\,^{\circ}C$ (point A on Fig. 8), and negative for $T > 1317\,^{\circ}C$ for Reaction (2) (point B on Fig. 8). It is critical to keep the temperature as high as possible to prevent the premature occurrence of the re-oxidation reaction implied by the reverse of Reaction (2). Fortunately, under conditions of increased p_{CO}, the re-oxidation temperature will be lowered, Fig. 9. Reactions (3) and (4) have controlling effects on the spatial location of reduction and re-oxidation in the plant. An excess of carbon controls the amount of CO necessary for reduction according to Boudouard reaction. For the carbo-reduction of metal oxides to be feasible, there should be a minimum ratio of CO to CO_2. This critical ratio shows the competition of Reactions (3) and (4). For example, at 1100 °C the ratio

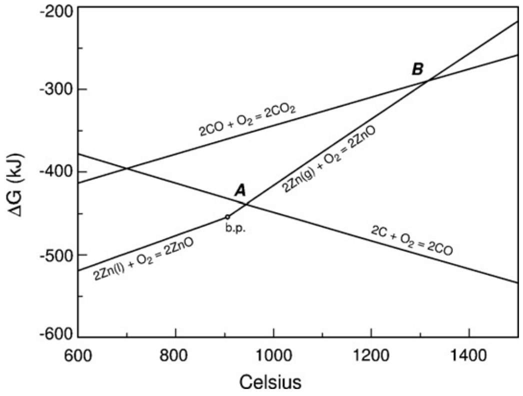

Fig. 8. Ellingham diagram showing free energy change of indicated reactions as a function of temperature, calculated using standard state thermodynamic data for the species.

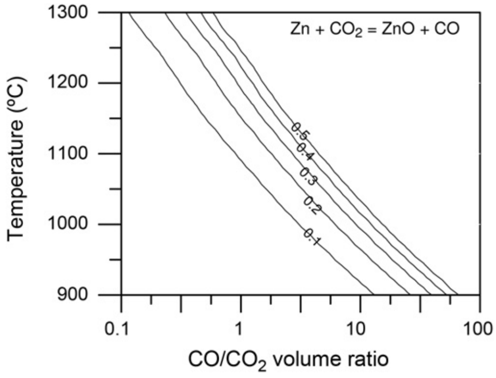

Fig. 9. Effect of temperature and gas composition on the partial pressure of $Zn_{(g)}$ (in atm). A decrease in temperature or CO/CO_2 causes a reduction in p_{Zn} due to increased oxidation. Recalculated and redrawn by the authors after Schoukens et al. [45]. Atmospheric pressure is assumed.

should be around 10 for the reduction stage (see Fig. 9). Therefore Zn does not go back to ZnO in the reduction zone as long as there is an excess of carbon and/or the critical ratio of CO/CO_2 for that temperature is exceeded.

A variety of zinc-containing raw materials can be used, including zinc ores (oxidic or sulfidic), zinciferous materials and flue dusts, lead blast furnace slags, mill slimes, electrolytic-zinc leach residues, skimmings from casting furnaces, off-grade zinc oxides and zinc ash from hot dip galvanization. Lead and chloride can be present in zinc ash and must be removed prior to the manufacture of ZnO.

Because of the generally lower purity of the feed material and the carbonaceous reductant, the final product is generally of lower quality compared to that produced by the indirect method and tends to have widely varying chemical properties and physical characteristics [31,36,46]. It may also contain traces of lead and cadmium [47]. Traces of sulfur are often present in ZnO produced by the American process (originating from the raw material) whereas ZnO produced by the indirect process is essentially sulfur-free [31,48]. Sulfur can be useful in some applications including rubber manufacturing but can be a harmful impurity in many other products.

The specific surface area of direct process ZnO is generally 1–3 $m^2 g^{-1}$. Standard ASTM D79-86 defines the properties expected for use as a pigment and shows that ZnO produced from the French process has higher minimum purity (>99%) than material produced by the American process (>98.5%). A maximum moisture content of 0.5% in these grades is also of importance [36]. In general, direct process ZnO is used in the paint and ceramic industries rather than for rubber [3].

Stationary-grate furnaces, moving-chain-grate furnaces, electrothermic furnaces and rotary kilns, including Waelz kilns can be used [49]. Recovery in rotary kilns is higher than in grate furnaces [49]. In the EU, only rotary kilns, known as Waelz kilns, are now used for the direct process. These kilns can be charged by a wide variety of feed materials, generally with a zinc content of between 60 and 75%. A Waelz kiln rotates at 0.4–0.7 rpm and is inclined about 2%. As a result, the solid feed travels slowly in the kiln with a residence time of about 8–10 h. By the time the charge reaches close to the discharge end, nearly all zinc is volatized leaving a slag behind. The volatilized gases, containing zinc vapor and CO, pass into a combustion zone where oxidation is completed by the suction of secondary air and, finally, ZnO is then cooled down and collected in bag filters. This system is designed to minimize fuel consumption as combustion reactions provide most of the energy needed in the reduction zone. A typical process flow diagram of this process is depicted in Fig. 10.

2.2.1.3. The spray pyrolysis process. In this process a solution of thermally-decomposable zinc-bearing salt is atomized and then thermally decomposed to ZnO in a spray pyrolysis tower, or similar apparatus. A high specific surface area is attainable, often >12 $m^2 g^{-1}$ [35]. Material produced by this method is homogenous with uniform particle shape and narrow size distribution and controlled purity [51,52]. Suitable precursors are aqueous solutions of a zinc salt such as zinc acetate, formate, carboxylate, nitrate or sulfate. Organic salts of zinc may be preferred to inorganic salts because of their lower decomposition temperatures. For example, the decomposition temperatures of zinc acetate, formate and sulfate are 237 °C, 553 °C [53] and 680 °C [35], respectively. However, selection of the precursor also depends on the cost, preprocessing solubility and stability, reactivity and toxicity [54]. In general, higher temperatures and more concentrated solutions result in lower specific surface area of the as-synthesized ZnO. For example at 500 °C a specific surface area of 35.6 $m^2 g^{-1}$ is reported to be obtained from a 32% w/v zinc acetate solution, but this drops to 12.5 $m^2 g^{-1}$ when the temperature is increased to 850 °C. The bulk density of the as-produced ZnO powders is very low around 100 $g L^{-1}$ [35]. A process flow diagram of the spray pyrolysis method is shown in Fig. 11.

A typical flame aerosol reactor for the production of nanoparticles consists of a droplet formation unit (atomizer), a heat-supply unit and an oxidant for the flame-assisted combustion (burner) and, finally, a filtration unit. The precursor composition, droplet size, flame temperature and also residence time in the reactor are controlling factors for the formation, growth and properties of nanoparticles of ZnO. Various designs for atomizers can be applied such as ultrasonic and gas-assisted pressurized atomizers [54].

2.2.2. Hydrometallurgical synthesis

Hydrometallurgical processes currently dominate the production of zinc metal [14] but are not as popular for the production of ZnO. One reason is that the ZnO they produce is often less pure and may contain a significant amount of water; another is that the particle morphology may be irregular and porous, unlike the equiaxed or blocky crystalline form of the pyrometallurgical grades. On the other hand, hydrometallurgical grades of ZnO are cheaper to produce and may have a high specific surface area and chemical reactivity, which may be desirable in some applications. The term 'active zinc oxide' is widely used to denote ZnO with very high specific surface area and chemical reactivity.

Many of the industrial hydrometallurgical processes for zinc or ZnO production use a significant proportion of zinc-containing

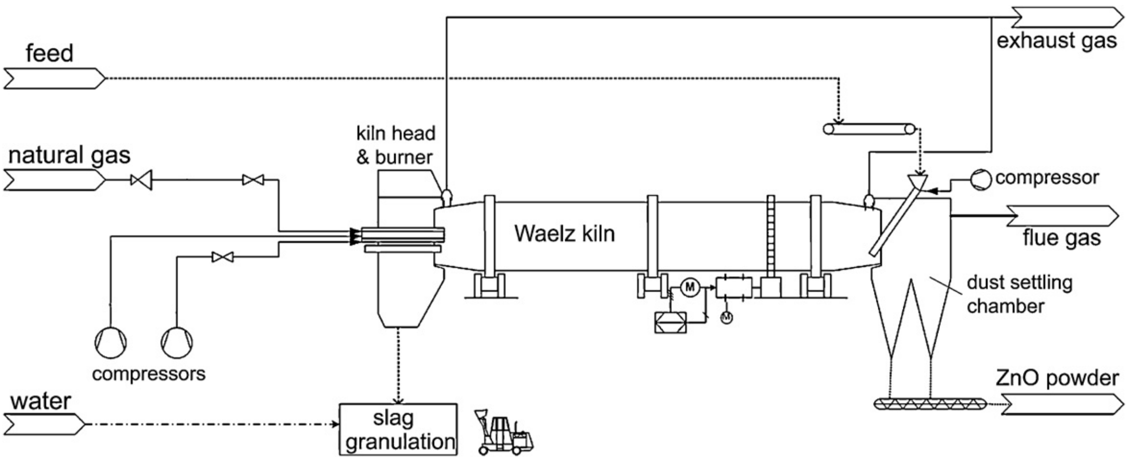

Fig. 10. A typical process flow diagram of the Waelz process, redrawn with permission from ValoRes GmbH [50] (private communication with Dr. Juergen Ruetten, ValoRes GmbH).

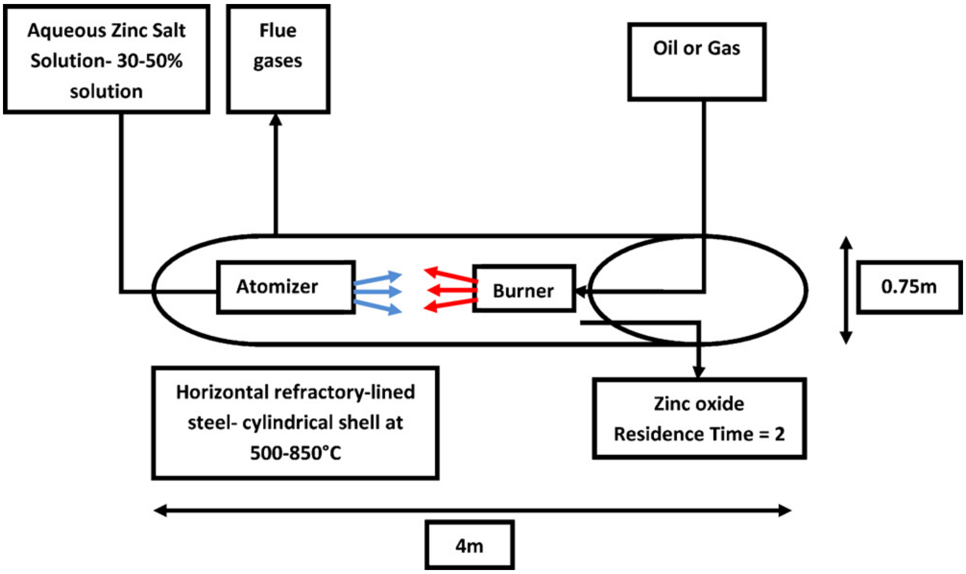

Fig. 11. Process flow diagram (PFD) of spray pyrolysis of aqueous solution of zinc salts to ZnO.

wastes such as the zinc ash from hot-dip galvanizing plants (Fig. 12) as input materials due to their availability and relatively lower prices.

In these processes, zinc-containing compounds are precipitated from aqueous solution, separated and then converted to ZnO by calcination. Direct precipitation of ZnO from aqueous solution at elevated temperatures is also possible [46,56]. Zinc oxide produced via wet chemical processes can be categorized into three main groups: (1) ZnO produced as a by-product of the production of sodium dithionate, (2) ZnO made by the reaction of a zinc salt such as zinc sulfate and a base such as ammonium or sodium hydroxide, followed by calcination or drying of the $Zn(OH)_2$ or ZnO produced, and (3) ZnO produced by a two-step reaction of zinc salts and carbon-containing bases such as sodium carbonate, ammonium bicarbonate or urea followed by calcination or alkaline treatment of the resultant basic zinc carbonate.

2.2.2.1. ZnO as a by-product from other processes. Zinc oxide produced as a by-product of an aqueous chemical reaction is considered to be a 'secondary type' according to the ASTM D4295 [31]. One of the main hydrometallurgical sources of ZnO is as a by-product in the synthesis of sodium dithionite ($Na_2S_2O_4$) (also known as sodium hydrosulfite) [3]. This substance is used as a reducing agent with major applications in the vat-dying of textiles and in the bleaching of wood pulp. The overall reaction for the production of ZnO from this process is given in Eq. (5) but in detail the process involves first the production of zinc dithionite followed by addition of soda ash or sodium hydroxide to produce sodium dithionite and to precipitate basic zinc carbonate.

$$2NaHSO_3 + Zn \rightarrow Na_2S_2O_4 + ZnO + H_2O \qquad (5)$$

The latter is then filtered and dried and converted to ZnO either by calcination or by alkali treatment [57–59]. The specific surface area of this grade is high ($>40\,m^2\,g^{-1}$) and therefore it can be considered as an "active" grade of ZnO.

2.2.2.2. Production of "active" zinc oxide by decomposition of hydrozincite. "Active" zinc oxide is an important grade of ZnO produced by wet-chemical routes. Descriptions of some variations in the process by which it can be prepared are available in the literature [60–63]. Active ZnO is considered to be superior to "white seal" ZnO (French process) in rubber compounding and rubber applications in terms of tensile strength and hardness and modulus at 300% [62]. A typical two-step process for its production is based on the formation and then decomposition of a basic zinc carbonate known as hydrozincite:

$$5ZnSO_4{\cdot}7H_2O + 5Na_2CO_3 \rightarrow Zn_5(CO_3)_2(OH)_6 + 5Na_2SO_4 + 3CO_2 + 32H_2O \qquad (6)$$

$$Zn_5(CO_3)_2(OH)_6 + \text{Heat} \rightleftharpoons 5ZnO + 2CO_2 + 3H_2O \qquad (7)$$

The decomposition reaction of hydrozincite is endothermic [64] and the reaction proceeds spontaneously only above about 154 °C,

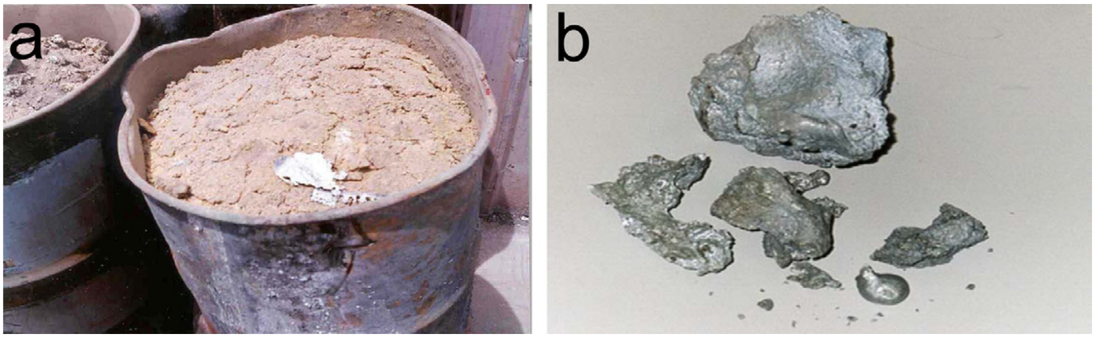

Fig. 12. (a) Zinc ash; (b) zinc dross. Photographs courtesy of Environment Australia. © Commonwealth of Australia 2001 [55].

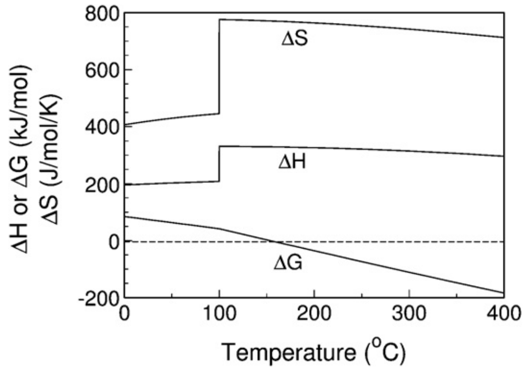

Fig. 13. Free energy change for reaction $Zn_5(CO_3)_2(OH)_6 \rightarrow 5ZnO + 2CO_2 + 3H_2O$ calculated by the authors using published thermochemical data [64,67].

Fig. 13. The very large specific surface area of "active" ZnO is produced when the CO_2 and H_2O are expelled from the hydrozincite lattice. Furthermore, at these low temperatures the ZnO that is formed from the hydrozincite cannot sinter, so this porosity can be retained. However, as shown in Fig. 13, it is thermodynamically favorable for the ZnO to revert to hydrozincite below 154 °C in the presence of CO_2 and H_2O although the rate of this reaction will depend on the specific surface area of the ZnO. Any ZnO that has been heated to high temperatures during manufacture (such as the pyrometallurgical grades mentioned earlier) will have a relatively low specific surface area and the rate of the reverse reaction will be normally be negligible, but material with higher surface area, such as that produced by decomposition of hydrozincite, is susceptible to the reverse carbonation reaction over a time period of weeks or months [65,66].

The reverse reaction relies upon the formation of a layer of adsorbed carbonic acid ($H_2O + CO_2$) and so will also depend on partial pressure of water p_{H_2O}, and that of CO_2, p_{CO_2}. At a moisture ratio $p_{H_2O}/(p_{CO_2} + p_{H_2O})$ below 0.1, ZnO shows no weight increase whereas the carbonation reaction occurs quickly at a ratio over 0.35, causing the properties of the ZnO to change significantly. In the intermediate range only a partial reversion occurs [65,68].

The relevant properties of wet-chemical grades of ZnO, such as specific surface area, porosity, morphology and quality, are variable and depend on the precursors, process conditions and many other factors. An important intrinsic property of the wet-chemical ZnO grades is the presence of abundant, stable, surface hydroxyl groups. Thermogravimetric analysis reveals the presence of these hydroxyl groups up to ~800 °C [56].

As for the pyrometallurgical routes, the purity of the starting materials used to make active ZnO is an important consideration. Zinc-bearing waste materials first undergo multi-stage physical and chemical extraction processes to yield purified zinc solutions such as zinc sulfate. The starting materials and purification process should be strictly controlled to ensure that no lead or cadmium, for example, is carried over into the final product or environment. These processes can involve acid/base leaching, filtration, precipitation/cementation and adjustment of pH and temperature.

For the calcination stage, a gas-fired rotary kiln can be utilized where, for example, basic zinc carbonate is fed to the high end of the kiln and the ZnO is collected from the lower end of the kiln. Hot gas travels counter-current to the solid charges. A schematic of this process, as depicted in US Patent 2603554, is shown in Fig. 14 [69]. Properties of the ZnO produced depend upon the identity of the material that is calcined, the calcination temperature profile and the residence time in the kiln. As a result, properties such as porosity, specific surface area and morphology of the particles can change dramatically.

It is also possible, in principle, to convert low surface area ZnO, typically the products of the indirect or direct processes, into an active grade of ZnO with a high specific surface area using a wet carbonation reaction to form basic zinc carbonates followed by separation and calcination of the product. Conversion of ZnO to basic zinc carbonate in the carbonation process may be as high as 76% [70].

2.3. Small-scale production routes

There are a large number of techniques available for the production of ZnO in small quantities or in a laboratory context. Some of these are mentioned below.

2.3.1. Precipitation of $Zn(OH)_2$ or ZnO from aqueous solutions of zinc salts

A typical one-step process for this type of wet-chemical process is based on Reaction (8) [56]:

$$ZnSO_4 + 2NaOH \rightarrow ZnO_{(s)} + Na_2SO_4 + H_2O \tag{8}$$

However specific surface area of the grades produced by Reaction (8) is generally limited to <30 $m^2\,g^{-1}$ which, while higher than that of ZnO produced by the pyrometallurgical processes, is still not as high as that of 'active' ZnO.

2.3.2. Solvent extraction and pyrolysis of zinc nitrate

A method to produce ZnO has been patented that includes an organic solvent extraction stage to extract zinc out of zinc-containing materials selectively, stripping of the organic phase with nitric acid to produce zinc nitrate and, finally, decomposition of the $Zn(NO_3)_2$ at a temperature above 200 °C to produce pure ZnO [46], Fig. 15. An important aspect of this process is that the nitric acid is then regenerated by aqueous scrubbing of the gases produced by decomposition, a step which would have marked economic advantages if performed efficiently.

2.3.3. Deposition of thin films

ZnO thin films are useful materials for piezoelectric devices such as surface acoustic wave (SAW) and bulk acoustic wave devices. Deposition of ZnO thin films may be achieved by methods such as chemical vapor deposition (CVD), metal organic chemical vapor deposition (MOCVD), pulsed laser deposition (PLD), molecular beam epitaxy (MBE) or laser MBE, reactive e-beam evaporation, rf or dc sputtering and planar magnetron sputtering [71–76].

2.3.4. Gas-phase synthesis

Gas phase synthesis is generally conducted in a closed chamber. The synthesis is performed within a temperature range of 500–1500 °C. Some common techniques include vapor phase transport (VPT) including vapor–solid (VS) and vapor–liquid–solid (VLS) growth, CVD, physical vapor deposition, MOCVD, thermal oxidation of pure Zn and condensation, microwave assisted thermal decomposition, seeded vapor phase (SVP) method, hydride or chloride vapor phase deposition (HVPE) [9,75]. ZnO nanorods can also be formed by an arc-discharge technique [77].

2.3.5. Miscellaneous other methods

Growth of ZnO from an aqueous solution is an attractive option for some morphologies because the process temperature can be below 100 °C. Large scale fabrication of nanostructure arrays can be achieved [71]. In some hydrothermal processes, the reaction takes place in a pressurized aqueous solution with a temperature that is above 100 °C. This technique is one of the main routes available for the growth of single crystals of ZnO (see Section 3.4.4). With this method, single crystals with volumes of several cubic centimeters can be formed. The production of homo- or hetero-epitaxically

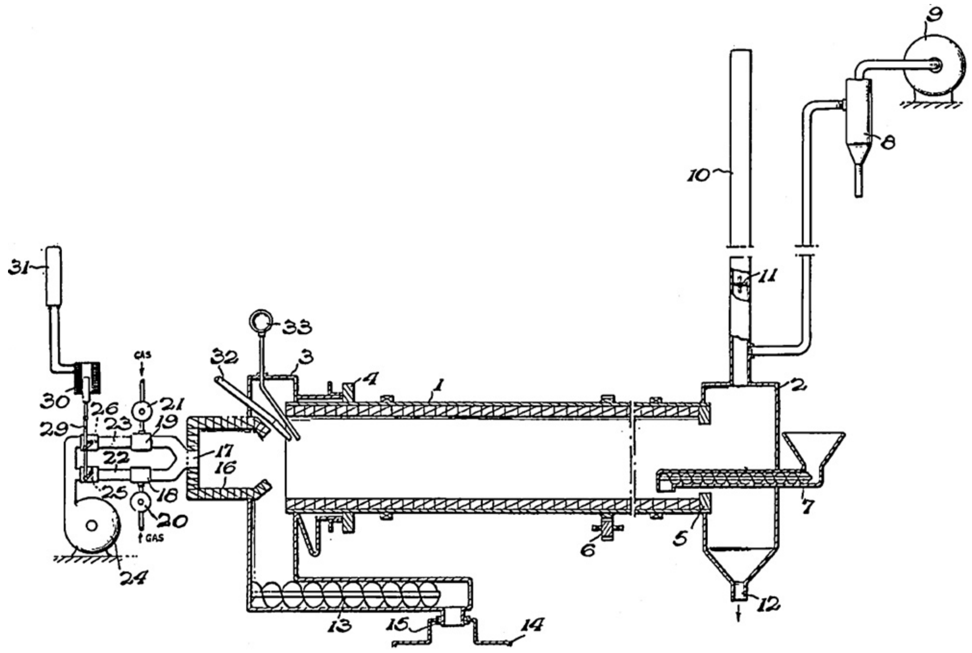

Fig. 14. Schematic of the rotary kiln for the calcination of basic zinc carbonate as depicted in US Patent 2603554 [69].

coated wafers of several square centimeters is also possible with hydrothermal processing. To do so, ZnO is dissolved in a base e.g. KOH at high temperatures and pressure, and is then precipitated at lower temperatures [5].

In solvothermal methods, which may be categorized under hydrothermal processes, the reaction takes place at moderate temperatures (generally 100–250 °C). In this process, an aqueous solution of an organic solvent such as ethanol, hydrazine or ethylenediamine is used instead of pure water [78–80]. The sonochemical technique invokes a hybridization of hydrothermal synthesis with sonication, and has been implemented using an ultrasonic probe to provide mechanical energy for the system. The time necessary for crystal growth may be reduced by sonochemical treatment [81].

Mechano-chemical processes (MCP) are yet another hybrid. Of course, wet or dry milling of big clumps of material to form powder is not a new technique; however, comminution to a particle size below about 1 micron is not usually feasible due to agglomeration of the particles and an increase in the viscosity of the charge. In the MCP processes milling is combined with a solid-state chemical reaction. This combination is suitable for the medium-scale production of nanoparticles because of its simplicity and relatively low cost but requires a relatively long reaction time. There is no solvent involved in this method. In the case of ZnO, there are three common reaction pathways, (1) milling of a mixture of zinc hydroxide carbonate and NaCl (as non-reacting diluent material) followed by calcination of the milled product to form ZnO and washing the mixture to remove NaCl, (2) milling a mixture of $ZnCl_2$ and Na_2CO_3 to form zinc hydroxide carbonate and NaCl and subsequent thermal decomposition of $ZnCO_3$ and (3) milling of a mixture of zinc acetate and oxalic acid, followed by a thermal decomposition of the product [82–85]. Wet-grinding to form nanoparticulate suspensions is also possible in principle, and has been reported for other metal oxides [86,87].

The composite hydroxide mediated (CHM) process is another relatively new small-scale technique. In this case the reaction to form ZnO occurs in a eutectic mixture of molten hydroxides. Due to the higher viscosity of the molten hydroxide system, mass transfer processes are slower than those of reactions conducted in water. However, the higher viscosity of the molten hydroxide system is reported to result in less agglomeration of the particles [88].

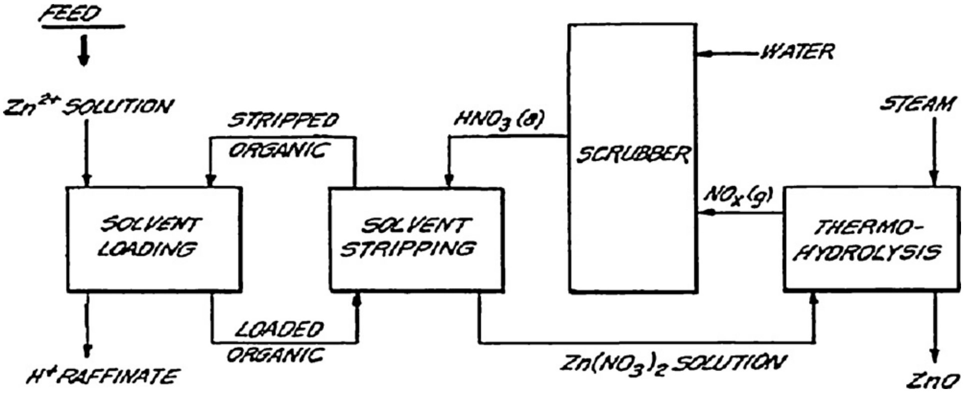

Fig. 15. Organic solvent extraction process for the production of zinc oxide [46].

3. Properties

Depending on end-use, ZnO may be considered as a bulk chemical or as a specialized semi-conductor. It has specific optical, electrical and thermal properties that are attractive for a range of very diverse applications. For example, its high refractive index (1.95–2.10) was useful in pigment applications, it can be an electrical conductor when suitably doped, and it is thermally stable to extremely high temperatures (at least ~1800 °C). The physical and chemical properties of ZnO powder ensure a large off-take as an additive in rubber. Alternatively, the high specific surface area of the 'active' grades permits them to be used in desulfurization processes in chemical plants. As a semiconductor, ZnO has applications in opto-electronics and in transparent conducting films. Awareness of its various properties is important, both for selection of this material for specific applications, and as input information for the producers of ZnO in its various forms.

3.1. *Crystal structures*

There are three crystal structures of ZnO: hexagonal wurtzite, cubic zinc-blende structure and a rarely-observed cubic rock-salt (NaCl-type). Under ambient conditions, the most thermodynamically stable structure is the wurtzite form. The zinc-blende structure is metastable and can be stabilized only by epitaxial growth on cubic substrates while the cubic rock-salt structure is usually only stable under extreme pressure (~2 GPa) [4].

3.2. *Toxicology*

Zinc oxide is generally categorized as a non-toxic material. Zinc oxide does not cause skin and eye irritation and there is no evidence of carcinogenicity, genotoxicity and reproduction toxicity in humans [17,89,90]. However, the powder can be hazardous by inhalation or ingestion because it causes a condition known as zinc fever or zinc ague. The symptoms of this syndrome are chills, fever, cough, and tightness in the chest. Therefore appropriate safety precautions should be observed when preparing, packaging, transporting and handling ZnO. According to the recent EU hazard classifications, zinc oxide is classified as N; R50-53 (very toxic for the aquatic environment or ecotoxic). Therefore packages of ZnO in these jurisdictions must be labeled "UN3077-Class 9, Environmentally Hazardous Substance" [91].

Soluble zinc compounds are considered ecotoxic for aquatic organisms despite them being necessary for humans, animals and plants in trace amounts [17,92]. The human body, for example, contains around 2 g of Zn and a daily intake of 10–15 mg is required for metabolism [17,93]. It has been shown that the ecotoxicity of ZnO to the model aquatic protozoan *Tetrahymena thermophila* is caused entirely by its solubilized fraction, i.e. the Zn^{2+} ion [93]. Toxicities of bulk ZnO, nano-ZnO and soluble Zn^{2+} are similar once their different solubilities are taken into account, with 4-h effect concentration (EC_{50}) values of about 4 or 5 mg bio-available Zn/L (5 ppm). These values are an order of magnitude lower than for soluble Cu^{2+} [93]. By comparison, the naturally occurring amount of Zn ions in seawater is three orders of magnitude smaller (5 ppb).

Zinc oxide has a long history of use in sunscreen compositions to block UV radiation, with the nanoparticulate form having been introduced for this application in the late 1990s. There have been occasional concerns voiced about possible adverse effects on human health or the environment. However, the current evidence shows that ZnO particles or nanoparticles do not penetrate viable skin cells and remain on the outer layer of undamaged skin (the stratum corneum) with low systemic toxicity [94–98]. Toxicity to the aquatic environment would depend on whether any ZnO washed off sunbathers was solubilized in, for example, the sea water, and whether the local environmental concentration of Zn^{2+} could thereby exceed the roughly 5 ppm threshold mentioned earlier.

3.3. *Morphology of zinc oxide particles*

The morphology of ZnO particles can be controlled by varying the synthesis technique, process conditions, precursors, pH of the system or concentration of the reactants. A wide variety of shapes are possible, Fig. 16. The French and American process zinc oxides have nodular-type (0.1–5 μm) or acicular-type (needle-shape, 0.5–10 μm) particle shapes. Wet-process ZnO may have a sponge-like form with porous aggregates being up to 50 μm diameter [17,31]. There are, however, a large number of other morphologies, each produced under some specific set of conditions. Many of these have been given whimsical names. The possibilities include nanorods [78,99], nanoplates [79,100], nanosheets [101], nanoboxes [100], irregularly-shaped particles (ISPs) [100], polyhedral drums [100], hexagonal prisms, nanomallets [100], nanotripods [102], tetrapods [103], nanowires [104], nanobelts [104,105], nanocombs and nanosaws [105], nanosprings and nanospirals and nanohelixes [99,105], nanorings [99,105], nanocages [99,105], nanoneedles [4,106], nanotubes [4,99,107], nanodonuts [4], nanopropellers [4], and nanoflowers [56,108].

3.4. *Industrial grades*

There are many industrial grades of ZnO in use. Differentiation between the grades is based on the purity, composition and specific surface area of the powder, and sometimes the process through which it is made. Although some grades are covered in national or international standards (e.g. Table 1) it seems that much ZnO is still supplied to somewhat looser designations. Some of these categories are listed in Table 2. However many of the companies producing ZnO have their own nomenclature too, and slightly different purity requirements are applied to the terms listed below by different manufacturers. Therefore, the minimum content of ZnO and/or maximum heavy metal impurity levels are probably a more reliable guide to quality.

3.4.1. *Bulk zinc oxide*

As mentioned earlier, most of the bulk ZnO in the world is produced by either the "French" or "American" processes. The specific surface area varies between 1 and 10 $m^2\,g^{-1}$ depending on process used. Such grades of ZnO are not considered as "active" due to their low specific surface area. Highly crystalline particles are formed during the high-temperature manufacturing process.

3.4.2. *Active zinc oxide by calcination of a carbonate*

Low crystallinity ZnO with high specific area (generally 30–70 $m^2\,g^{-1}$ or greater) is known as "active" ZnO, as mentioned in section 2.2.2.2. Specific surface areas as high as 200 $m^2\,g^{-1}$ may be achieved by carefully controlling the temperatures of precipitation and calcination [111]. Material with such a high surface area will be very susceptible to the reverse carbonation reaction described in section 2.2.2.2.

3.4.3. *Other 'wet-process' ZnO*

Zinc oxide produced by other wet-chemical processes, such as precipitation, has a specific surface area that is intermediate between that of ZnO produced by the high-temperature methods and that produced by the decomposition of a carbonate. The surface area of regular (i.e., not "active") wet-process ZnO is normally in the range of 10–30 $m^2\,g^{-1}$ but can attain a maximum of around

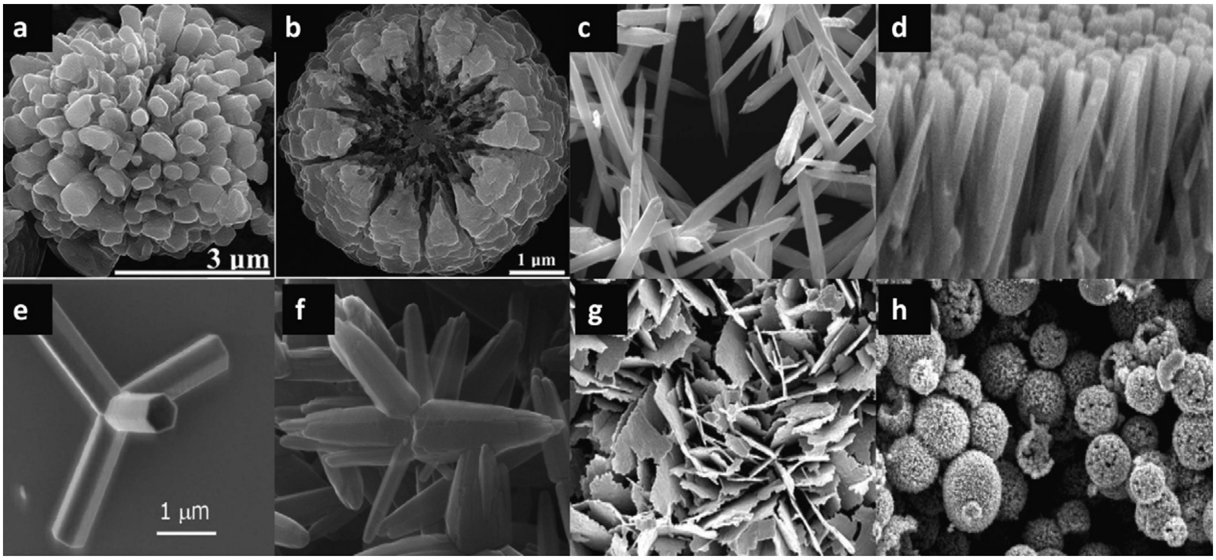

Fig. 16. SEM images of ZnO showing various morphologies; (a) and (b) are reprinted with permission from [80], (c) from [81], (d) from [71], (e) from [109], (g) from [101], (h) from [110] and (f) is synthesized by the authors. Reproduced with permission from the various sources cited.

Table 2
Industrial grades of zinc oxide. Data are adapted from the product datasheets from industrial producers: PT. Indo Lysaght Indonesia, US Zinc in the USA, Umicore Zinc Chemicals and Silox in Belgium, IEQSA in Peru and Grillo Zinkoxid GmbH in Germany.

ZnO Grade	Nominal purity (%)	Specific surface area ($m^2\,g^{-1}$)	Production process
Gold Seal	99.995	4–7	French Process
Pharma Grade	99.8–99.9	3–9	French Process
White Seal	99.8	3–5	French Process
Green Seal	99.6–99.7	4–10	French Process
Red Seal	99.5	3–5	French Process
American Grade	98.5–99.5	Max. 3	American Process
Active Grade	93–98	Min. 30	Wet process
Feed Grade	90–99	–	Various

50–60 $m^2\,g^{-1}$ by carefully controlling the process conditions such as concentration of the base or feeding method [56].

3.4.4. *ZnO single crystals*

Zinc oxide single crystals, Fig. 17, are of interest due to potential applications in electronics. They are *n*-type irrespective of the growth method used. Synthesis of *p*-type ZnO single crystals has been proven to be quite difficult so far [8,112], although some success has been claimed for *p*-type polycrystalline films [113–115]. Diverse methods may be used for single crystal growth, including hydrothermal growth at temperatures around 350–450 °C and pressures up to 2500 bar, vapor phase transport growth at temperatures around 1100–1400 °C, or growth from a pressurized melt of salts with low melting temperature (e.g. $ZnBr_2$) [8,10,116].

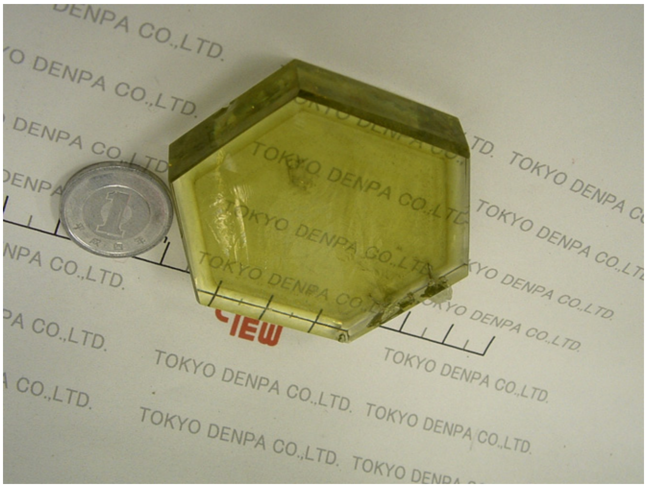

Fig. 17. Zinc oxide single crystal, produced by the hydrothermal method. Image courtesy of Tokyo Denpa Co., Ltd. Japan.

The hydrothermal growth method yields the largest crystals but is slow, with a growth rate of 0.1–1 mm/day [116,117]. Crystal growth by the vapor phase methods is faster with a rate of around 7–8 mm/day. Crystal growth from a melt is also reported to have higher growth rate than that of hydrothermal methods [112,118–120].

3.5. *Optical properties*

Much of the recent surge in research interest in ZnO has been motivated by possible optoelectronic applications [4,5,7,121]. This is because there appears to be a possibility of replacing the GaN-based compounds currently being used in optoelectronic devices operating in the blue or UV range (for example, LEDs, laser diodes and photodetectors) with a cheaper and non-toxic alternative such as ZnO. Selection of ZnO is due to the similarity of its band gap energy (3.37 eV at RT) with that of GaN (3.39 eV at RT) and, importantly, the larger exciton binding energy of ZnO (60 meV) compared to that of GaN (18–28 meV) [122]. This would be useful in light emitting devices. Band-gap engineering of ZnO is also possible. For example, alloying with CdO decreases the band gap [8] while alloying with MgO increases the band gap [8,121]. The compound

Mg/$Cd_{1-x}Zn_xO$ has a band gap that is potentially tunable between 2.3 and 4.0 eV [8]. Emission properties of ZnO nanoparticles are influenced by many factors such as synthesis method, morphology of the nanoparticles, dopants and ligands used for surface coating [8,10,121–123]. Zinc-based phosphors have been known for decades, although the precise mechanism of their operation is still said to be controversial [124,125].

3.6. Electrical, thermal and magnetic properties

Zinc oxide was one of the first semiconductors to be extensively investigated [10,126] but the lack of a reliable *p*-type variant has hampered efforts to use it in many types of devices.

3.6.1. Piezoelectricity, pyroelectricity and thermoelectricity

In 1960, it was discovered that ZnO is a piezoelectric semiconductor with a large electromechanical coupling coefficient (piezoelectric crystals can transform mechanical energy into an electric signal or vice versa). The tetrahedral coordination in ZnO crystals results in a non-centro-symmetric structure and consequently piezoelectricity and pyroelectricity. This led to the first electronic application of ZnO as a thin layer for surface acoustic wave devices. Other applications can be in resonators, controlling tip movement in scanning probe microscopy, or as air or liquid vibration sensors [10,105,122].

Doped ZnO, especially Al-doped ZnO, is a *n*-type oxide thermoelectric compound [127,128]. Unfortunately the all-important figure-of-merit of ZnO is still inferior to many other kinds of thermoelectric substances.

3.6.2. Ferroelectricity, magnetism and ferromagnetism

Ferromagnetism can be induced in ZnO by doping with either ferro- or paramagnetic elements such as Fe, Co, Ni or Mn, Cr and Li, or nonmagnetic elements such as Ti, V, Cu. While semiconductor materials are used for microprocessors, magnetic materials are used for memory devices. Materials that share both of these properties, sometimes referred to as dilute magnetic semiconductors (DMS), are of potential interest for a new generation of devices. Interest in ZnO as a DMS has been intensified by theoretical calculations which suggest that it could hold its ferromagnetism at relatively high temperatures by doping with some 3*d* transition metals. In addition, its optical transparency might provide a transparent ferromagnetic material which would open up new device possibilities. However, synthesis, reproducibility and understanding of such materials are still a matter of much debate [10,129–132].

3.6.3. Electrical conductivity

The conductivity of ZnO depends significantly on its content of charge carriers, which is in turn highly influenced by its stoichiometry. The latter can be adjusted by the oxygen or zinc partial pressure during high temperature processing. In addition, annealing in a reducing atmosphere containing hydrogen can have a large effect on electrical conductivity. In contrast, hydrothermally grown ZnO crystals show very high resistivities due to the solvents used containing atoms such as Na, K or Li that can readily provide charge compensation in a defective lattice [10]. Electrical conductivity of ZnO, as in most other semiconductors, increases with temperature.

In piezoelectric devices, ZnO must have a very high resistivity ($>10^8\ \Omega$cm). This can be provided by doping with lithium for example, by means of which the resistivity can be increased to $10^{12}\ \Omega$cm. On the other hand, for applications, such as solar-cells, which might require a transparent conducting oxide, very high conductivity of ZnO thin-films is a prerequisite. For these purposes resistivities as low as $2 \times 10^{-4}\ \Omega$cm have been achieved by high doping levels of B, Al, Ga or In. While undoped ZnO crystals show carrier concentrations as low as 10^{15} cm^{-3}, In-doped materials show carrier concentrations around 10^{20} cm^{-3} [10,133]. However, as mentioned previously, a generally applicable process to achieve stable *p*-type ZnO with high conductivity has not been found yet. It is believed that one problem is self-compensation in the lattice of the ZnO originating from the native defects or hydrogen impurities [114,134]. The lowest *p*-type resistivity values reported so far are around $0.5\ \Omega$cm for example by N, Ga, As or P-doping [112]. Obtaining a stable high-conductivity *p*-type ZnO would provide a breakthrough in the fabrication of homo-epitaxial LEDs, laser diodes and thin film solar cells [8,112,115,135,136].

3.6.4. Heat capacity, thermal conductivity, thermal expansion coefficient

Zinc oxide has relatively high heat capacity and thermal conductivity [23]. The specific heat capacity for ZnO is reported to be about 40 J K^{-1} mol^{-1} which increases to around 50 J K^{-1} mol^{-1} at 630 °C [67]. Thermal conductivity at room temperature is about 50 WK^{-1} m^{-1} for bulk ZnO but this drops to 15 W K^{-1} m^{-1} as the temperature or porosity increase [128,137]. Zinc oxide has a relatively low coefficient of expansion at room temperature (between 3 and 8×10^{-6} K^{-1} which increases as the porosity or temperature increase [137].

3.6.5. Thermochromism

Crystalline ZnO is thermochromic, changing from white to yellow when the temperature is increased to >300 °C [17] and then from yellow to white upon cooling. This is probably because of the formation of crystal lattice defects due to a loss of oxygen and the formation of the non-stoichiometric $Zn_{1+x}O$, with x increasing with temperature.

3.7. Surface properties

The surface properties of ZnO particles or thin films play a significant role in diverse fields, for example in sensing, catalysis or optoelectronics. As a result, the topic has been extensively studied [4,11,138]. Absorption of molecules onto the ZnO surface has been examined with some attention focused on the adsorbates for methanol synthesis from syn-gas (H_2, CO, CO_2) [11,139]. The wettability of ZnO surfaces has also been examined; flat ZnO substrates exhibit the maximum water contact angle of 109° [140]. Super-hydrophobic ZnO has been prepared by surface treatment with fatty acids and reversibly switchable wettability between super-hydrophilicity and super-hydrophobicity has been observed by alternation of UV irradiation or oxygen plasma treatment [140–142]. The hydrophobicity of ZnO additives is an important issue in polymer blending when seeking to obtain a homogeneous particle distribution or grafting of monomers onto the metal oxide. Since most polymers are hydrophobic and ZnO is hydrophilic, the surface of the particles surface may be modified for better compatibility with the polymer matrix [143–145].

4. Applications

The uses of ZnO have changed markedly over time. Some major uses, such as in photocopy paper as a photoconductive ingredient [146] (which was the second largest volume consumed in the 1970s [23]) and in linoleum have almost disappeared [3]. Furthermore ZnO is not the principal white pigment in paint anymore. Today its major uses are in the rubber industry, followed by ceramics [3], but it has many niche applications such as, for example, in drilling fluids for the oil and gas industry [147,148]. Most recently, ZnO is being investigated for applications such as LEDs, transparent transistors, solar cells and memory devices [4,5] and as the basis of a transparent conducting oxide for consumer devices [10]. The more important of these applications are discussed briefly below.

4.1. Rubber

The major application of ZnO (more than half of the total use) is currently in the rubber industry where it is used as a vulcanizing activator (a substance applied in small doses to increase the effectiveness of the vulcanization accelerator). Early un-accelerated vulcanization processes used ~8 parts per hundred rubber (phr) of activator and required temperatures above the sulfur melting point for several hours. Organic accelerators allowed the amount of sulfur and vulcanization times to be significantly reduced but a significant breakthrough in the vulcanization process involved activators such as ZnO [19,149].

Zinc oxide is also used as a curing or cross-linking agent for halogen-containing elastomers such as neoprene or polysulfides [150]. Metallic oxides not only change the rate of cure but also the ‘scorch’ (i.e. premature vulcanization caused by heat during rubber processing) in neoprene [151]. In cable insulators such as ethylene propylene diene monomer (EPDM) rubber, the incorporation of ZnO imparts low water absorption and longer lifetime. It is also used in pressure sensitive adhesives (e.g. in epoxidized natural rubber) [152,153].

The addition of ZnO also considerably improves the thermal conductivity of rubber, which is crucial to dissipate the heat produced by deformation under load or cyclic stress, for example in vibration mounts or when a tire rolls. There is also evidence that the inclusion of ZnO in rubber compounds improves the abrasion resistance. It has also been found that ZnO improves the heat resistance of the vulcanizates. ZnO additions also contribute to the processing of uncured rubber by decreasing the shrinkage of molded products and improving the cleanliness of the molds. Finally, the presence of ZnO appears to increase the bonding between rubber and metallic inserts, such as steel wire [149].

French process ZnO of the ‘Red Seal’ purity level is a typical example of the material used in rubber tires. However, ‘active’ ZnO can be used for inner tubes, latex gloves and similar items with thin sections.

During the vulcanization process, only the small quantity of ZnO at the surface of the particles is involved. Therefore, the efficiency of ZnO use in vulcanization can be improved by the maximization of the interfacial area between ZnO particles and accelerator. This depends on the particle size, shape and specific surface area. However, production, de-agglomeration and dispersion of small particles of ZnO are difficult and smaller ZnO particles may unintentionally diminish some desired rubber rheology characteristics [151,154]. Standard ASTM D4620-02 (the standard test method for evaluating the effective surface area of ZnO in rubber) mentions that the specific surface area of ZnO can significantly affect cure activation and vulcanization properties. Longer cure times indicate lower surface area and vice versa [155].

Zinc oxide must be dispersed properly in the rubber to impart the required properties. This is normally achieved by high intensity mechanical mixing, but in some cases a coating of co-activator fatty acids (particularly propionic acid or stearic acid, 0.2–0.4% by weight) prior to its incorporation into the rubber might be of benefit. These co-activator fatty acids make the ZnO surface hydrophobic and improve dispersion times into organic media [156,157]. Another benefit of application of surface-treated ZnO is that such ZnO retards the initial cure which decreases the scorching of rubber while yielding the optimum cure in approximately the same time as untreated ZnO. French or American process ZnO is suitable for the surface-treatment with fatty acids. A drawback of the surface-treated ZnO is that it is extremely dusty. Dustiness is related to the low bulk density of the particles, which causes significant disadvantages in handling, such as increased cost of transportation, process control problems and, possibly, an unpleasant working environment [156].

In recent years, due to the environmental and economic concerns in relation to the amount of zinc in rubber products, there is a tendency for minimization of the zinc content. To reduce the necessary amount of ZnO, the activity of the particles should be increased. Therefore the availability of Zn^{2+} ions at the surface of the crystals should be maximized [157]. Some suggested options include the application of ‘active zinc oxide’, use of the so-called ‘nano zinc oxide’, and prior chemical reaction between the accelerators, stearic acid and the oxide before addition into the rubber matrix. Reported data indicate the possibility of reducing ZnO levels without impairing the properties of the vulcanizates [92,150,151,157]. In the vulcanization of solution styrene-butadiene rubber (s-SBR) other ways to reduce the amount of zinc in the rubber compositions include the application of CaO, MgO, zinc-m-glycerolate or zinc clay (e.g. 5 phr) as good alternatives for ZnO without damaging the cure properties. Zinc-bearing clays can be produced by modification of commonly used clays such as montmorillonite with zinc ions. By application of 2.5–5 phr of zinc clay (equivalent to 0.15–0.3 phr of pure ZnO) in s-SBR composition, physical and curing properties of the rubber remained unchanged compared to the 3 phr of pure ZnO. This change is associated with an order of magnitude reduction in the amount of zinc used [92,157].

4.2. Ceramics and concrete

The second largest application of ZnO is in ceramics [3] in particular the tile industry [22]. Both the French or American process ZnO are suitable. The relatively high heat capacity, thermal conductivity and high temperature stability of ZnO coupled with a comparatively low coefficient of expansion are desirable properties in the production of ceramics. In glazes, enamels or ceramic formulations, ZnO affects the melting point and optical properties of the glaze. Zinc oxide as a low expansion, secondary flux improves the elasticity of glazes by reducing the change in viscosity as a function of temperature and helps prevent crazing and shivering. By substituting ZnO for BaO and PbO, the heat capacity is decreased and the thermal conductivity is increased. Zinc in small amounts improves the development of glossy and brilliant surfaces. However in moderate to high amounts, it produces matte and crystalline surfaces [23,158,159]. With regard to color, zinc has a complicated influence. It can improve or damage blues, browns, greens, pinks and is not recommended with pigments or glazes containing copper, iron, or chromium [158].

Zinc oxide acts as a metallic oxide flux in the preparation of frits and enamels for ceramic wall and floor tiles or for sanitary and tableware ceramic applications. Its fluxing action starts at around 1000 °C (e.g. in Bristol glazes). Zinc oxide may be reduced to metallic zinc under reducing conditions in the gas-fired kiln followed by volatilization some time later. These properties are useful for low fire glazes and as a result ZnO is quite common in fast fire applications [158,160].

Zinc oxide in concrete provides longer processing time and improves its resistance against water [5]. In the manufacture of Portland cement, ZnO can be used in the raw material mixture for the production of cement clinker [161]. Its addition in small amounts to Portland cement retards the setting and hardening effectively (at 0.25% ZnO addition: hydration is almost zero up to 12 h; at 1% addition: hydration does not begin up to 2 days) and improves the whiteness and final strength [159,161]. Zinc oxide may also be used in quick-setting phosphate cements [161].

4.3. Plastics and linoleum

Zinc oxide may provide useful benefits when added to a plastic polymer. Once again this is commonly in the form of the French or American process material. Properties such as improved heat resistance, mechanical strength and water and fire resistance are imparted to acrylic polymers, polyvinylidene fluoride (PVDF), epoxy resins and nylon-6-6. Zinc oxide may be used as a stabilizer in polyolefin resins such as high density polyethylene (HDPE), polypropylene (PP) and unsaturated polyesters, polychlorofluoroethylene and poly-vinyl-halides such as PVC. In these matrices it provides UV absorption properties, thermal stability and increased tensile strength. Zinc oxide-stabilized PP and HDPE are used in safety helmets, stadium seating, insulation, pallets, bags, fibers and filaments, agricultural and recreational equipment. Zinc oxide also improves the dye-ability of polyester fibers and the antistatic, fungistatic and emulsion stability of vinyl polymers [159,162–168].

In the production of linoleum, ZnO acts as a coloring agent which is mixed with all components such as linoleum cement, organic and inorganic fillers in a mixing unit. A typical linoleum composition may contain approximately 40% binder, 30% organic fillers, 20% inorganic mineral fillers and 10% coloring agents, including up to 5% ZnO [169,170].

4.4. Pigments and coatings

Although now largely superseded by TiO_2, ZnO remains an important white inorganic pigment in niche applications. Pigments made of ZnO are known as 'zinc white' or 'Chinese white' or 'flowers of zinc', with the term 'zinc white' now reserved for ZnO pigment produced by the French process [17]. The pigment may be purchased in the dry form or as a paste in oil [17,36]. An important property of white pigment is its low light absorbance together with high dispersion of radiation in the visible region (wavelengths of 400–800 nm). However, the scattering power depends on the particle size and also the wavelength of the incident beam [17]. Therefore by controlling the particle size, it is possible to engineer the desired scattering power to some extent.

Replacement of linseed-oil based exterior paints with latex-based ones during 1980s caused a significant decline in the demand for ZnO in the paint industry. However this trend was partially reversed during 1990s due to a ban in some countries on mercury-containing latexes (mercury has been used as a fungicide and for mold control in the latex) and introduction of ZnO into the latex due to its fungistatic properties [22]. Direct process ZnO is preferred in these applications due to its lower reactivity with resin systems.

On the other hand, ZnO as a pigment cannot compete for hiding power with TiO_2. Hiding power is the ability of a coating to mask the color of the substrate. It is related to the ability of a particle to scatter light, which in turn is directly related to refractive index. The average refractive index of rutile crystal (2.73) is considerably higher than that of ZnO (2.02) [18], a factor that in large measure explains why TiO_2 pigments now dominate the paint industry. Zinc oxide can also cause blistering when water penetrates into the coating and, as a result, its application in primers is not recommended. However, ZnO in paint contributes to mildew protection, UV absorption, hiding power and neutralization of acids formed during paint oxidation so it still has some applications, particularly in anti-fouling paints for ships [3]. ASTM D79-86 provides information on ZnO additions to paint. An important point is that the ZnO pigment must contain less than 0.5% moisture content. Therefore the French or American process ZnO materials are used, which have very low moisture and volatile matter content. Wet-chemical ZnO, with higher moisture content and surface hydroxyl groups, cannot generally be used in such applications. There have been very significant changes to paint formulations over the last few decades, and a very large number of standards or specifications related to the use of ZnO in paints have been cancelled or withdrawn. Therefore, care should be taken to acquire the most recent information before using ZnO in a modern paint formulation.

Zinc oxide also has a potential application as an energy-saving coating on windows [6]. As described in Section 3.6.3, ZnO becomes modestly electrically conductive when doped with elements such as Al or Ga, hence it acquires the ability to reflect infrared radiation. It can therefore be used as a component of a multilayer coating system for energy-saving or heat-rejecting windows. In these applications the visible part of the spectrum passes through the coating but the infrared radiation is either reflected back into the room (saving energy in cold weather) or it is reflected from outdoors (rejecting radiant heat in hot weather). The ZnO coating can be applied by physical vapor deposition in a vacuum chamber, using sputter targets manufactured from very pure ZnO powder. However, the market is currently dominated by pyrolytic SnO_2 coatings because these are cheaper to produce.

It is also reported that the sulfide scavenging properties of ZnO can be useful for the corrosion-resistant tin coatings applied on the inside of steel cans used in the food packaging industry. Fine particles of ZnO incorporated in the coating can react with the trace amounts of H_2S given off during the cooking of foodstuffs such as corn. The reaction of ZnO with H_2S forms white ZnS. This prevents from the formation of unsightly (black) tin sulfide stains that would be caused by the reaction between H_2S and tin coatings [18].

4.5. Cosmetics, medical and dental

A wide range of cosmetic products e.g. moisturizers, lip products, foundations, mineral make-up bases, face powders, ointments, lotions and hand creams make use of ZnO [94]. One reason is that ZnO helps cosmetics adhere to the skin but a more important motivation is that ZnO is a broad-spectrum UV absorber which effectively attenuates UV radiation in both the UVA (320–400 nm) and UVB range (290–320 nm). It is photo-stable and has one of the broadest UV attenuation spectra amongst the sunblocks approved by regulatory authorities such as the USA's FDA [171,172]. Performance of ZnO particles for UV attenuation depends on particle size with an optimal size of 20–30 nm. However it is generally used in particle size range of 30–200 nm. To facilitate its dispersion in the compositions, particles are generally surface-treated with inert coating materials, such as silicon oils, SiO_2 or Al_2O_3 [94].

Clinically, ZnO promotes wound healing and keeps wounds moist and clean. High surface area ZnO (active grade) can be used in lotions or creams for the treatment of acne or of fungal infections such as athlete's foot (*Tinea pedis*). Active ZnO inhibits the growth of bacteria such as *Propionibacterium acnes* which results in less of the sebum (an oily substance secreted by the sebaceous glands in mammalian skin) being split into the free fatty acids which in turn act to inflame the follicle wall. ZnO may also be used in anti-dandruff shampoos and in the treatment of nappy rash [173].

As an ingredient in dry deodorants to reduce wetness under the arm, ZnO can be used between 0.05 and 10% by weight with average particle size in the range of 0.02–200 microns. ZnO may be used to provide a pH range desirable for deodorants designed for use on sensitive skins [174].

Zinc salts such as chloride and sulfate are useful in dental materials such as dentifrice pastes, filling material, cements and impression materials, but may cause an unpleasant lingering taste. ZnO may alleviate this problem in toothpaste, for example [175]. In dentifrice compositions, 0.1–10% ZnO is generally added as an anti-plaque, anti-gingivitis, anti-bacterial or tartar agent. Anti-plaque properties of compositions containing ZnO are improved by formation of zinc ions which slows tartar formation. Typical compositions of toothpaste, tooth gel and tooth powder containing ZnO are disclosed in the patent literature, see for example [176]. It is recognized in the field that the useful effect of the Zn is from soluble Zn^{2+} ions rather than from ZnO itself which, as mentioned previously, is comparatively inert.

4.6. Catalysts

It was discovered in Germany in the 1920s that methanol was the major product of the hydrogenation of carbon monoxide over mixed zinc and chromium oxides [177]. Today, methanol is a very important commodity in the chemical industry. A methanol synthesis catalyst must be active for about four years and must also be selective to avoid formation of other unwanted species such as methane or ethanol. The catalytic process for synthesis of methanol uses synthesis gas, a mixture of H_2, CO, and CO_2. Originally a high-pressure (100–350 bar) process over ZnO/Cr_2O_3 catalyst at 320–450 °C was applied but this was replaced by a lower-pressure process (50–100 bar) over $Cu/ZnO/Al_2O_3$ catalyst at 200–300 °C patented in 1965 by Imperial Chemical Industries [177,178]. So far the best methanol productivity reported is over catalyst prepared by the co-precipitation of Cu, Zn, and Al carbonates. The resulting mixed metal hydroxy-carbonates are then calcined at around 300–500 °C to form the mixed metal oxides. The ratio of the oxides is variable depending on the manufacturer, and falls in the range 40–80% CuO, 10–30% ZnO and 5–10% Al_2O_3 [177,179,180].

Alkali-promoted ZnO catalysts can also be used in the production of *iso*-butyl alcohol from synthesis gas at temperatures above 400 °C [49]. Zinc oxide has been also used as a formose catalyst. It heterogeneously catalyzes formaldehyde condensation to a complex mixture of formose sugars at slightly acidic conditions [181]. Other uses of ZnO include as a catalyst for conversion of cyclohexanol to cyclohexanone in the course of the production of caprolactam, $(CH_2)_5C(O)NH$, which is a precursor for nylon 6 [49].

4.7. Desulfurization

The reaction $ZnO + H_2S \rightarrow ZnS + H_2O$ has a favorable ΔG of <-75 kJ mol^{-1} between 0 and 1000 °C. Therefore, ZnO can serve as a scavenger for H_2S gas in a variety of fluids and gases, particularly hydrocarbon gases containing H_2S or other sulfur-containing compounds and industrial flue gases [182,183]. For instance in gas-to-liquid production plants, natural gas feedstocks may be desulfurized using ZnO fixed-bed reactors. To lower the sulfur content of process streams to an acceptable level [70,182], the ZnO specific surface area should be above 20 m^2 g^{-1} and preferably in the range 50–200 m^2 g^{-1}. It is typically used in the form of granules or pellets. Operating temperatures may be between −10 °C to +200 °C with a maximum temperature below 300 °C [184]. Although ZnO can be regenerated, its recovery involves calcination at temperatures around 500 °C which releases SO_2 [185]. A schematic of a purification process using ZnO and typical desulfurization reactors and ZnO absorbent are shown in Fig. 18.

4.8. Oil and gas well drilling fluid

Drilling fluids or "muds" in oil and gas industries are used to control formation pressure, cool the bits and carry cuttings from the drill holes to the surface. During the drilling process, H_2S can be formed by the action of sulfate-reducing bacteria under anaerobic conditions and can diffuse into the drilling muds. This toxic and corrosive gas should be controlled to reduce health hazards and damage to pipelines and equipment. The reaction kinetics and absorption capacity of ZnO make it a useful absorbent for H_2S in drilling fluids with the advantage that spent ZnO sorbent is non-toxic [147]. A very large specific surface area is helpful in this application. 'Nano-ZnO' with a crystal size of <30 nm and specific surface area of >40 m^2 g^{-1} is suitable. For example, nano-ZnO samples produced by spray pyrolysis and with specific surface area over 44 m^2 g^{-1} removed 100% of H_2S within 15 min in a simulated aqueous drilling fluid. In contrast, bulk ZnO with the specific surface area of 5 m^2 g^{-1} and a crystal size of about 250 nm removed only 2.5% of the H_2S in 90 min [147].

Another important issue in the formulation of drilling fluids is the effect of various constituents on their density and viscosity. Barium sulfate is used as a weighting compound in vertical wells, but is not optimum for horizontal wells which require that such an additive be soluble in acid [148]. To address the problem, ZnO – which has a density of 5.6 g cm^{-3} *vs.* 4.5 g cm^{-3} for $BaSO_4$ – has been proposed for use as weighting agents in such drilling fluids [148].

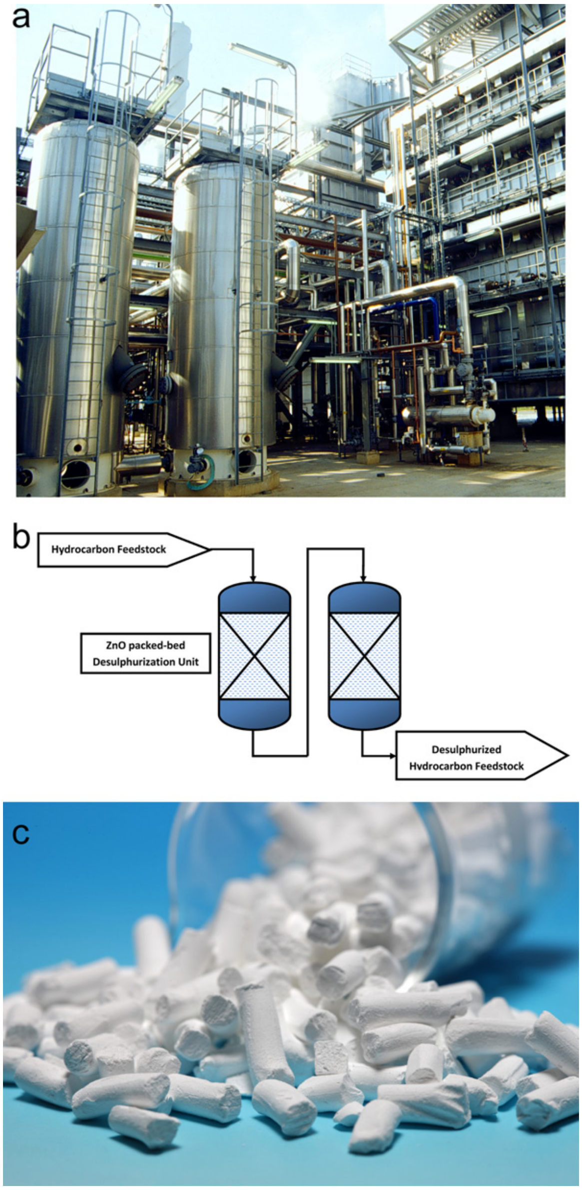

Fig. 18. (a) An industrial desulfurization unit; (b) A schematic diagram of a simplified hydrocarbon feedstock purification unit using ZnO as a desulfurization absorbent; (c) An example of a ZnO desulfurization absorbent. By permission from Haldor Topsøe, Denmark.

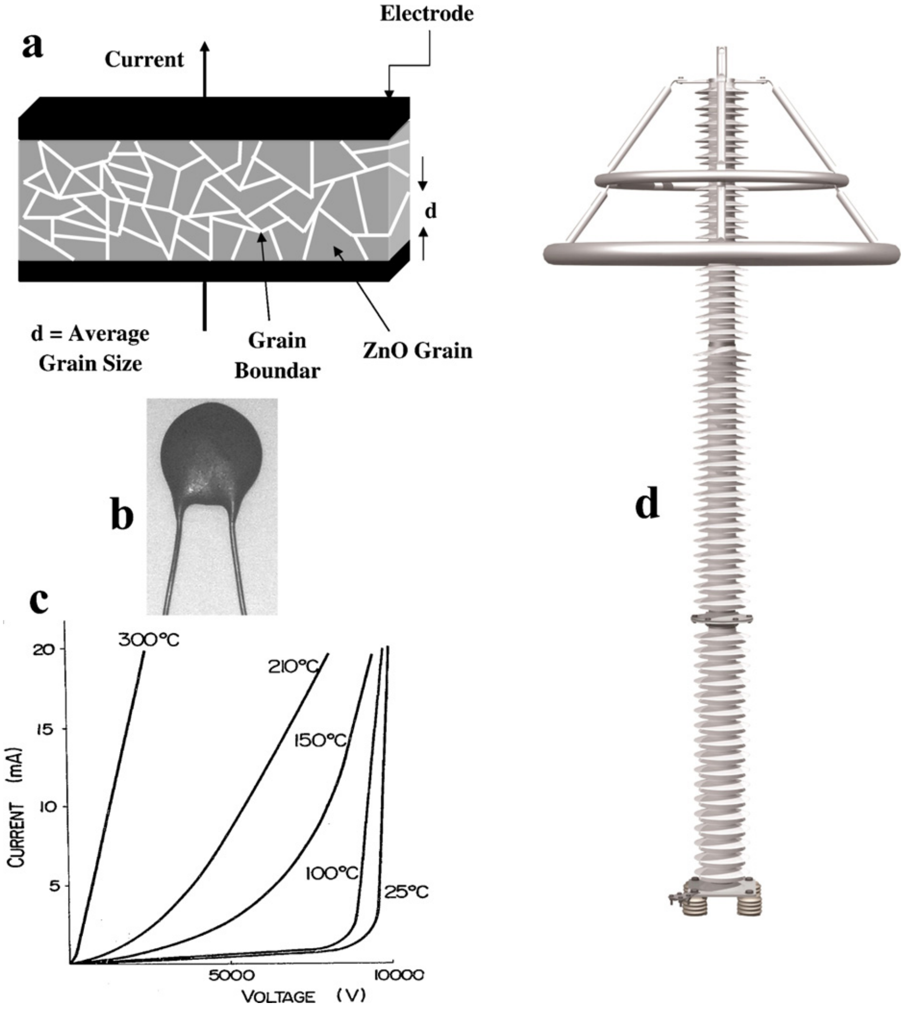

Fig. 19. (a) Schematic of microstructure of a ZnO varistor [10]; (b) Small size varistor; (c) Temperature dependence of *I–V* curve of ZnO varistor [186]; (d) A typical silicone-rubber-housed ZnO surge arrester type PEXLIM P330-YH420 suitable for protection in 420 kV systems reproduced by permission from ABB, Sweden.

4.9. *Varistors and soft ferrites*

Varistors are protective electronic devices with an extremely nonlinear current-voltage curve at ambient temperature, Fig. 19. As the voltage increases and reaches a certain voltage (breakdown value), a dramatic increase in current occurs [10,186]. Zinc oxide in this ceramic form acts as a resistor below the surge voltage and a conductor above that and can provide protection against damaging power surges or transients. The *I–V* characteristic of a varistor is also a function of the temperature. As the temperature increases, it loses its non-linear characteristics and leaks more readily.

The first ZnO-Bi_2O_3-based varistor was developed by Matsuoka in Japan in 1969. Today commercially available varistors are mostly based on a polycrystalline matrix of ZnO (grain size around 10 μm) combined with other additives such as oxides of Bi, Co, Cr, Mg, Mn, Ni, Pr, Sb, Si and Ti with contents above ~0.1 mol%. ZnO-based varistors are widely used in electrical devices, including household appliances, automotive circuitry, portable electronics, high voltage power transmission, avionics and lightning arresting applications. The size of a ZnO varistor depends on the application and varies from a few millimeters for integrated circuit boards to 1 m for high voltage surge arresters. ZnO varistors are relatively cheap with a long life span and can withstand high currents and energies. Their switching response is about 500 ps [186,187].

Large surge arrestors are made of a stack of individual ZnO varistors of up to 10 cm in diameter. Internal ZnO blocks are manufactured by premixing and pressing the ZnO (e.g. the French process grade) and other metal oxides into the mold. Then the pressed shape is sintered at temperatures above 1000 °C for several hours followed by slow cooling ($\sim$100 K h^{-1}) to form a solid block. The solid block is next coated by a conductive layer followed by stacking the blocks together and sealing them in a vessel made of a ceramic material or molded rubber [186–188]. Detailed processes to manufacture ZnO-based varistors are disclosed in the US Patents 5250281 and 4262318 [186,187].

Zinc ferrite, $ZnFe_2O_4$, is an important sorbent material for high-temperature desulfurization of coal gas. A catalytic grade of zinc ferrite can be manufactured by calcination of a 1:1 mol ratio of zinc oxide and iron oxide mixture [189]. ‘Soft’ zinc ferrites such as $Mn_xZn_{(1-x)}Fe_2O_4$ or $Ni_xZn_{(1-x)}Fe_2O_4$ are also important ferromagnetic materials for electronic applications such as transformers, electromagnetic gadgets, antenna rods, magnetic recording heads, noise filters, choke coils, information storage, medical diagnostic and biomedical devices and magnetic amplifiers [190–192]. The term ‘soft’ refers to their low magnetic coercivity. Zinc ferrites containing other elements such as Mg, Cu are also used in some specialized electronic applications [193].

4.10. *Fertilizers, animal feed and dietary supplements*

Zinc is an essential micronutrient in all organisms including humans and is required for healthy growth and metabolism, and

Table 3
Chemical purity of a typical feed grade zinc oxide [200].

Zn	Min. (%)	72.0
Pb	Max. (%)	0.04
Cu	Max. (%)	0.01
Cd	Max. (%)	0.0001
As	Max. (%)	0.005
Cl	Max. (%)	0.1

normal functioning of the immune system [194,195]. Zinc deficiency has a role in physical growth, morbidity and mortality from infections (such as diarrhea and pneumonia) particularly in young children and also adversely effects the health of the mother and fetus during pregnancy and lactation [5]. The efficiency of zinc absorption from the diet is relatively low, in the range of 15–35% for adults. It is estimated that around one-third of the world's population lives in zinc-deficient areas and are therefore at risk [196].

Water-soluble or insoluble zinc fertilizers are used to provide traces of Zn in deficient soils. These are especially important for rice, corn, potato, beans and oil palm where relatively large amounts may be used. The zinc-containing material may be applied directly, or blended with another product such as urea [197]. Alternatively, ZnO could be added to the composition of a pesticidal-micronutrient to provide the required zinc for spray application to crops [23,198], or suspended in water with a dispersant such as calcium lignosulphonate.

Free-flowing 'feed grade' ZnO is a special grade with Zn content between 72 and 79%, ZnO content of 90–99% and (usually) a high bulk density between 1.6 and 2.4 $\mathrm{g\,cm^{-3}}$ which can be easily handled, stored in silo trucks and weighed automatically. Feed grade ZnO is mostly used in animal feed for piglets, cats, dogs, cattle or poultry. There is some ambiguity concerning the method by which feed grade ZnO should be manufactured. Edwards and Baker [199] examined the efficacy of four grades of 'feed grade' ZnO in the North American chicken industry and found that they varied widely. Furthermore, the materials used had been manufactured by at least three processes: the direct process (in a Waelz kiln), the sodium dithionate process and the French process. Table 3 shows the chemical composition of a typical 'feed grade' ZnO.

Direct fortification of food is considered an effective and economic method to increase dietary zinc intake and adsorption in humans too [196]. Zinc oxide and to a lower extent zinc sulfate (the two cheapest zinc chemicals commonly used by food industries) may be added to wheat, rice and maize flours, for example, or to breakfast cereals or snack bars [194,201–203]. Obviously, only the purest ZnO, i.e. pharmaceutical grade, should be used.

4.11. *Zinc oxide in chemical synthesis*

Zinc phosphate, $Zn_3(PO_4)_2$, is used in corrosion-resistant paints for metal structures and as a filler in the manufacture of vulcanizates to increase heat-resistance. It is also used as an anti-galling agent in the couplings of drill strings for the oil and gas industry. Zinc phosphate, which is insoluble in water, can be prepared by a reaction between ZnO and phosphoric acid in an aqueous medium [204].

Zinc borate ($x\mathrm{ZnO}\cdot y\mathrm{B_2O_3}\cdot z\mathrm{H_2O}$) is a white powder with low water solubility and high dehydration temperature. It has applications in polymer compositions as a fire retardant and as smoke suppressant and in the wood, textile and cement industries (ZnO is also considered a fire-retardant, for example in nylon 6,6 [164]). Zinc borate may be prepared by a reaction between ZnO and boric acid in an aqueous medium at temperatures around 90–100 °C [205,206].

Zinc dialkyldithiophosphates (ZDDPs) are oil soluble coordination compounds used in the lubricant industry as anti-wear and anti-oxidant agents. Metal dialkyldithiophosphates were developed by Herbert Freuler and patented in 1944 [207]. Zinc oxide plays an important role in the production of ZDDPs. First, dialkyldithiophosphate is synthesized by reacting powdered phosphorous pentasulfide (P_2S_5) with alkyl alcohol, then the dialkyldithiophosphate is neutralized by ZnO to yield the zinc dialkyldithiophosphate [208].

Zinc diacrylate used in golf balls can be prepared by reacting acrylic acid with ZnO-fatty acid mixture in a liquid medium [209].

Zinc stearate can be manufactured from zinc oxide. One application for it is in the tire industry, where it may be used to dress the steel molds to assist with release of the tire. It may also be added to the initial blend for the rubber, but generally in far smaller quantities than ZnO itself.

4.12. *Miscellaneous applications*

ZnO in phosphors: Phosphors are compounds (mainly of the transition metals) that luminesce with a characteristic output spectrum under certain conditions of optical excitation. A phosphor known as 'ZnO:Zn' has been used for decades in CRTs and other devices where an electron beam must be converted to light (green in this case). ZnO may also be used as a precursor in the manufacture of other phosphors, such as $Zn_2SiO_4{:}Mn^{2+}$ which is used as green phosphor in thin-film electroluminescence displays [10].

Smoke-producing devices: Military smokes are used to temporarily obscure objects from visible or infrared observation. The fine airborne dispersion of liquid droplets or particulate solids causes light to be scattered. Opacity, duration of effect, cost, toxicity and dispersion properties of screening smokes are important factors in this field [164,210]. Optimum scattering is obtained when the particle size of the aerosol is about the same as the wavelength of light to be screened. Zinc oxide-hexachloroethane smokes are well-known in this industry. A typical composition contains aluminum powder, ZnO and hexachloroethane (HCE). All the constituents are in solid form and as a result can be compacted in small volumes for applications such as smoke grenades, smoke pots, and artillery shells. Reaction between HCE and ZnO forms zinc chloride-water smoke. However $ZnCl_2$ smoke produced from this reaction is relatively toxic and can cause severe respiratory symptoms [210,211].

ZnO in paper: Another niche application for ZnO is in specialized paper coatings, high pressure laminates and wallpaper. It can improve the cohesive strength of paper coatings. High purity ZnO (such as the French process ZnO) has photoconductive properties. It can hold negative electrostatic charge which can be discharged when UV or deep blue radiation is applied. This characteristic was exploited in papers used for electrostatic photocopying between about 1965 and 1985. In this case, a coating of ZnO mixture with a resinous binder was applied on the paper [146,212].

Corrosion inhibition: A corrosion inhibitor is an additive to a fluid or gas that decreases the corrosion rate of adjacent metallic structures. Zinc oxide is a cathodic inhibitor and slows the corrosion by inhibiting the reduction of water to hydrogen gas. For example, in alkaline aluminum batteries, ZnO can inhibit the corrosion of aluminum anode [213].

Polymer-modified-asphalt: Polymer-modified asphalts (PMAs) such as those modified by incorporation of elastomeric polymers (e.g. polybutadiene) are used in applications requiring improved physical and mechanical properties compared to non-modified asphalt compositions. To prepare PMAs, activators and accelerators are applied to accelerate the crosslinking reaction. Zinc oxide and mercaptobenzothiazole are conventional activator and cross-linking agent materials, respectively [214].

Fungistat: Zinc oxide and its derivatives contribute effectively to the control of fungi in many different types of applications. Zinc oxide is not a fungicide per se, rather it is a fungistat; i.e., it inhibits the growth of fungi, such as mildew on the surface of exterior house paints. Its fungistat effect increases with its surface area. ZnO inhibits the growth of mycelium or the germination of spores. However it does not kill the spores or prevent their germination after exposure to a more favorable environment. It can, however, be added to fungicides for fortification to take advantage of its fungistatic property [215].

5. Potential and emerging applications

There are several emerging applications of ZnO in the area of electronics and optoelectronics, driven by specific optical or electrical characteristics of this semiconductor.

5.1. Liquid crystal displays

Transparent conductive oxides (TCOs) are currently used in a large variety of consumer goods, including liquid crystal displays. In general, they are based on indium tin oxide (ITO). However, there are concerns that indium resources will be insufficient to service future growth and there is an active quest for alternative or cheaper materials. Zinc oxide films that have been doped with *n*-type dopants such as Al, Ga and In are promising candidates to fill this requirement. These materials may be deposited by magnetron sputtering, and are of special interest due to their high conductivity and optical transparency, high thermal stability and relatively lower cost [10,133,216,217].

5.2. Light emitting diodes (LEDs)

A large exciton binding energy is an important factor in the design of LEDs. Zinc oxide, with the relatively high exciton binding energy of 60 meV, shows promise in blue/UV light emitters. The field has recently been reviewed by Choi et al. [218]. A challenge for the production of ZnO-based light emitters, however, is producing reliable, low-resistivity *p*-type ZnO, a problem which is not yet resolved [218]. Zinc oxide is currently being explored for applications such as in UV lasers [123,219], in blue light emitting diodes [123], and in organic LEDs [6,10].

5.3. Spintronics

Dilute magnetic semiconductors are potentially important materials for spintronics with proposed applications in, for example, integrated memory devices and microprocessors. As described in Section 3.6.3, doped materials such as ZnO:Mn are of interest because of their ability to exhibit ferromagnetism above room temperature. This field is still in its earliest phases, however, and no significant commercial application of semi-conductor spintronics has emerged yet [129].

5.4. Solar cells

Zinc oxide has a role in two disparate aspects of photovoltaic technology. First, use of transparent, conductive ZnO in the front electrodes of solar cells can eliminate the shadow effect related to metal-finger contacts and is also cheaper than the alternative indium oxide electrodes [6,10]. Secondly, n-type ZnO films may also be used within the photovoltaic structure itself, for example as a tunnel junction in amorphous silicon cells or as part of the p/n junction in $Cu(In,Ga)(S,Se)_2$ cells [10].

5.5. Sensors and actuators

The sensitivity of the electrical resistivity of ZnO to gases such as ethanol, acetylene, CO, NO and NO_2 makes it potentially useful for sensing applications. A drawback, however, is its poor selectivity [7]. Zinc oxide nanowires may be useful in room temperature sensing applications and, for example, a glucose sensor based on ZnO nanorods has been reported [220].

The piezoelectric property of ZnO makes it suitable for applications in acoustic microscopy, bulk acoustic wave (BAW), acousto-optic and surface acoustic wave (SAW) devices [221] for use in telecommunications industries (e.g., in mobile phones and base stations), piezoelectric sensors, or torque or pressure sensors. A SAW ZnO sensor has been studied for its potential application in wine differentiation [222].

5.6. ZnO in textiles

The application of ZnO (produced by the wet chemical process) to fabrics such as cotton and polyester may impart beneficial antimicrobial characteristics, enhanced whiteness, resistance to UV radiation and anti-static properties [60,223]. However, large-scale application of ZnO in the textile industry has not yet occurred to our knowledge. In any case, in our opinion the commercial penetration of such a product into OECD markets will very likely run into consumer concerns regarding the safety of nano-particles. While a clear medical case can be readily made for use of ZnO or other nanoparticles in a product such as sunscreen, their use in consumer clothing might be harder to sell.

6. Conclusions

Zinc oxide has been an important industrial material for centuries and is currently the subject of considerable new interest. It has a combination of physical properties (such as relatively high electrical and thermal conductivity, optical absorption in the ultraviolet and very high temperature stability), chemical properties (such as stability at neutral pHs and mildly antimicrobial action), and techno-economic attributes (such a ready availability and reasonable cost) that have ensured its use in an exceedingly wide range of industries.

Methods of production of ZnO have evolved continuously. The larger scale pyrometallurgical processes produce crystalline ZnO powders for the rubber and other large scale industries, but the niche applications are served by an extraordinary variety of small-scale production methods, with the choice of technique matched to the end-use properties required. There does not seem to be any feasible substitute at present for the use of ZnO in rubber, and this application is likely to remain the dominant one for decades to come. However, given the very versatile and useful nature of ZnO as a material, it is possible that new and unanticipated applications for ZnO will arise and become economically important. Current experience shows that the new applications are as likely to be supplied by one of the smaller-scale production techniques described here, as by the pyrometallurgical ones, so from a production point-of-view, the field remains lively and interesting.

Although ZnO has been used in cosmetic and medical applications for thousands of years, there has of late been a campaign in some countries within the OECD to alert the public to its potential ‘toxicity’. Certainly ZnO is not totally inert, of course, and if it was it would not be of value in many of its current applications which rely upon a small but controlled degree of chemical reactivity. Nevertheless, the issue seems to be over-rated in general. As shown here, more than half of all ZnO production goes into the rubber of motor car tires, which gradually abrade away during use anyway. The urban and roadside environment has therefore been well covered by now in particulate ZnO, but that issue hardly rates any comment in the literature.

Zinc oxide has enjoyed a variety of uses over the last century, some of which (such its use in photocopying) have appeared and then disappeared a few decades later in quite a dramatic fashion. However, in our opinion the useful set of physical and economic attributes of this material will ensure that it will continue to be considered for an impressively diverse range of existing and future applications.

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