

# Aerosol Science and Technology: History and Reviews

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**RTI** Press

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Library of Congress Control Number:

2011936936

ISBN: 978-1-934831-01-4

doi:10.3768/rtipress.2011.bk.0003.1109

[www.rti.org/rtipress](http://www.rti.org/rtipress)

### **About the Cover**

The cover depicts an important episode in aerosol history—the Pasadena experiment and ACHEX. It includes a photograph of three of the key organizers and an illustration of a major concept of atmospheric aerosol particle size distribution. The photograph is from Chapter 8, Figure 1. The front row shows Kenneth Whitby, George Hidy, Sheldon Friedlander, and Peter Mueller; the back row shows Dale Lundgren and Josef Pich. The background figure is from Chapter 9, Figure 13, illustrating the trimodal atmospheric aerosol volume size distribution. This concept has been the basis of atmospheric aerosol research and regulation since the late 1970s.

This publication is part of the RTI Press Book series.

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# History of Manufacture of Fine Particles in High-Temperature Aerosol Reactors

Sotiris E. Pratsinis

This chapter reviews the historic development of aerosol reactors for the manufacture of commercially available fine particles, placing emphasis on flame-made carbon black, titanium dioxide ( $\text{TiO}_2$ ), and silicon dioxide ( $\text{SiO}_2$ ), which dominate the aerosol-made material market by volume and value, followed by particles made in hot-wall reactors (zinc oxide [ $\text{ZnO}$ ], nickel [ $\text{Ni}$ ], tungsten carbide [ $\text{WC}$ ], and others). Early discoveries have shaped this industry: carbon black can be used to reinforce tires, and carbon black made from flare gas in oil fields is equivalent to that made from natural gas. Carbon black engineers were some of the first to introduce the fractal characterization of aerosol particles. Also the competition between coagulation and sintering for synthesis of fractal-like or ramified particles seems to have been reported first in reference to the manufacture of fumed silica. The success of DuPont's research on the aerosol synthesis of titania is best illustrated by the fact that DuPont started using the process in 1951 but DuPont's competitors did not build similar plants for  $\text{TiO}_2$  production for more than 12 years. Despite such technologies being developed through trial and error, aerosol engineers today understand the mechanisms controlling the characteristics of these particles. In this chapter, the role of process variables on particle characteristics is highlighted. Such understanding guides the rational design and operation of aerosol reactors for synthesis of a number of commodities today. It also enables aerosol technology to develop a score of new processes and products, such as catalysts, sensors, biomaterials, photonics, and even nutritional supplements and functional devices to name a few that have evolved from academic laboratories and start-up companies.

## Introduction

Smoke has been used throughout human history: in prehistoric drawings on cave walls and art in ancient Egypt, India, Greece, and China; as a preservative for meat and fish by Romans and Scandinavians; and even as a means of telecommunications by ancient Trojans and American Indians. Flame-made particles have special structure and high purity, resulting in unique products such as carbon black and fumed silica for light guides (Ulrich, 1984). Furthermore, gas phase (aerosol) technology involves fewer process steps than liquid phase technology, and separation of product particles from gases is easier than from liquids because it does not involve liquid by-products and costly effluent cleaning (Pratsinis & Mastrangelo, 1989). As such, it is no surprise that aerosol processing is preferred over wet chemistry processes for many industrial uses, including production of titania pigments (chloride vs. sulfate processes) and cleaning effluent streams (gas vs. wet scrubbing). Very recently, it has been shown that aerosol processes can make metastable materials such as low-temperature barium carbonate ( $\text{BaCO}_3$ ) for  $\text{NO}_x$ -storage and reduction (NSR) catalysts (Strobel et al., 2006a) or tungsten trioxide ( $\epsilon\text{-WO}_3$ ) for highly selective sensors of acetone, a diabetes marker in the human breath (Righettoni et al., 2010).

Historically, aerosol manufacturing technologies have been developed around specific products that predominately use flame or hot-wall reactors. Today flame reactors produce 90% (by value and volume) of aerosol-made commodities, including carbon black, pigmentary titania, and fumed silica (Stamatakis et al., 1991; Wegner & Pratsinis, 2003a). Hot-wall reactors have been used to manufacture ZnO, Ni, iron (Fe), and nonoxide ceramics (e.g., tungsten carbide). The early development of aerosol reactor technology was driven solely by product discovery and application (e.g., the reinforcement of rubber by carbon black was developed specifically for the production of tires for motor vehicles).

With the paucity of scientific information available in the early 20th century, the ability to construct and continuously operate huge units for aerosol manufacture of such materials at really high production rates was a miracle of engineering. Although much is known about soot formation, this knowledge may be of little relevance to materials manufacture (Skillas et al., 2005). When soot is viewed as a nuisance or a pollutant, there is little motivation for detailed characterization and performance evaluation, which are the focus of the carbon black industry. Typically, soot formation research

focuses on understanding pathways for soot's suppression. In contrast, the materials industry focuses on the development and characterization of soot after particle formation (e.g., the development of particle morphology, structure, surface, and crystallinity), especially at the high concentrations that are of most interest for the efficient and sustainable manufacture of such particles. As a result, the development of aerosol reactor technology is closely associated with the performance of its specific products.

This chapter reviews the historic evolution of this technology for the manufacture of today's particulate commodities so that one may better understand the factors that may guide the future manufacture of other aerosol-made products such as electroceramics, catalysts, and sensors. As such, this chapter does not cover synthesis of films, coatings, or deposits that are made by aerosol processes, including suspended droplets or particles deposited in a molten state on surfaces at high temperatures by flames, plasma, or torches, or at low temperatures by high-pressure sprays or electrospraying. This technology is called "thermal spray coating," as reviewed by Clyne and Gill (1996), or just "spray coating" or "combustion chemical vapor deposition" (Hunt et al., 1993); and Tricoli and colleagues (2010) have recently reviewed its use for gas sensors. This chapter also does not discuss the manufacture of optical fibers involving oxidation of precursor vapors and deposition of fine silica-based particles and eventual fiber drawing (Rowell, 1986). One should note, however, that aerosol science truly guided the design and operation of optical fiber preforms by modified chemical vapor deposition because aerosol thermophoresis dominated the yield of this process. The present chapter excludes materials made by spray pyrolysis or aerosol decomposition because this is a small (albeit increasing) market, especially for select ceramic materials (Kodas & Hampden-Smith, 1999). Similarly, I do not address nanoparticle synthesis in plasma and laser reactors, including laser ablation, because of their limited contribution to large-scale manufacture materials until recently. Nevertheless, several excellent studies have been published on the topic: Vollath (2007) has reviewed plasma synthesis of materials, focusing on microwave plasmas that allow even organic coatings on nanoparticles; Semaltianos (2010) has examined nanoparticle synthesis by laser ablation; and Van Erven and colleagues (2009) have focused on the scale-up of laser reactors.

The present chapter focuses on the history of the development of aerosol reactors for synthesis of *commercially available* fine particles (carbon black,

titania, silica, zinc oxide, and nickel), emphasizing the flame and hot-wall reactors that dominate this field. Other authors provide additional insight into various aspects of aerosol reactors:

- Ulrich (1984) gives an excellent overview of flame aerosol technology for materials manufacture that ought to be read by anyone working in this field.
- Gurav and colleagues (1993) superbly review nearly 350 papers on aerosol processing of materials in a special issue of *Aerosol Science and Technology* that contains some seminal articles in the field.
- Rosner (1997) gives an outstanding account of combustion synthesis of commodity gases, particles, and films.
- Wooldridge (1998) and Pratsinis (1998) tutorially review flame reactors and models for synthesis of particles until the mid-1990s, outlining how flame variables affect product particle size and morphology.
- Kudas and Hampden-Smith (1999) describe a broad spectrum of pertinent applications of aerosol processing of materials, and the second edition of Friedlander's (2000) classic aerosol textbook addresses dynamics of irregularly shaped particles that are so relevant to this technology.
- Swihart (2003) critically reviews the state of the art in vapor synthesis of materials, focusing on methods and processes.
- Strobel and colleagues (2006b) summarize the recent, rapid development of heterogeneous catalysts by flame aerosol technology.
- Roth (2007) highlights recent experimental, diagnostics, and modeling aspects of particle formation in flames for materials processing.
- Strobel and Pratsinis (2007) review how flame aerosol technology can be used to make various sophisticated materials for sensors, biomaterials, electroceramics, and even nutritional supplements.
- Biskos and colleagues (2008) review aerosol generation and characterization methods for nanoparticles.
- Athanassiou and colleagues (2010) show how ceramics and even metals are made in scalable flame aerosol reactors.
- Camenzind and colleagues (2010) review how aerosol-made nanoparticles affect the mechanical and optical properties of nanocomposites.

- Pratsinis (2010) shows how critical is aerosol technology to nanoscale manufacturing: from functional materials to sophisticated devices.

Finally, it should be noted that aerosol synthesis of materials has recently expanded rapidly as the potential of aerosol technology has become recognized across scientific disciplines. Furthermore, academic laboratories and start-up companies have recently developed a number of new aerosol processes for synthesizing novel materials; because this chapter examines the use of aerosol in large-scale commercial manufacture, it does not cover these new developments because they have not yet reached their full commercial scale. As such, there is much more in recent literature than is discussed here, especially with new processes and products being developed in both industrial and academic laboratories.

I start by looking at the manufacture of carbon black. Carbon black was the first flame-made product to attain industrial status; from prehistoric times, it has been used to make inks, and since the early 20th century, it has been used to reinforce rubber tires. Each automobile tire contains about 20% carbon black by weight. I then discuss  $\text{TiO}_2$ , the largest (by volume and value) ceramic material made in flame aerosol reactors, followed by fumed silica and its diverse applications, mostly as a flowing aid to particulate commodities in a multitude of applications (e.g., cosmetics, food, and drugs) and as the basic material for optical fibers. Finally, I discuss particles—such as ZnO, WC, and filamentary Ni (which is the leading aerosol-made metal today)—that are made in hot-wall reactors.

## **Carbon Black**

Carbon black is the oldest aerosol that is still manufactured today. Its history is well documented in encyclopedias and specialized books (Cabot, 1979; Kühner & Voll, 1993; Collin, 2000; Wang et al., 2004). In short, carbon black was first made in India and Egypt at prehistoric times and was systematically manufactured for pigments in China by pyrolysis of vegetable oils, using the “lampblack” process at about 1500 BC. This process involves the evaporation and pyrolysis of hydrocarbon vapors in a closed chamber to which a controlled amount of air is supplied. Carbon black is formed in the gas phase (aerosol) and is deposited by thermophoresis onto the smooth walls and ceilings of the chamber; it is then scraped from the surfaces of the chamber and is suspended in fluids for various applications.

The lampblack process was rather simple because only one parameter, the supplied air, controlled the carbon black's characteristics. Simplicity, however, was accompanied by a lack of flexibility because selective evaporation of the volatile oil fraction from the evaporating pans during manufacturing required systematic removal of the remaining heavy residue from the pans. Lampblack carbon black had a broad particle size distribution caused by its exceedingly broad residence time distribution resulting from the inhomogeneous mixing of incoming air and freshly formed carbon black over the pans. Flexibility was also limited because manufacturers were required to replace small with larger pans for evaporation of oil when shifting the average particle size from fine to large. Today, only large carbon blacks, up to 500 nm primary particle size, are made by the lampblack process (Kühner & Voll, 1993).

In the late 19th century, "channel" or "gas" carbon black was discovered. This form of carbon black had a finer texture than the carbon black produced by the lampblack process, making it attractive for use in more viscous printing ink. Its raw material was natural gas (in the United States) or vaporized oil from coal tar distillates (in Europe). The combustion plume impinged on cold surfaces at the bottom of water-cooled channels (hence "channel carbon black") or rotating drums, where it was collected. The yield of this process was 3%–5%, and a large fraction of carbon black ended up in the atmosphere, making the smoke from these plants visible from far away (Kühner & Voll, 1993). This form of carbon black had a finer structure (primary particle size 10–30 nm) than lampblack because of its short high-temperature residence time. It appealed successfully to the dominant ink industry at the time and contributed to discovering the reinforcing role of carbon black on natural rubber.

After the discovery of the reinforcing role of carbon black in tires (by the turn of the 20th century) and the beginning of automobile mass production after World War I, the demand for natural gas increased rapidly. Gas suppliers could store natural gas and distribute it at will, controlling the market. At that point, Thomas Cabot, whose family owned a small carbon black company in Pennsylvania, discovered that flare gas from oil fields was as good as natural gas for synthesizing gas carbon black and shifted the carbon black feedstock from natural to flare gas, which was cheaply available. From 1925 to 1930, Cabot Corporation built nine such plants, becoming one of the carbon black technology leaders, which still is today (Cabot, 1979).

Further improvements in handling carbon black, including pelletization to reduce dust problems, allowed shipping and distribution of carbon black over



great distances. However, the inherently low yield of the channel/gas process and the onset of World War II pushed engineers to develop the furnace process in 1941. This is a classic aerosol reactor that allows scalable, single flame synthesis of carbon black with flexible characteristics such as variable primary and agglomerate size, variable structure, and even variable primary particle porosity. A change in raw material to aromatic-based feedstock facilitated the current dominance of the furnace process; more than 80% of carbon black is made by this process today. Other carbon blacks include thermal and acetylene carbon black. The former is made by a batch process, whereas the latter has a very small primary particle size, a graphitic structure, and a high degree of aggregation, leading to the high conductivity that makes acetylene carbon black attractive for electrical applications (Kühner & Voll, 1993).

The development of a single reactor for carbon black synthesis by the furnace process and its flexibility in product characteristics emphasized the need for a better scientific understanding for process scale-up. Indeed, right after World War II, there was a huge need for carbon black to reinforce natural and synthetic rubber. The first attempts to characterize agglomerates were made in the carbon black industry. Medalia and Heckman (1969) introduced new ways to characterize agglomerate particles by optical microscopy in their effort to link carbon black reinforcing performance to carbon black characteristics and furnace process design and operation. By counting the primary particles in agglomerates,  $N_p$ , they reported a power law relating agglomerate size (radius of gyration),  $R$ , to the fractal dimension,  $D_f$ , introduced 10 years later by Mandelbrot (1982):

$$N_p \sim R^{D_f} \quad (1)$$

In fact, carbon black particles are frequently cited as fractal applications by Mandelbrot (1982) and others. According to the early patent literature, a lot of industrial research focused on reactor design, wall deposits, and additive use for the control of agglomeration (Mezey, 1966).

The lack of basic studies on carbon black formation and growth is most amazing given its history and industrial volume. Notable exceptions to this are the chemical kinetics of benzene pyrolysis for carbon black formation (Ivie & Forney, 1988) and the carbon black reactor model of Skillas and colleagues (2005) that interfaces aerosol dynamics with fluid mechanics. Most

of the prevailing understanding of carbon black formation and growth relies, however, on fuel lean soot formation (Donnet & Bansal, 1993). Accordingly, carbon black is made by nucleation followed by surface growth, coagulation, and partial oxidation. During carbon black formation, fuel-rich combustion takes place because about half of the fed carbon is combusted to pyrolyze the rest and form carbon black in a gas mixture containing mostly products of incomplete combustion, hydrogen ( $H_2$ ), and traces of oxygen ( $O_2$ ) that may give different surface growth rates than classic soot formation models. Necks between carbon black primary particles are probably formed when carbon black is rather soft and liquid, containing lots of hydrogen, which should happen at low rather than at high temperatures, when hard, graphitic structures are created. This process contrasts starkly with aggregate formation of ceramic particles by sintering, in which complete coalescence takes place at high temperatures (Koch & Friedlander, 1990).

As a result, there is considerable uncertainty in present carbon black models that qualitatively predict the effect of process variables on carbon black characteristics (Skillas et al., 2005). Additionally, in the dominant furnace process, the carbon black plume is quenched much faster than in ceramic flame-made aerosols because the carbon black plume is also a fuel (containing carbon and  $H_2$  from hydrocarbon pyrolysis) and can be readily oxidized. In fact, water injection is used to quench carbon black aerosols right after they exit the burner rather than relying on gentle cooling through pipe walls, as with pigmentary titania. Depending on the cooling rate, the surface of carbon black primary particles may become porous, releasing carbon monoxide (CO) and  $H_2$  later on (Kühner & Voll, 1993).

This scientific uncertainty, however, has not prevented the construction and operation of carbon black plants all over the world for more than a century. In fact, the production volume of carbon black is more than 3 times that of the next aerosol-made material ( $TiO_2$ ), and its value is almost twice that of  $TiO_2$  (Wegner & Pratsinis, 2003a). The evolutionary growth of this process has reached a point at which the design of some of its components are quite close to their optimum.

So it is not an overstatement that carbon black manufacture is an engineering marvel that produces a commodity that is quite modern, considering that it is also the cheapest nanostructured material available in the market today. Nevertheless, improved understanding of the process can have a large impact on its economics, because carbon black is a high-volume commodity. In fact, the fraction of combusted and pyrolyzed hydrocarbon

produced by the furnace process is critical for this industry. Furthermore, understanding the production process could help to reduce the prices of today’s costly carbon nanotubes, making them available for a score of applications (Pratsinis, 2010). Last, but not least, safety and occupational health issues, including detailed air-quality monitoring, play an important role during carbon black production (e.g., Kuhlbusch & Fissan, 2006). Such issues become increasingly important for manufacture of all nanostructured materials. As a result, the carbon black industry experience is invaluable in the regard.

### Titania, TiO<sub>2</sub>

Manufacturing of TiO<sub>2</sub> constitutes the second largest industrial aerosol commodity (in value and volume) after carbon black. About 5 million tons of titanium dioxide are made annually, representing 85% of worldwide use of titanium metal. Most TiO<sub>2</sub> is used as pigment for paints (65%), plastics (20%), and paper (10%), with the rest being used for specialty applications including catalysts, sunscreens, and, very recently, photocatalysts. Today, about 60% of TiO<sub>2</sub> is made in aerosol reactors by the so-called “chloride” process, which involves ore chlorination, distillation of titanium tetrachloride (TiCl<sub>4</sub>), and oxidation of the TiCl<sub>4</sub> vapor at high temperatures (Figure 1). The remaining TiO<sub>2</sub> is made by the older “sulfate” process, in which ore is dissolved in sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), followed by precipitation and separation of iron sulfate (FeSO<sub>4</sub>) from the liquid titanium sulfate [Ti(SO<sub>4</sub>)<sub>2</sub>] that, upon

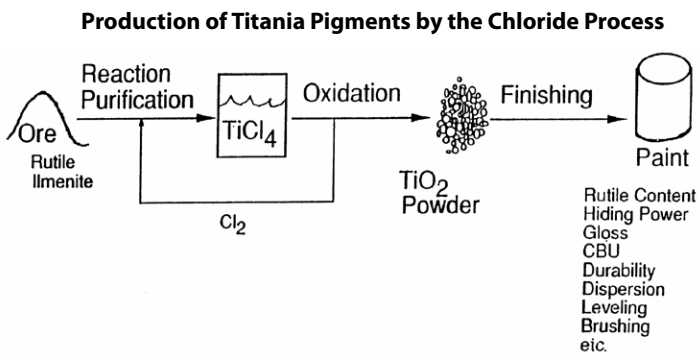


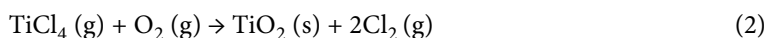
Figure 1. Schematic of the chloride process: Pure TiCl<sub>4</sub> made by chlorination of rutile or ilmenite ores is purified by distillation and fed to the flame reactor (oxidizer). There, mostly TiO<sub>2</sub> (about 200 nm) in primary particles is produced and led to a series of wet processes (finishing) to be suspended in paints while by-product Cl<sub>2</sub> is recycled for ore chlorination.

heating, decomposes and precipitates out  $\text{TiO}_2$ . The chloride process was developed first by DuPont, currently the largest producer of  $\text{TiO}_2$ , with 25% of worldwide production, followed by Cristal (formerly Millennium and SCM Co.) with about 20%, and Tronox (formerly Kerr-McGee) with 13% (Bohnet, 2003).

The use of  $\text{TiO}_2$  as a superior white pigment has been known since 1916, but initially the high manufacturing cost of the wet sulfate process prohibited its widespread use. By 1930, DuPont was the largest US producer of lithopone ( $\text{ZnS}/\text{BaSO}_4$ ), the white pigment of choice at that time. However, as  $\text{TiO}_2$  quality and price became competitive with lithopone's, DuPont realized that, within a few years, its leadership in this market would be undercut. DuPont then evaluated the patent landscape for manufacturing of  $\text{TiO}_2$  by the sulfate process, carried out its own research, and bought a sulfate  $\text{TiO}_2$  patent-holding company. By 1934, DuPont had decided to make its own sulfate plant for  $\text{TiO}_2$  manufacture.

DuPont's early success in the  $\text{TiO}_2$  business was its marketing, as early as 1941, of sulfate-made rutile  $\text{TiO}_2$  that had 20% higher hiding power than anatase, because of a higher refractive index of rutile, 2.72, than that of anatase, 2.55 (Hounshell & Smith, 1988). Manufacture of  $\text{TiO}_2$  by present-day methods produces pigments with a closely controlled size distribution and average particle size, and this probably explains its success over other white pigments (Hounshell & Smith, 1988). The opacity of  $\text{TiO}_2$  is an exceptionally strong function of particle size (Kingery et al., 1976). In fact, there is little tolerance in particle size variation (about 10%) by pigment manufacturers. When, in the late 1980s, I had remarked that this could not be detected reliably by then-current aerosol instruments, one DuPont engineer replied that their accountants would detect such a difference, given DuPont's production volume!

DuPont's dominance in  $\text{TiO}_2$  markets relies on its industrial development of the chloride process:



Although the process was discovered as early as 1928, a series of DuPont patents starting in 1949 covered a number of process aspects and details, including the use of additives such as  $\text{AlCl}_3$  to promote rutile formation and many ways to prevent deposits on the  $\text{TiCl}_4$  injection orifice and reactor

walls (Mezey, 1966). The scale-up of the chloride process was direct from bench to commercial scale, without having the benefit of a pilot plant. The process was effectively piloted at full scale until a really workable process emerged (Hounshell & Smith, 1988). The success of DuPont's research and development effort is probably best illustrated by the fact that although the company started chloride-process  $\text{TiO}_2$  production in 1951, it was 12 more years before any corporate competitors were able to build chloride-like plants for  $\text{TiO}_2$  production. In fact, DuPont's chloride process is one of the best-kept secrets in the business (Mezey, 1966). Rumor has it that other DuPont plants bought proprietary additives for the chloride process and delivered them internally to the chloride sites. In the mid-1960s, chloride-like plants were built by Tioxide in the United Kingdom, followed by Kronos in Germany and Kerr-McGee in the Netherlands (which now operates under the name "Tronox") and in Saudi Arabia (which now operates under the name "Cristal"). A chloride-like process was introduced in Japan in 1974 by Sangyo Ishihara, although related patents had been awarded in Japan since 1958. In Asia, the first DuPont chloride plant was built in Taiwan in 1994, and the biggest one is planned for Dongying, China, about 500 km south of Beijing on the Pacific coast.

Nevertheless, other manufacturers (e.g., Tioxide, Cristal, and Kronos, to list a few) have developed similar but legally unique processes. In these processes, the precursor,  $\text{TiCl}_4$ , is typically obtained from chlorination of rutile or ilmenite ores containing either 95% or 50%, respectively, titanium, as well as iron, vanadium, and other metal oxides (Figure 1). High-purity  $\text{TiCl}_4$  is obtained by distillation and is fed as vapor to the aerosol reactor (oxidizer) unit, where it is oxidized or burned at  $1,000^\circ\text{C}$ – $1,500^\circ\text{C}$  with an  $\text{O}_2$ –CO flame, air, external heating, or preheating  $\text{TiCl}_4$  with  $\text{O}_2$  at intermediate temperatures (Clark, 1975; Wiseman, 1976). Typically the exothermic  $\text{TiCl}_4$  oxidation reaction sustains the process and facilitates particle growth to the optimal crystallite size of about 200 nm (Mezey, 1966). To assure synthesis of rutile or anatase crystallites, 0.5%–2%, respectively, of aluminum- or silicon-based promoters or catalysts are co-oxidized with  $\text{TiCl}_4$  (Mezey, 1966; Wiseman, 1976).

Titania particles for pigments are made at high concentrations by  $\text{TiCl}_4$  oxidation at nearly stoichiometric conditions and grow by coagulation, surface growth (Spicer et al., 2002), and sintering (Kobata et al., 1991) in

turbulent flows ( $Re = 10^5 - 10^6$ ) at or near atmospheric pressures (1–4 bars) (Xiong & Pratsinis, 1991), forming agglomerates and aggregates (Figure 2) of primary particles (Grass et al., 2006). By-product chlorine gas is recycled for ore chlorination. To minimize fusion or necking of the  $TiO_2$  particles and formation of large hard agglomerates (or aggregates), their temperature has to be reduced to less than  $600^\circ C$  (Mezey, 1966). Titania particles leaving the oxidizer (flame aerosol reactor) are typically soft agglomerates, several micrometers in diameter, consisting of smaller (about 500 nm) hard agglomerates (aggregates) that contain even smaller (about 200 nm) primary particles (Heine & Pratsinis, 2007). As a result, special milling (grinding) is used to break up the soft agglomerates before feeding them to the finishing plant where their surfaces are coated and conditioned for suspension in paints or compounding in polymer or paper matrixes. Aggregate formation can be controlled by adding alkali metal halides (e.g., potassium chloride [KCl] as in soot formation) in the presence of  $AlCl_3$  or  $SiCl_4$  (Xiong et al., 1992a; Akhtar et al., 1994).

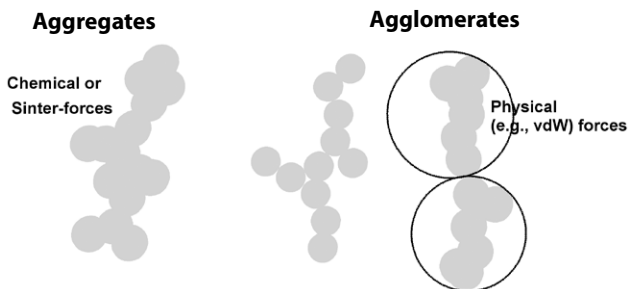


Figure 2. Structure of flame-made particles: Aggregates of primary nanoparticles (or hard-agglomerates) are held together by chemical (e.g., sinter) forces while agglomerates (or soft-agglomerates) of primary particles and/or aggregates are held together by physical forces.

Source: Derived from Tsantilis and Pratsinis (2004).

In contrast with the carbon black process, the ensuing global (Pratsinis et al., 1990) and detailed (West et al., 2009) kinetics of  $TiCl_4$  oxidation in the gas phase and on the surface of freshly formed  $TiO_2$  particles (Ghoshtagore, 1970) are known. Today, the role of process parameters on  $TiO_2$  size, morphology, and crystallinity is well understood. The essential concept is the *particle residence time at high temperature*. In premixed flame reactors, perfectly spherical titania particles of increasing diameter are formed at increasing distances (or residence times) away from the burner (Arabi-Katbi et al., 2001) in both upward and downward flame configurations (Arabi-Katbi

et al., 2002). These particles attain the self-preserving number size distribution (George et al., 1973) having a geometric standard deviation,  $\sigma_g$ , of 1.45 in excellent agreement with theory (Tsantilis et al., 2002). Increasing precursor concentration increases enthalpy and  $\text{TiO}_2$  concentration, which results in producing larger particles by coagulation and sintering without altering their polydispersity (Arabi-Katbi et al., 2001).

Compared with premixed flames, diffusion flames allow for more parameters to control a broader range of characteristics of the produced titania and other oxides. In a classic diffusion flame, the fuel (any hydrocarbon or hydrogen) and  $\text{TiCl}_4$  or other precursor are in the center stream, surrounded by the oxidant (air or oxygen) in the outer stream. The product particle size and rutile fraction decrease with increasing oxidant flow rate as particle concentration, visible flame height, and particle residence time at high temperature are reduced for constant flow rate of precursor  $\text{TiCl}_4$  (Zhu & Pratsinis, 1996) or titanium isopropoxide (TTIP) (Stark et al., 2001). This decrease in size comes from reducing the coagulation rate by dilution with the added oxidant gas and reducing the sintering rate by cooling from the additional, effectively inert, oxidant gas stream. The rutile fraction decreases by increased oxidant flow rate, reduced high temperature particle residence time, and higher oxygen concentration.

The particle morphology is affected drastically by the oxidant flow rate in diffusion flames. At low oxidant flow rates, long laminar diffusion flames result in spherical nonagglomerated particles, whereas at high flow rates, agglomerates of much finer particles are made (Wegner & Pratsinis, 2003b). The increased oxidant flow rates gradually transform a laminar diffusion flame to a turbulent, effectively premixed flame in which the rapid gas cooling prevents the coalescence of colliding titania clusters, resulting in the collected agglomerates.

Replacing oxygen with air in diffusion flames reduces particle size and rutile fraction, although the visible flame height is increased. Clearly, air flames have longer residence times, but at lower temperatures than oxygen flames (Zhu & Pratsinis, 1996). For constant oxidant flow rate, increasing Ti-precursor flow results in larger primary particles regardless of whether  $\text{TiCl}_4$  (Pratsinis et al., 1996) or TTIP (Stark et al., 2002) is used as the precursor. The rutile fraction increases with TTIP concentration but not with  $\text{TiCl}_4$  at constant fuel ( $\text{CH}_4$  or  $\text{H}_2$ ) concentration. When the latter is increased (Pratsinis et al., 1996), the rutile fraction increases as particles experience higher temperature residence times in agreement with the thermodynamics

of anatase-to-rutile transformation. Interestingly enough, this trend has a limit, because further increasing the fuel flow rate reduces the rutile fraction although the primary particle size increases, indicating that the high-temperature particle residence time is sufficient for grain growth but not for the anatase-to-rutile transformation (Stark et al., 2002).

The most fascinating effect of oxidant composition, however, is on particle morphology. By gradually changing the oxygen content of the oxidant stream, product particles transform from necked aggregates or hard agglomerates (pure air) to perfect colloidal-like spheres (pure O<sub>2</sub>). Pure O<sub>2</sub> accelerates fuel consumption so that particles experience a higher maximum temperature than when oxidized with air, and because the fuel is consumed faster than with air, they experience a steeper cooling with O<sub>2</sub> (Zhu & Pratsinis, 1996). Using O<sub>2</sub> as an oxidant, particles can grow more before the end of coalescence. When full coalescence ends, it does so abruptly, preventing neck formation between colliding particles by their omnipresent Brownian motion, which can only lead to soft agglomerates (Grass et al., 2006).

A major challenge in the development of chloride aerosol reactors has been identifying materials of construction that will hold up to high temperatures and corrosive atmospheres. Early development was conducted on quartz reactors, and plants had several glass blowers skilled at repairing damage to quartz reactors. That skill has disappeared from chloride plants. As materials development in the area of high-temperature alloys has progressed, precious metal use in the process has decreased. The heaters for vaporization of AlCl<sub>3</sub>/TiCl<sub>4</sub> used to be made out of platinum, and some chloride plants had the world's largest inventories of platinum. This is no longer the case because the heaters are now made of high-quality metal alloys. Quartz did have its advantages. The early developers were strong adherents of the adage "seeing is believing"; the quartz allowed the flow patterns in the burner and reactor to be visually observed, and this helped to refine aerosol reactor design before the days of computational fluid dynamics. Developments to reduce thermophoretic deposition attracted a lot of attention: the method of choice was knocking the pipe walls, either manually or with vibrators. A common practice for preventing wall deposit was to judiciously inject large particles to "scrape" such deposits from reactor walls. Process efficiency drove the search for particles that were easier to use, and the industry settled on sand and salt—one insoluble in water and the other soluble.

Currently, the TiO<sub>2</sub> pigment industry grows at about 3% annually, especially as new markets are evolving in India and China, making



new investments attractive. Furthermore, there is growing interest in manufacturing finer  $\text{TiO}_2$  (less than 50 nm in diameter) for photocatalytic, cosmetic, ultraviolet (UV) protection, and other applications. Wet-made  $\text{TiO}_2$  (e.g., by Sachtleben Chemie) and Evonik's flame-made P25  $\text{TiO}_2$  cater to these markets. The latter is mostly (70%) anatase and is approximately 50 nm in primary particle diameter with a ramified morphology that is made by the oxychloride flame aerosol process employed widely for fumed silica manufacture (as discussed in the subsequent section). Most of today's research on aerosol-made  $\text{TiO}_2$  focuses on nanoparticles for catalysts, sensors, films by laser flame synthesis by the NanoGram Corporation, low pressure flames (Lindackers et al., 1994), and flame spray pyrolysis (Teoh et al., 2007), to name a few.

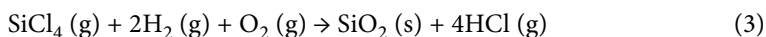
## Silica, $\text{SiO}_2$

Fumed silica is the third largest industrial aerosol commodity by value and the fourth largest by volume. As with carbon black, it is made solely by aerosol technology. Most of it is used as a flowing aid in a wide spectrum of applications including paints, microelectronics, pharmaceuticals, and cosmetics. Synthesis of fumed silica by combustion of  $\text{SiCl}_4$  in an oxy-hydrogen flame was discovered in the late 1930s by scientists at Degussa (now part of Evonik) who were looking for a replacement for carbon black as a reinforcing agent for rubber. However, it was never used as such because fumed silica quickly captured other more profitable markets as a flowing aid. Right after World War II, Cabot sold it in the United States. When the US market grew large enough, Cabot cross-licensed Degussa's process and built a plant producing about 1,500 tons of fumed silica in the United States in 1958 (White & Duffy, 1959). Today Evonik, Wacker, and Cabot dominate the worldwide market in fumed silica.

Manufacturing of fumed silica is somewhat similar to the chloride process for manufacturing  $\text{TiO}_2$ . In fact, manufacture of optical fiber preforms by the modified chemical vapor deposition process involving  $\text{SiCl}_4$  oxidation in pipe flow resembles the chloride process for  $\text{TiO}_2$ , although the product is deposited on the pipe walls instead of being collected (Rowell, 1986). A major difference between these two flame-made oxides lies in their sintering characteristics. The fumed silica has a primary particle diameter of 7–60 nm, whereas that of  $\text{TiO}_2$  made at identical conditions is almost an order of magnitude larger (Xiong et al., 1993). Fumed silica aggregates (hard agglomerates) are typically about 200–300 nm in diameter, consisting of

several primary particles. As a result, fumed silica possesses very high surface area, necessitating special care in its handling (e.g., removal of adsorbed chlorine), because impurities are picked up easily. In fact, the preservation of the “fluffiness” of fumed silica imposed by its highly ramified structure is essential for many of its applications.

Today, the dominant route for synthesis of fumed SiO<sub>2</sub> relies on the oxychloride process for oxidizing various silica precursors, especially SiCl<sub>4</sub>:



In particular, the capacity and flexibility of a given plant to employ alternative chlorosilane precursors (e.g., by-products of microelectronics processing) and cheap H<sub>2</sub> along with the ability to sell hydrochloric acid (HCl) is essential for the success of an industrial fumed silica synthesis unit. In fact, the location of any new plant is largely decided on these factors, as the history of existing units amply tells. For example, the decision to build Cabot's first unit in Tuscola, Illinois, was influenced by the existence of a nearby plant that could supply it with H<sub>2</sub> and buy its by-product HCl (White & Duffy, 1959). This continues today, as with Cabot's plant in Rheinfelden, Germany, where chemicals are shared with Evonik's fumed silica plant.

As with TiO<sub>2</sub>, a number of patents cover various process aspects for fumed silica manufacture (Mezey, 1966). In the current oxychloride process, high-purity tetrachlorosilane (SiCl<sub>4</sub>) or other chlorosilanes are obtained and fed as vapor to the aerosol reactor (oxidizer) unit where they are burned at 1,000°C–1,500°C with an H<sub>2</sub>–O<sub>2</sub> flame (Bohnet, 2003). Again, the heat of that flame and the exothermic chlorosilane oxidation reaction sustain the process, facilitating particle growth by coagulation and sintering that result in the desired product. Excess heat is converted to electric energy and supplied to the local electric network.

Ulrich (1971) presented the first systematic investigation of a flame-made material, fumed silica, in premixed laminar and turbulent jet flames. He showed that aerosol coagulation by Brownian motion, rather than by turbulence, is the dominant particle formation mechanism in these reactors. He quantitatively explained particle growth with increased residence time by Brownian coagulation and predicted that these particles reach a self-preserving size distribution in the free-molecular regime. In fact, he published this distribution a year ahead of Lai and colleagues (1972), who have been

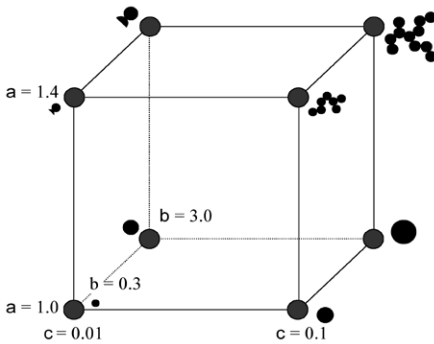
largely credited for it. This was proven experimentally by measuring the sizes of flame-made titania from micrographs at Tioxide, United Kingdom (George et al., 1973). Thermophoretic sampling was used for particle collection to infer the significance of surface growth of flame-made  $\text{TiO}_2$ . This sampling technique was systematically introduced by Dobbins and Megaridis (1987) and effectively opened up the “black box” of combustion synthesis of materials.

Product  $\text{SiO}_2$  particles grow by coagulation and sintering in turbulent flows at or slightly below atmospheric pressure, forming aggregates (hard agglomerates) and soft agglomerates of primary particles (see Figure 2 in this chapter, which is derived from Tsantilis & Pratsinis, 2004). The existence of such aggregates is established by small-angle X-ray or neutron scattering, because aggregates exhibit two distinct slopes of intensity versus frequency (inverse particle size), whereas nonaggregates exhibit only one slope (Kammler et al., 2004). Fumed  $\text{SiO}_2$  particles are collected mostly by baghouse filters, preceded by cyclones (Mezey, 1966) for all but high-purity silica products. As pointed out above, emphasis is put on  $\text{SiO}_2$  surface treatment by removing attached HCl from its surface (de-acidification), typically in fluidized beds with or without chemical reaction (Flesch et al., 2008). In addition, the hydrophilic surface of fumed silica can be treated with organic functional groups to become hydrophobic for selected applications.

The detailed chemical kinetics of  $\text{SiCl}_4$  oxidation in  $\text{O}_2$ - $\text{H}_2$  flames have been presented by Hannebauer and Menzel (2003). The effect of flame parameters on silica characteristics is also reasonably well understood. For example, as with  $\text{TiO}_2$ , increasing the oxidant flow rate in a diffusion flame dilutes the aerosol and reduces its high-temperature residence time, reducing flame height and primary particle size and increasing the extent of aggregation (Mueller et al., 2004). Similarly, nonaggregated, perfectly spherical fumed silica can be made by replacing oxidant air with  $\text{O}_2$  in diffusion flames (Zhu & Pratsinis, 1997). Recently, it has been shown that coagulation and growth of agglomerated fumed silica (e.g., Aerosil or Cab-O-Sil 380, HDK 440) at industrial manufacturing conditions may not follow classic coagulation theory. At high concentrations, these fractal-like particles quickly grow and occupy far more space than dictated by their solid volume fraction, causing their effective volume fraction to increase rapidly and more quickly reach gelation conditions that may force restructuring and fragmentation in industrial aerosol flow reactors (Heine & Pratsinis, 2006). It

should be noted, however, that there is uncertainty about the sintering rate of silica even though expressions have been proposed in the literature (Tsantilis et al., 2001), which is important because detailed aerosol reactor models are developed by combining aerosol and fluid dynamics (Johanessen et al., 2000).

Today, fumed silica consumption is growing at a rate of 4% annually, which is faster than the consumption of any other aerosol-made commodity. Some of the leading manufacturers of fumed silica have established a quantitative understanding of the oxychloride process by interfacing particle dynamics with computational fluid dynamics. That way, the effect of process variables on some fumed silica features can be described in considerable detail (Mühlenweg et al., 2001). Figure 3 pictorially summarizes this understanding, showing how the morphology and primary particle size can be determined by a “cube” of temperature, precursor concentration, and cooling rate. Such diagrams greatly facilitate the design and operation of industrial aerosol reactors, as well as training of personnel, process maintenance, and new product development.



*Figure 3. Summary of coupled particle dynamics and fluid mechanic simulations showing qualitatively the conditions for synthesis of particles with selected size and morphology as a function of (a) temperature, (b) cooling rate, and (c) concentration.*

Source: Adapted from Mühlenweg et al., 2001.

## ZnO, Ni, WC, and Other Materials

ZnO is the fourth largest aerosol-made product by value and the third largest by production volume, with a worldwide annual consumption of about 600,000 tons. Almost all ZnO is made by aerosol processes—the so-called “French” and “American” processes that produce 85% and 14%, respectively, of commercially manufactured ZnO (Bohnet, 2003). The French process was put into industrial practice in 1840, making it the second industrial aerosol material manufacturing process after the lampblack process for carbon black. The difference between the French and American processes lies in how Zn

vapor is generated: by boiling Zn metal (in the French process) or by reducing Zn minerals with coke (in the American process) (Bohnet, 2003). In these processes, Zn vapor is oxidized with air, resulting in micron-sized ZnO particles that are used mostly as accelerators for curing or vulcanizing natural or synthetic rubber.

Despite ZnO's long history of aerosol manufacture, its formation fundamentals have been studied the least (Tani et al., 2002). There is no straightforward way to use the French and American processes to synthesize nanosized ZnO, which has a number of promising applications in microelectronics, quantum dots, UV filters, and other uses. For these applications, ZnO is typically made by wet chemistry (e.g., Meulenkamp, 1998). However, flame technology is capable of making filamentary ZnO (Jensen et al., 2000) with closely controlled crystallite size by SiO<sub>2</sub> doping, exhibiting even quantum dot behavior (Mädler et al., 2002b).

Many sizes and morphologies of Ni powder are made in industrial hot-wall aerosol reactors. Typically, the metal is reacted with CO, forming nickel tetracarbonyl [Ni(CO)<sub>4</sub>] that is thermally decomposed in these reactors, resulting in micron and submicron metal particles by nucleation, surface growth, and coagulation (Wasmund & Coley, 2009). This process was developed and patented in Germany in the mid-1920s by A. Mittasch at I. G. Farbenindustrie for producing Fe and Ni equiaxed multi-micron-sized single particles (Trout, 1938). It was later adapted for use at Inco's nickel refinery in the United Kingdom for making products such as Type 255, a filamentary Ni powder that is used to make porous metal electrodes, coatings, and catalysts. Today more than 20,000 tons per year of Ni powder are made by this process, and recent basic understanding of its fundamentals led to synthesis of Ni nanopowders (Wasmund & Coley, 2006). Recent studies in microwave reactors have elucidated the gas-phase synthesis of filamentary Fe nanoparticles from iron pentacarbonyl [Fe(CO)<sub>5</sub>] decomposition (Giesen et al., 2004).

Probably the latest success story of aerosol-made materials is the manufacture of ultrafine WC for cutting tools by rapid carbothermal reduction, a process that was originally developed by Dow Chemicals for the manufacture of borides, nitrides, and carbides by pyrolysis of powder mixtures of metal salts and starch flowing down graphite tube reactors heated above 2,000°C and followed by rapid cooling (Weimer et al., 1991; Weimer et al., 1994). Despite the solid precursors employed by this process, the fine structure characteristics of the product powder are determined by coagulation

and sintering, because they can be inferred by the aerosol dynamics of similar carbides such as boron carbide ( $B_4C$ ) (Xiong et al., 1992b). Likewise, silicon carbide (SiC) grains grow by sintering on the surface of carbon primary particles resulting in SiC that is quite fluffy (Johnson et al., 2002). Today, about 500 tons/year of the world's finest WC are made by rapid carbothermal reduction.

Hot-wall reactors—which use “spray roasting,” “pyrolysis,” or “decomposition” processes—are used to manufacture a spectrum of materials (e.g., ferrites; Li et al., 1993), typically mixed oxides or metal/ceramics. Hot-wall reactors are known for their excellent control of temperature and, as a result, phase composition of the product. For example, Alam and Flagan (1986) first used such reactors for the aerosol synthesis of silicon for semiconductors. Silicon synthesis in such reactors has been scaled up, resulting in aggregated nanoparticles (Knipping et al., 2004), whereas plasma reactors have been used to manufacture nonaggregated luminescent silicon nanoparticles (Mangolini et al., 2005; Gupta et al., 2009), which are being explored by start-ups. Such processes have attracted renewed interest in photovoltaic applications of silicon, and the academic community has studied hot-wall reactors more than any other aerosol reactor because a number of fundamental processes such as nucleation, condensation, evaporation, sintering, and coagulation can be isolated and studied with close control of temperature and residence time for materials synthesis by spray pyrolysis (Kodas & Hampden-Smith, 1999).

Recently, both Cabot and Evonik have begun marketing fumed alumina made by the oxychloride process, similar to  $SiO_2$  and P25  $TiO_2$ , mostly for chemical-mechanical polishing in microelectronics. A special consideration is that aluminum chloride ( $AlCl_3$ ) vapor is supplied to the process by sublimation. A number of other oxides are possible by this technology, as Kreichbaum and Kleinschmidt (1989) have shown.

Mixed oxides can have some unique properties, such as iron oxide ( $Fe_2O_3$ )/ $SiO_2$  made in a premixed methane ( $CH_4$ )- $O_2$  flame or a  $H_2$ - $O_2$ -argon (Ar) premixed low-pressure flame. The thermal decomposition of the iron precursor  $Fe(CO)_5$  is much faster than the thermal decomposition of the Si-precursor (hexamethyl di-silane [ $Si_2(CH_3)_6$ ] or silane [ $SiH_4$ ]). Consequently, the iron oxide particles are formed first in the flame and are later encapsulated by  $SiO_2$ . Such powders exhibit superparamagnetic properties and are commercially available (Roth, 2007).

A number of new small start-up companies make fine particles by aerosol technology using flames, plasmas, lasers, and other high-energy sources for specialized applications such as microelectronics, photonics, and nanocomposites. It is worth mentioning Admafine, a joint venture between Toyota and Shin-Etsu, which makes perfectly spherical alumina or silica particles that are 100–500 nm in diameter and are either pure or contain zirconia or titania from combustion and oxidation of metal vapors at very high temperatures. As business interests focus on high-value products, small companies such as Nanogram in Milpitas, California; nGimat in Atlanta, Georgia; Tal in Michigan; and Turbobeads, HeiQ, and Nanograde in Zurich, Switzerland, to name only a few, use flame aerosol technology to make such products. To that effect, combustion of sprays of organic solutions similar to the furnace process for carbon black (Kühner & Voll, 1993) but for ceramics (Sokolowski et al., 1977; Lewis, 1991; Bickmore et al., 1996; Mädler et al., 2002a) and flame pyrolysis of sprays of aqueous solutions of inorganic precursors (Marshall et al., 1971; Purwanto et al., 2008) relieve the constraint of using vaporizable precursors and create unprecedented opportunities for synthesizing sophisticated materials beyond the simple oxides of the recent past (Strobel & Pratsinis, 2007). Most notably, Johnson Matthey, a leading manufacturer of heterogeneous catalysts, actively explores such aerosol technology for synthesizing a wide spectrum of nanomaterials (Figure 4).



*Figure 4. A flame aerosol reactor pilot plant at the Johnson Matthey Research Center, UK. This plant offers synthesis of various nanoparticle compositions by flame spray pyrolysis within the NanoCentral alliance ([www.nanocentral.eu](http://www.nanocentral.eu)).*

Photo: Courtesy of Dr. Peter Bishop, Johnson-Matthey Co.

## Conclusions

Aerosol reactors are used today to manufacture commodities such as carbon blacks, fumed silica, pigmentary titania, ZnO, and filamentary nickel. More than 90% of these products, by both volume and value, are made in flame aerosol reactors that were built initially by persistent engineering with little formal input from aerosol science. Nevertheless, in the last 20 years, significant developments in aerosol and combustion science and engineering have given the design and operation of such reactors a firm scientific basis.

Aerosol science is now challenged to describe the dynamics of ramified or fractal-like aerosol particles from low to high concentrations, as dictated by the economic manufacture of aerosol-made materials. Coagulation and surface growth rates of such particles still need to be better understood, because they determine all particle sizes, especially those of agglomerates. Sintering or coalescence rates also need to be better understood (especially when additives or impurities are present on the particle surface) because they determine primary particle and aggregate diameters that are critical to all applications. Nucleation rates of such materials are also unknown and can be quite important when producing nanoparticles with a diameter of only a few nanometers. For most of these materials made at high production rates, coagulation washes out (so to speak) the effect of nucleation because precursors are rapidly consumed and product particles attain self-preserving distribution by coagulation. Developing aerosol processes and scaling them up would greatly facilitate their adoption for the manufacture of new materials and the devices that contain them.

There is currently a strong interest in aerosol reactors for manufacturing materials and devices, but there has already been a sizeable investment in materials made by conventional (e.g., wet chemistry) routes, so aerosol reactors will not replace these materials overnight. Nevertheless, the capacity of flame spray aerosol reactors (Figure 5), in particular, to form new materials, nanothin hermetically layered particles (Teleki et al., 2008; Phillips et al., 2009; Guo et al., 2010), and even highly porous (98%) nanostructured semiconducting micropatterns on electronic circuitry (Tricoli et al., 2008) creates the opportunity to make products with new properties and functionalities. These products include catalysts (Strobel et al., 2006b), sensors (Tricoli et al., 2010), transparent but radiopaque dental prosthetics (Schulz et al., 2005), phosphor particles (Camenzind et al., 2005; Purwanto et al., 2008) and films (Kubrin et al., 2010), lithium-ion battery materials





*Figure 5. A flame spray pyrolysis aerosol reactor at the Swiss Federal Institute of Technology (ETH Zurich) for continuous synthesis of mixed noble metal and ceramic nanopowders up to 1 kg/h.*

Photo: Courtesy of the author.

(Ernst et al., 2007), nutritional supplements (Rohner et al., 2007) with rigorous physiological evaluation (Hilty et al., 2010), anti-fogging films made by in situ grown silica nanowires (Tricoli et al., 2009), and even highly durable sorbents for CO<sub>2</sub> sequestration (Lu et al., 2009). Thus, some of these products may soon appear on the market. Furthermore, synthesis of metal and metal alloys, as well as nonoxide ceramics, can be carried out in scalable flame (Athanassiou et al., 2010) and plasma reactors (Phillips et al., 2009) at respectable production rates (Ryu et al., 2010), even in a laboratory-scale (0.5–2 g/min) plasma reactor, promising many opportunities for aerosol technology to contribute to the rapidly evolving field of nanomaterials and its breadth of applications.

## **Acknowledgments**

I acknowledge financial support from the European Research Council, the Swiss National Science Foundation, and the Commission for Technology and Innovation. I also greatly appreciate comments by G. Skillas (Degussa AG), R. Strobel and M. Eggersdorfer (ETH Zurich), G. D. Ulrich (University of New Hampshire), K. Okuyama (University of Hiroshima, Japan), A. Weimer (University of Colorado), E. Wasmund (INCO) and literature suggestions by B. Diemer (DuPont).

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