

## COATING PROCESSES, POWDER

### 1. Introduction

Powder coating is a process for applying coatings on a substrate using heat fusible powders. Materials used in the process are referred to as coating powders, finely divided particles of organic polymer, either thermoplastic or thermosetting, which usually contain pigments, fillers, and other additives. After application to the substrate, the individual powder particles are melted in an oven and coalesce to form a continuous film having decorative and protective properties associated with conventional organic coatings.

The origin of powder coating technology dates back to the late 1940s when powdered thermoplastic resins were applied as coatings to metal and other substrates by flame spraying. In this process, a powdered plastic was fed through a flame spraying apparatus where the plastic particles are melted and propelled by the hot gases to the substrate. A patent issued in Great Britain to Schori Metalising Process, Ltd. in 1950 described a process for forming a coating in which powdered thermoplastics were applied to a heated substrate by dipping or rolling the heated article in the plastic powder (1). This process was difficult to practice, however, and never achieved commercial success.

A major breakthrough in powder coating occurred in the mid-1950s, when Erwin Gemmer conceived the fluidized-bed coating process, in which a heated object is dipped into a fluidizing bed of powder. Gemmer was involved in developing flame spraying processes and materials in the laboratories of Knapsack-Griesheim (Hoechst) a manufacturer of specialty gases and was searching for a more efficient method than flame spraying for coating objects with powder. The first patent applications were filed in Germany in May 1953, and the basic patent was issued in September 1955 (2). The first U.S. patent was issued in 1958 (3), and the Polymer Corporation, Reading, Pa., acquired rights to the Knapsack-Griesheim patents. The Polymer Corporation mounted an aggressive effort to develop, license, and sell fluidized-bed coating technology in North America. However, acceptance of this coating process was rather slow. In 1960, the annual sales of coating powders in the United States were below 450 metric tons (mt) in part because of a lack of expertise in the methodology. In addition, the available

powder coating materials were expensive, efficient production techniques had not been worked out, and volume of production was low.

Today, powder coating is widely accepted, with thousands of installations in the factories of original equipment manufacturers (OEMS) and custom coating job shops. It is the preferred method for coating many familiar items such as lawn and garden equipment, patio and other metal furniture, electrical cabinets, lighting, shelving and store fixtures, and many automotive components.

In the fluidized-bed coating process, the coating powder is placed in a container having a porous plate as its base. Air is passed through the plate causing the powder to expand in volume and fluidize. In this state, the powder possesses some of the characteristics of a fluid. The part to be coated, which is usually metallic, is heated in an oven to a temperature above the melting point of the powder and dipped into the fluidized bed where the particles melt on the surface of the hot metal to form a continuous film or coating. By using this process, it is possible to apply coatings ranging in thickness from  $\sim 250$ – $2500\text{ }\mu\text{m}$  (10–100 mils). It is difficult to obtain coatings thinner than  $\sim 250\text{ }\mu\text{m}$  and, therefore, fluidized-bed applied coatings are generally referred to as thick-film coatings, differentiating them from most conventional paint-like thin-film coatings applied from solution or as a powder at thicknesses of  $20$ – $100\text{ }\mu\text{m}$  (0.8–4 mils) (see THIN FILMS, FILM FORMATION TECHNIQUES).

In the electrostatic spray process, the coating powder is dispersed in an air stream and passed through a corona discharge field where the particles acquire an electrostatic charge. The charged particles are attracted to and deposited on the grounded object to be coated. The object, usually metallic and at room temperature, is then placed in an oven where the powder melts and forms a coating. By using this process, it is possible to apply thin-film coatings comparable in thickness to conventional paint coatings, ie,  $20$ – $75\text{ }\mu\text{m}$ . A hybrid process based on a combination of high voltage electrostatic charging and fluidized-bed application techniques (electrostatic fluidized bed) has evolved as well as triboelectric spray application methods (see COATING PROCESSES, SPRAY COATINGS). Powder coating methods are considered to be fusion-coating processes; ie, at some time in the coating process the powder particles must be fused or melted. Although this is usually carried out in a convection oven, infrared (ir), resistance, and induction heating methods also have been used. Therefore, with minor exceptions, powder coatings are factory applied in fixed installations, essentially excluding their use in maintenance applications. Additionally, the substrate must be able to withstand the temperatures required for melting and curing the polymeric powder, limiting powder coating methods to metal, ceramic, and glass (qv) substrates for the most part, although recently some plastics and wood products have been powder coated successfully.

Compared to other coating methods, powder technology offers a number of significant advantages. These coatings are essentially 100% nonvolatile, ie, no solvents or other pollutants are given off during application or curing. They are ready to use, ie, no thinning or dilution is required. Additionally, they are easily applied by unskilled operators and automatic systems because they do not run, drip, or sag, as do liquid (paint) coatings. The reject rate is low, the finish is tougher and more abrasion resistant than that of most conventional paints (see PAINT). Thicker films provide electrical insulation, corrosion protection,

and other functional properties. Powder coatings cover sharp edges for better corrosion protection. The coating material is well utilized: overspray can be collected and reapplied. No solvent storage, solvents dry off oven, or a mixing room are required. Air from spray booths is filtered and returned to the room rather than exhausted to the outside. Moreover, less air from the baking oven is exhausted to the outside, thus saving energy. Finally, there is no significant disposal problem because there is no sludge from the spray booth wash system. Any powder that cannot be reclaimed and must be discarded is not considered a hazardous waste under most environmental regulations. Whereas the terms coating powder and powder coating are sometimes used interchangeably, herein the term coating powder refers to the coating composition and powder coating to the process and the applied film.

Coating powders are frequently separated into decorative and functional grades. Decorative grades are generally finer in particle size and color and appearance are important. They are applied to a cold substrate using electrostatic techniques at a relatively low film thickness, eg, 20–75  $\mu\text{m}$ . Functional grades are usually applied in heavier films, eg, 250–2500  $\mu\text{m}$  using fluidized-bed, flocking, or electrostatic spray coating techniques to preheated parts. Corrosion resistance and electrical, mechanical, and other functional properties are more important in functional coatings (see CORROSION AND CORROSION CONTROL).

Coating powders are based on both thermoplastic and thermosetting resins. For use as a powder coating, a resin should possess: low melt viscosity, which affords a smooth continuous film; good adhesion to the substrate; good physical properties when properly cured, eg, high toughness and impact resistance; light color, which permits pigmentation in white and pastel shades; good heat and chemical resistance; and good weathering characteristics, ie, resistance to degradation by ultraviolet (uv) light, hydrolysis, and environmental pollutants. The coating powder should remain stable on storage at 25°C for at least six months and should possess a sufficiently high glass-transition temperature,  $T_g$ , so as to resist sintering on storage.

The volume of thermosetting powders sold exceeds that of thermoplastics by a wide margin. Thermoplastic resins are almost synonymous with fluidized-bed applied thick-film functional coatings and find use in coating wire, fencing, and corrosion resistant applications, whereas thermosetting powders are used almost exclusively in electrostatic spray processes and applied as thin-film decorative and corrosion resistant coatings.

Thermoplastic resins have a melt viscosity range that is several orders of magnitude higher than thermosetting resins at normal baking temperatures. (See Table 1). It is, therefore, difficult to pigment thermoplastic resins sufficiently to obtain complete hiding in thin films, yet have sufficient flow to give a smooth coating since incorporation of pigments reduces melt flow even further. In addition, thermoplastic resins are much more difficult to grind to a fine particle size than thermosetting resins, so grinding must usually be carried out under cryogenic conditions. Because powders designed for electrostatic spraying generally have a maximum particle size of  $\sim 75 \mu\text{m}$  (200 mesh), the thermoplastic powders are predominant in the fluidized-bed coating process where heavier coatings are applied and a larger particle size can be tolerated. Fluidized-bed powders typically contain only  $\sim 10$ – $15\%$  of particles  $< 44 \mu\text{m}$  (325 mesh),

Table 1. Physical and Coating Properties of Thermoplastic Powders<sup>a</sup>

Property	Vinyls	Polyamides	Polyethylene	Polypropylene	PVDF <sup>b</sup>
melting point, °C	130–150	186	120–130	165–170	170
preheat/postheat temperatures, °C <sup>c</sup>	290–230	310–250	230–200	250–220	230–250
specific gravity	1.20–1.35	1.01–1.15	0.91–1.00	0.90–1.02	1.75–1.90
adhesion <sup>d</sup>	G–E	E	G	G–E	G
surface appearance <sup>e</sup>	smooth	smooth	smooth	smooth	sl OP
gloss, 60° meter	40–90	20–95	60–80	60–80	60–80
hardness, Shore D	30–55	70–80	30–50	40–60	70–80
resistance <sup>e,f</sup>					
impact	E	E	G–E	G	G
salt spray	G	E	F–G	G	G
weathering	G	G	P	P	E
humidity	E	E	G	E	G
acid <sup>g</sup>	E	F	E	E	E
alkali <sup>g</sup>	E	E	E	E	G
solvent <sup>g</sup>	F	E	G	E	G–E

<sup>a</sup> All powders require a primer and pass the flexibility test, which means no cracking under a 3-mm dia mandrel bend.

<sup>b</sup> Poly(vinylidene fluoride) = PVDF.

<sup>c</sup> Typical ranges.

<sup>d</sup> E = excellent; G = good.

<sup>e</sup> OP = orange–peel effect; sl OP = slight orange–peel effect.

<sup>f</sup> F = fair; P = poor.

<sup>g</sup> Inorganic; dilute.

whereas the high end of the particle-size distribution ranges up to ~200  $\mu\text{m}$  (70 mesh). Most thermoplastic coating powders require a primer to obtain good adhesion and priming is a separate operation that requires time, labor, equipment, and typically involves solvents. In automotive applications, some parts are primed by electrocoating. Primers are not usually required for thermosetting powder coatings.

## 2. Thermoplastic Coating Powders

Thermoplastic resins used in coating powders must melt and flow at the application temperatures without significant degradation. Attempts to improve the melt flow characteristics of a polymer by lowering the molecular weight and plasticizing or blending with a compatible resin of lower molecular weight can result in poor physical properties or a soft film in the applied coating. Attempts to improve the melt flow by increasing the application temperature are limited by the heat stability of the polymer. If the application temperature is too high, the coating shows a significant color change or evidence of heat degradation. Most thermoplastic powder coatings are applied between 200 and 300°C, well above the generally considered upper temperature limits for adequate heat stability. However, the application time is short, usually  $\leq 5$  min. The principal polymer types are based on plasticized poly(vinyl chloride) (PVC) [9002-86-27], polyamides (qv), and other specialty thermoplastics. Thermoplastic coating powders have one

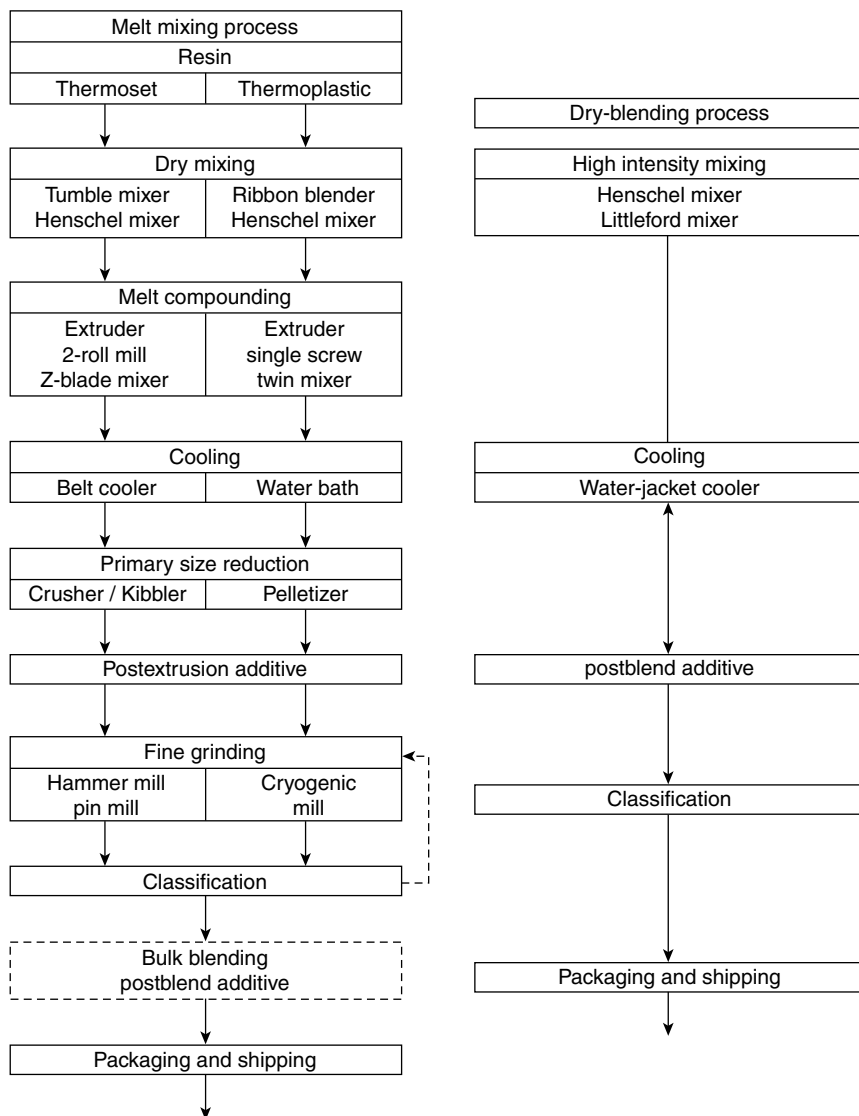
advantage over thermosetting coating powders: They do not require a cure and the only heating necessary is that required to complete melting or fusion of the powder particles. Thermoplastic resins have applications in coating wire, fencing, and other applications where the process involves continuous coating at high line speeds. Typical properties of thermoplastic coating powders are given in Table 1.

**2.1. PVC Coatings.** All PVC powder coatings are plasticized formulations [see VINYL POLYMERS, VINYL CHLORIDE and POLY(VINYL CHLORIDE)]. Without plasticizers (qv), PVC resin is too high in melt viscosity and does not flow sufficiently under the influence of heat to form a continuous film. Suspension and bulk polymerized PVC homopolymer resins are used almost exclusively because vinyl chloride–vinyl acetate and other copolymer resins have insufficient heat stability. A typical melt-mixed PVC coating powder formulation is given in Ref. 4. Dispersion grade PVC resin is added in a postblending operation to improve fluidizing characteristics (5). Additional information on the formulation and application of PVC coating powders can be found in Ref. 6. Whereas most PVC coating powders are made by the dry-blend process, melt-mixed formulations are used where superior performance, such as in outdoor weathering applications and electrical insulation, is required (see Fig. 1). Almost all PVC powder coatings are applied by the fluidized-bed coating process. Although some electrostatic spray-grade formulations are available, they are very erratic in their application characteristics. The resistivity of plasticized PVC powders is low compared to other powder coating materials and the applied powder quickly loses its electrostatic charge. Dishwasher baskets are coated with fluidized-bed PVC powder. Other applications are various types of wire mesh and chain-link fencing. PVC coatings have a very good cost/performance balance that is difficult to match with any of the other thermoplastic materials. Properly formulated PVC powders have good outdoor weathering resistance and are used in many applications where good corrosion resistance is required (see CORROSION AND CORROSION CONTROL). These coatings are also resistant to attack by most dilute chemicals except solvents. In addition, PVC coatings possess excellent edge coverage.

Powder coatings as a class are superior to liquid coatings in their ability to coat sharp edges and isolate the substrate from contact with corrosive environments. PVC coatings are softer and more flexible than any of the other powder coating materials. Primers used for PVC plastisols generally have been found suitable for powder coatings as well (7).

**2.2. Polyamides.** Coating powders based on polyamide resins have been used in fusion-coating processes from the earliest days. Nylon-11 [25587-80-9] has been used almost exclusively; however, coating powders also have been sold based on nylon-12 [24937-16-4]. The properties of these two resins are quite similar. Nylon-6 [25038-54-4] and nylon-6,6 [32131-17-2] are not used because the melt viscosities are too high.

Polyamide powders are prepared by both the melt-mixed and dry-blend process. In the latter, the resin is ground to a fine powder and the pigments are mixed in with a high intensity mixer (see Fig. 1). Melt-mixed powders have a higher gloss, eg, 70–90 on the Gardner 60° gloss meter, whereas dry-blended powders have a gloss in the range of 40–70. Because the pigment is not dispersed in the resin in the dry-blend process, it must be used at very low concentrations,



**Fig. 1.** Flow diagram for coating powder manufacture.

usually  $<5\%$ . Even in melt-mixed formulations, the concentration of pigment and fillers (qv) seldom exceeds  $\sim 20\%$  of the composition.

Nylon coating powders are available for both electrostatic spray and fluidized-bed application. Nylon coatings are very tough, resistant to scratching and marring, have a pleasing appearance, and are suitable for food contact applications when properly formulated. These coatings are used for chair bases, hospital furniture, office equipment, knobs, handles, and other hardware. Because of expense, nylon is generally applied only to premium items. Nylon coatings have good solvent and chemical resistance and are used for dishwasher baskets, food

trays, hot water heaters, plating and chemical-etching racks, and large diameter water pipes in power-generating stations. For maximum performance, a primer is used. Nylon coating powders are discussed in more detail in Ref. 8.

**2.3. Other Thermoplastic Coating Powders.** Coating powders based on polyethylene [9002-88-4] and polypropylene [9003-07-1] have been available for many years but have achieved limited commercial success (see OLEFIN POLYMERS). A primary problem in using polyolefin-based powders is poor adhesion to metal. However, ethylene copolymers functionalized with acrylic acid, sold under the tradename Envelon (9), and certain grades of ionomer resins (10) have been formulated into coating powders and are enjoying some measure of commercial success. Self-adhering clear coatings based on a combination of ionomer resins and high melt index ethylene/acrylic acid copolymers are described in a recent patent (11).

Thermoplastic polyester coating powders achieved some commercial success during the mid-1980s; however, these were eventually replaced by nylon coating powders in functional coatings and thermosetting polyester powders in decorative applications because of lack of any unique characteristics or price advantages (see POLYESTERS, THERMOPLASTIC).

Coating powders based on poly(vinylidene fluoride) (PVDF) [25101-45-5] are available and are used in architectural applications where long-term exterior performance is required. Most are modified with thermoplastic acrylic polymers (12) or other fluoropolymer resins containing comonomers to improve melt flow and application characteristics (13). A method for preparing pigmented PVDF powders that does not require melt compounding and cryogenic grinding is described in Ref. 14.

Several other thermoplastic powders are available based on specialty polymers such as ethylene-chlorotrifluoroethylene (E-CTFE) [25101-45-5], poly(phenylene sulfide) (PPS) [25212-74-2], and tetrafluoroethylene-ethylene copolymers [68258-85-5] (see FLUORINE COMPOUNDS, ORGANIC, POLYMERS CONTAINING SULFUR). Such powders are used in functional applications where resistance to corrosion and elevated temperatures are required. They are usually applied by fluidized-bed coating techniques but can also be applied by electrostatic techniques to a heated substrate (15). Extremely high application temperatures in the range of 250–350°C are required for these polymers because of high melting point and high melt viscosity.

### 3. Thermosetting Coating Powders

Thermosetting coating powders, with minor exceptions, are based on resins that cure by addition reactions. Thermosetting resins are more versatile than thermoplastic resins in the formulation of coating powders in that: many types are available varying in melt viscosity, functional groups, and degree of functionality; numerous cross-linking agents are available, thus the properties of the applied film can be readily modified; the resin/curing agent system possess a low melt viscosity allowing application of thinner, smoother films, and necessary level of pigments and fillers required to achieve opacity in the thin films can be incorporated without unduly affecting flow; gloss, textures, and special effects can be

Table 2. Physical and Coating Properties of Thermosetting Powders

Property	Epoxy	Polyurethane <sup>a</sup>	Polyester <sup>b</sup>	Hybrid	Acrylic <sup>c</sup>
fusion range, °C	90–200	160–220	160–220	140–210	100–180
cure time <sup>d</sup> , min	1–30 <sup>e</sup>	15–30	5–15	5–15	5–25
storage temp, °C <sup>f</sup>	30	30	30	30	20
adhesion <sup>g</sup>	E	G–E	G–E	G–E	G–E
gloss, 60° meter	5–95	5–95	40–95	20–95	80–100
pencil hardness <sup>h</sup>	H-4H	H-2H	H-4H	H-2H	H-2H
flexibility	E	E	E	E	F–P
resistance to:					
impact	E	G–E	G–E	G–E	F
overbake	F–P	G–E	E	G–E	G–E
weathering	P	G–E	G–E	P–F	G–E
acid <sup>i</sup>	G–E	F	G	G	F
alkali <sup>i</sup>	G–E	P	F	G	P
solvent	G–E	F	F–G	F	F

<sup>a</sup> Hydroxy function-blocked isocyanate cure.<sup>b</sup> TGIC (triglycidyl isocyanurate) Hydroxy alkylamide cure.<sup>c</sup> GMA(glycidyl methacrylate)type cured with DDA (dodecanedioic acid).<sup>d</sup> Value is given at 160–200°C, unless otherwise indicated.<sup>e</sup> At 240–135°C.<sup>f</sup> Maximum value is given.<sup>g</sup> E = excellent; G = good; F = fair; P = poor.<sup>h</sup> Refers to highest degree of lead hardness at which coating can be marred.<sup>i</sup> Inorganic; dilute.

produced by modifying the curing mechanism or through the use of additives; and manufacturing costs are lower because compounding is carried out at lower temperatures and the resins are friable and can be ground to a fine powder without using cryogenic techniques. The properties of thermosetting coating powders are given in Table 2.

Ideally, the appearance of a powder coating should equal that of a water borne or solution coating at the normal thickness range, eg, 20–60  $\mu\text{m}$  ( $\sim 1\text{--}2$  + mils). While significant advances have been made in the formulation and application of powder coatings over the last 10 years, it is more difficult to apply powders uniformly in thin films that match the smoothness and appearance of conventional liquid finishes. However, the gap is closing rapidly. Automotive powder clear coats have been applied by BMW to several models on a production basis since 1998. As of May 2000, over 1000 car bodies per day are being powder coated on completely automated lines (but at a film thickness still higher than desired) (16).

In order to retain their particulate form and free-flow characteristics, coating powders must resist sintering or clumping during transportation, storage and handling. To maintain these properties,  $T_g$  of the formulated powder must be at a minimum of  $\sim 40^\circ\text{C}$  and preferably  $>50^\circ\text{C}$ . In the case of epoxy resins, because of their highly aromatic backbone, the necessary  $T_g$  is attained at a relatively low molecular mass. In contrast, polyester resins require linear comonomers to achieve the desired degree of flexibility leading to a lower  $T_g$ . Thus, to attain the desired  $T_g$ , higher molecular mass resins must be used resulting in



Table 3. Melt Viscosity, Glass-Transition Temperature and Equivalent Weight of Various Thermosetting Resins

Resin Type	Equiv. Weight	T <sub>g</sub> , °C	Melt Viscosity, mPa·s (cP) at Indicated Temperatures, °C	
epoxy resins			175	200
“2” Type	600–750	50–60	500–1000	<sup>a</sup>
“3” Type	700–850	55–65	1000–2000	200–400
“4” Type	850–1000	60–70	2000–3000	1000
“7” Type	1500–2500	80–85	9000–10,000	10,000
polyester resins				
acid functional	750–2800	50–64		3000–6500
hydroxyl functional:				
general purpose	560–1870	50–55		3000–6000
high T <sub>g</sub> .	1400–1800	60–70		6500–8500
acrylic resins				
acid functional	750–1600	55–68		3000–8000
hydroxyl functional	1250	60		5000
glycidyl methacrylate	510–560	39–56	390–470	<sup>a</sup>

<sup>a</sup> Too low to measure.

higher melt viscosities (17). At an equivalent range of  $T_g$ , polyester resins have a melt viscosity ~10 times higher than for epoxy resins (see Table 3).

The surface tension and melt viscosity are the main parameters affecting film formation and the flow of thermosetting coating powders (18). While a high surface tension promotes the coalescence and flow of molten powder particles, a low surface tension is necessary to wet the substrate. So-called, “flow control additives” are used in almost all coating powders to eliminate surface defects such as craters and pinholes. A more accurate term would be “surface tension modifiers”, since this is their primary effect. They are believed to function by creating a uniform surface tension at the air–surface interface of the molten coating as a result of the partial compatibility (19). The most widely used flow control additives are acrylic oligomers (20). Most are primarily based on *n*-butyl acrylate [9003-49-0] and copolymers of ethylacrylate and 2 ethy-hexyl acrylate [26376-86-3] (see ACRYLIC ESTER POLYMERS).

While there is little difference between the surface tension lowering effects of various acrylic flow additives (21) monomer composition and molecular mass can have a significant effect on the flow and orange peel of the final coating (22). The relationship between flow and melt viscosity of the binder resin(s) is more obvious. Significant efforts on the part of resin manufacturers have been made to optimize the melt viscosity of the polymers while still maintaining the required  $T_g$ . Monomer composition (23), molecular mass, and functionality (24) are among the most important variables. The degree of reactivity between the resin and curative has a significant effect on flow and smoothness. For ideal flow and leveling of the coating, the time between melting of the powder and the start of cross-linking should be maximized. Most resins are intended for use with a particular curing agent, so the functionality of the resin is designed accordingly. Rapid heating of the applied powder layer, ie, high curing temperatures, results in the lowest level of melt viscosity, but also in a faster increase in

viscosity once the cross-linking starts (25). Chemorheological measurements have proven useful in determining the most desirable resin/curing agent reactivity and functionality in specific thermosetting systems (26). Optimum curing conditions can be predicted based on the reaction kinetics of the coating powder (27). In addition to the chemical and rheological factors already mentioned, smoothness of the cured coating is also related to the structure of the electrostatically deposited powder layer. The initially applied powder layer is much more porous than would be expected from random close packing of particles and shows appreciable powder segregation and patterning. A comprehensive study of powder application, coalescence, and flow indicates orange peel, with its millimeter length scale and micron-scale amplitude, arises partly from incomplete leveling of the largest scales of unevenness originally present in the deposited powder layer (28). Previous studies have also noted the relationship between clusters or large agglomerates of particles and orange peel (29). Finer particle size powders eliminate some of the large agglomerates and result in smoother films (30), but finer particles are more cohesive, less free flowing, and more difficult to manipulate (31).

The higher degree of orange peel exhibited by powder coatings in comparison to conventional liquid coatings is a fundamental shortcoming. Determining the ultimate cause of this deficiency and correcting it will lead to even greater acceptance and use of powders in finishing processes.

**3.1. Formulation.** In many respects, the formulation of coating powders is similar to that for conventional paints. The resinous binder plays a major role in the basic properties of the final coating such as exterior durability, chemical resistance, flexibility and impact resistance, and, to some extent, appearance. Whereas in conventional paints solid ingredients such as pigments and fillers are dispersed in the liquid vehicle using a mill, in coating powders, the solid ingredients are dispersed in the molten binder in an extruder. Paint dispersions must be stabilized to prevent pigment agglomeration and settling. Flooding, floating, and pigment agglomeration are not a problem in a solid binder so rheological and dispersing additives are not necessary and are seldom used in coating powders. A significant formulating advantage for conventional paints is that there are few constraints on the  $T_g$  of the binder resins; they can even be liquids. In addition to the binder resin(s), curing agents, which can range from crystalline solids to polymers, flow agents, additives, pigments, and fillers are utilized in coating powders. An important formulating variable is the ratio of pigments and fillers to the binder, the pigment/binder or P/B ratio. Typical pigment/binder ratios used in formulating various types of coating powders are listed in Table 4. In general, the P:B ratios used in coating powders are much lower than for conventional paints since there are no other liquid ingredients present to wet out the pigments. Thus the pigment volume concentration in coating powders is correspondingly lower and seldom exceeds ~25%. Higher levels of pigments or fillers significantly reduce the flow out of coating powders resulting in a rough grainy coating.

In addition to the acrylate flow control additives, silicones, primarily the polyether modified types and fluoropolymer flow agents, are also used. Care must be exercised when using powders with differing flow additives or significantly different binder resins since cross-contamination can occur resulting in

Table 4. **Pigment: Binder Ratios for Various End Use Applications**

Pigment: binder ratio	% Pigment and fillers	Approximate PVC <sup>a</sup>	Application
0.01–0.10	1–9	0.3–2.9	transparent, flamboyant, clear metallic, special effects
0.1–0.2	9–17	2.9–5.7	high chroma, high DOI, automotive exterior durability, high flexibility
0.2–0.6	17–37.5	5.7–15	general purpose, appliance, furniture, fixtures, lawn and garden
0.6–1.0	37.5–50	15–23	low cost, anticorrosive, electrical insulation, pipe coatings
1.0–1.2	50–55	23–26.5	primers, textures, functional coatings, economy grades
>1.2	>55	>26.5	specialized applications, zinc rich primers

<sup>a</sup> Pigment volume concentration calculated using pigments and fillers having a specific gravity of 4.0.

loss of gloss, surface imperfections, and loss of smoothness. These incompatibilities arise from differences in the surface tension of the various powders (32). Low melting thermoplastic additives such as benzoin [119-53-9] are used in coating powders to promote bubble release and air entrapment (33). Many of the additives used in coating powders, such as uv absorbers, light and heat stabilizers, and mar and slip agents, have their basis in conventional coatings. However, others, such as electrostatic or tribocharging additives and postblend additives mixed with the finished powder to improve dry, free-flow characteristics (34) are unique to coating powders.

Many of the pigments used in conventional paints are also used in coating powders. These include inorganic pigments such as titanium dioxide, nickel/titanium rutile, iron oxides, and complex inorganic pigments. Lead- and cadmium-based pigments have not been used for many years in the United States and Europe and are being phased out in the rest of the world. Typical organic pigments used include phthalocyanine blues and greens, various azo types, quinacridones, carbazoles, diketo-pyrrolo pyrroles, among others. Generally, inorganic pigments are used to provide opacity, while organic pigments are used for their chroma or saturation. Because of their high surface area and high binder demand, organic pigments cannot be used at very high levels, ie, >5–6% before a noticeable reduction in flow and increase in orange peel of the coating starts to occur. Therefore, as a rule of thumb, the level of inorganic pigments should be maximized and the level of organic pigments should be minimized, while meeting the requirements for opacity and chroma. As noted, even inorganic pigments with their higher opacity and lower binder demand are not used at levels in coating powders as high as in paints. To obtain complete opacity with a white coating powder containing 30% TiO<sub>2</sub> (P/B ratio = 0.46) a film thickness of 89  $\mu\text{m}$  is required. The addition of only 0.001% carbon black reduces the thickness required for complete hiding to 63 and 37  $\mu\text{m}$  with the addition of 0.005% (35).

Fillers such as calcium carbonate, blanc fixe and barium sulfate [07727-43-7] and wollastonite [13983-17-0] are used in coating powders to modify gloss, hardness, permeability, and other coated film characteristics and to reduce costs (36). Clays and talcs are seldom used, except in textured coatings, because of their

high binder demand and adverse affect on flow and smoothness. Silicas are usually avoided due to their abrasiveness during extrusion and grinding, with the exception of colloidal silica used as a postextrusion additive.

Matting or flattening agents are employed to control gloss, which is dependent on microscopic surface smoothness (37). Thus, nonmelting or incompatible thermoplastic resins of proper particle size such as Teflon and polypropylene are used to disrupt surface smoothness and reduce gloss (38). Similarly, incompatible waxes concentrate at the surface of the coating, also reducing gloss but resulting in a waxy feel, which is prone to showing blemishes, eg, fingerprints. Coarse grades of fillers such as barytes, calcium carbonate, or wollastonite are also used for gloss control, usually with other techniques. Curing agents having widely different reactivities cause a two-stage polymerization to occur, resulting in incompatible domains and impaired microscopic surface smoothness (39). In a similar fashion, low gloss is achieved by mixing two powders varying significantly in reactivity (40). Gloss can be controlled over a wide range using combinations of glycidyl methacrylate functional resins with acid functional polyester resins (41). In summary, there are many methods of gloss control available to the coating powder formulator covering the full range of gloss in both interior and exterior durable systems.

**3.2. Special Finishes.** Clear coatings are formulated using curing agents and flow additives, which have a high degree of compatibility with the resin. Conventional uv and hindered amine light stabilizers can be added to improve exterior durability. Metallic finishes can also be prepared but the metal flake must be added after the powder has already been ground to prevent break up of the metallic flakes and preserve the metallic appearance (42).

Hammertones, veins, and other special effects are prepared by the judicious addition of surface tension lowering ingredients, eg, silicones or flow control/resin master batches, usually in conjunction with a dry blended metallic or mica flake pigment. Textured coatings are produced by controlling the flow and particle size of the powder particles as well as with nonmelting polymers of controlled particle size. Wrinkle finishes are obtained using selected curing agents and catalysts (43).

**3.3. Epoxy Coating Powders.** Thermosetting coating powders based on epoxy resins  $C_{15}H_{16}O_2 \cdot (C_3H_5ClO)$ , [25068-38-6] have been used longer than any other resin system. The reason that is solid epoxy resins were commercially available when thermosetting coating powders were being developed and had the necessary combination of low molecular mass,  $T_g$ , and melt viscosity (see Table 3). Further, a variety of latent curing agents were also known that allowed the development of stable, one component powders. Early efforts to develop powders based on dry-blend processing methods, such as by ball milling, were generally not commercially acceptable because the resultant coatings were low in gloss, lacked smoothness, and good appearance, especially with greater than minimal levels of pigments and fillers. These problems were overcome when powders were processed by melt mixing, eg, extrusion (see Fig. 1 and related text). The earliest powders were based on dicyandiamide [461-58-4] a latent curing agent. However, these powders were too slow curing, requiring 15–30 min at 200°C, to achieve full properties. A wide variety of catalysts for the dicyandiamide epoxy reaction were evaluated, but the clear choice after several years of trial and error were

imidazoles, especially 2-methyl imidazole [693-90-1]. Dicyandiamide has a high melting point and limited solubility in epoxy resins. Dicyandiamide derivatives having aromatic substitution were developed, which are more compatible with epoxy resins, easier to disperse, and more reactive while still retaining their latency. Typical of these substituted dicyandiamide derivatives are *o*-tolyl biguanide [93-69-6] and 2,6-xylenyl biguanide (44). Highly reactive, compatible, and low melting curatives are also prepared by reacting an epoxy resin with excess imidazole. Another class of curatives, developed somewhat later, are the linear phenolics. These have the same structure as epoxy resins but are terminated with bisphenol A [80-05-07] rather than epoxide groups and contain significant levels of free bisphenol A. Since they have a functionality of only 2, the functionality of the epoxy resin in the binder must be increased, usually by blending with an epoxidized phenol novolak resin to give an average functionality of  $\sim 2.5$ – $3.0$ . The epoxy/phenolic hydroxyl reaction is relatively slow for many applications so an imidazole catalyst is often included in the formulation (45). Most of these curatives are still used today in both decorative and functional epoxy coating powders and provide compositions that cure in the typical range of 10–15 min at 180–200°C or in the low temperature range of 15–20 min at 140–180°C.

Many other types of curing agents have been evaluated in formulating epoxy-based coating powders but have found use in only specialized applications. Conventional phenol or cresol novolak resin curatives impart a high degree of cross-link density but result in rather brittle coatings with undesirable color. Aromatic amines give very reactive, fast curing systems but are marginal in storage stability and their health and safety characteristics are questionable. Of course, primary aliphatic amines cannot be used because they react even at room temperature and cannot be compounded at elevated extrusion temperatures. Dihydrazides have also been evaluated but their cost/performance base can seldom justify their use. Many anhydride curing agents have been considered but only a few have found their way into commercial formulations. For a time, trimellitic anhydride [552-30-7] cured powders catalyzed with metal-organic salts were used in the formulation of very reactive, fast cure powders, such as used for coating concrete reinforcing bars (rebars) and pipe coatings (46). However, health and safety concerns led to the decline in use of this chemistry. Benzophenone tetracarboxylic dianhydride yields highly cross-linked coatings with very good heat and chemical resistance and is used in specialized functional applications (47).

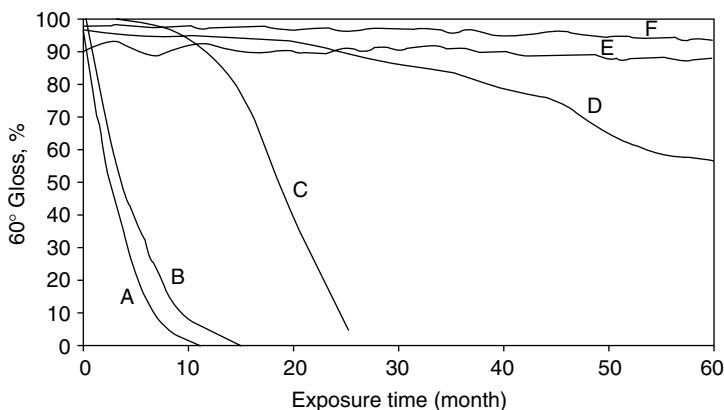
Decorative epoxy powders are used in a wide variety of applications, eg, for lighting fixtures, garden equipment, motor control cabinets, and many automotive under the hood items including coil spring shock absorbers, mechanical parts, and even engine blocks. Low melt viscosity resins of the “3” type are most widely used in decorative applications (see Table 3). Type “4” resins and higher with a higher molecular mass and melt viscosity are more often used in functional applications such as for electrical insulation and corrosion resistance where thicker coatings are needed and a higher degree of edge coverage is necessary. Epoxy powders are used almost exclusively in rebar and pipe coatings (48). In outdoor applications, epoxy coatings chalk readily and lose gloss; however, they protect the substrate for many years. Figure 2 compares the gloss retention of epoxy coatings with other thermoset types on exterior exposure.

**3.4. Epoxy-Polyester Hybrids.** A major class of interior grade coating powders is based on a combination of epoxy and acid functional polyester resins. As noted, epoxy resins cured with anhydrides have desirable properties but never gained a high degree of commercial acceptance. Most anhydrides are respiratory irritants and are difficult to work with. Also, they are hygroscopic and the reactivity of coating powders cured with anhydrides varies on storage depending on the ambient humidity and the degree of conversion of the anhydride to acid. On the positive side, anhydride cured powders possess heat resistance and good color stability in contrast to the tendency for most amine cured powders to discolor on exposure to heat or exterior exposure. Therefore, programs were initiated in the research facilities of polyester resin manufacturers to develop resins that retained the desirable characteristics of anhydrides while eliminating their undesirable characteristics. This work resulted in the development of acid functional, relatively linear, saturated polyester resins specifically designed for curing bisphenol A based epoxy resins. The original resins developed had an acid number of 70–80 (equiv. weight range 700–800) so they were used at 50:50 ratio with “3” type epoxy resins (see Table 3). The functionality is  $\sim 2.5$ –3, to provide good curing characteristics and cross-link density when used with the essentially bifunctional epoxy resins. Because polyester resins are less expensive than epoxy resins, higher equivalent weight polyester resins were subsequently developed, which are used at a stoichiometric ratio of 60:40 and even 70:30 ratios to epoxy resin. Properties of these polyester-epoxy hybrids are similar to those of a straight epoxy, but differ in several respects. The overbake resistance (resistance to color change after extending curing) and resistance to discoloration on exposure to sunlight is superior. Because the cross-link density for hybrid coating powders is generally less than for straight epoxies, cured hybrid coatings are inferior in solvent resistance and hardness. They are also somewhat inferior in salt spray and corrosion resistance. Polyester resins, having a higher melt viscosity than epoxy resins (see Table 3), result in the hybrids having more orange peel than epoxy based coatings, especially at the higher polyester/epoxy ratios.

The reaction rate between the carboxyl end groups of the polyester and the epoxide groups of the epoxy resin is generally quite slow, requiring a catalyst to obtain a practical baking time. Catalysts are frequently mixed with the polyester resin by the resin manufacturer. The ideal catalyst should exhibit good reactivity at the desired baking temperature, eg, 150–180°C, while providing good flow and shelf stability (50). Tertiary amines, amic acids, and quaternary phosphonium compounds are effective catalysts for the epoxy-carboxyl reaction (51,52).

Epoxy-polyester hybrid coatings are marginally better than straight epoxy based coatings in gloss retention on exterior exposure (Fig. 2) but generally are not recommended for exterior applications. For the most part, applications for the hybrid powders are the same as those for decorative epoxy coating powders. The latter are being replaced by the hybrid coating powders and are increasing in market share in the United States. In Europe, hybrid coating powders are the most widely used powder type (see Table 5).

**3.5. Polyester-TGIC Cured.** A principal class of exterior durable powder coatings is based on acid functional, saturated polyester resins cured using TGIC [02451-62-9] (see Fig. 2). This system was first developed in Europe



**Fig. 2.** Gloss retention in outdoor exposure in Florida for various powder coatings: A, epoxy; B, epoxy-polyester hybrid; C, polyester TGIC, HAA, and urethane (dark brown); D, super durable polyester TGIC, HAA, and urethane (dark brown); E, super durable polyester, clear, no light stabilizers; F, GMA acrylic, clear, light stabilized. (After Ref. 49,74).

in the early 1970s. The acid functional polyester resins used in TGIC cured coating powders are similar to those used in epoxy polyester hybrids. However, the resins for curing with TGIC have a higher equivalent weight, typically in the range of 1600–1900 and a lower degree of functionality. Thus most resins are used at a 93:7 ratio of resin to TGIC. Acid functional resins are normally prepared by a two-step process: the reaction of excess polyol and dibasic acids followed by esterification of the hydroxyl terminated resin using dibasic acids or anhydrides (53). This technique yields a resin where the functional groups are at the end of the molecule rather than occurring randomly along the polymer chain. The excellent exterior durability of polyester resins cured with TGIC is primarily a result of the nonaromatic structure of TGIC in contrast to that of the bisphenol A based epoxy resins used in polyester/epoxy hybrid coating powders. Monomer composition of the resin also plays a significant role. It is recognized that the exterior durability of polyester powder coatings is affected by factors other than resistance to uv radiation. Accumulation of moisture on the surface of the coatings, especially at elevated temperatures (darker colors) and exposure to oxygen leads to hydrolysis, oxidation, and degradation of the resin.

**Table 5. 1998 Thermoset Powder Coatings Production by Resin Type<sup>a</sup>**

Resin type	North America (%)	Europe
epoxy	15.0	8.5
epoxy–polyester hybrid	35.7	54.0
polyester–carboxyl	22.6	29.0
polyester–hydroxyl	21.6	4.0
acrylic and other	5.1	4.5
<i>total</i>	<i>100.0</i>	<i>100.0</i>

<sup>a</sup> Ref. 119.

Environmental factors such as acid rain or alkaline bird droppings as well as cyclic heating and cooling also contribute to molecular breakdown and loss of properties. For these reasons, accelerated weather testing now frequently includes cyclic exposure to elevated temperatures and moisture as well as uv light (54).

The recent development of so-called "super durable polyesters" has validated the cyclic accelerated weathering approach. Super durable polyester resins are based almost exclusively on isophthalic acid while most standard resins contain terphthalic acid as well. Super durable polyesters are highly resistant to hydrolysis and degradation by uv light (55,56), which helps to account for their superior exterior durability. Compared with a standard TGIC cured polyester powder coating in a dark color, which loses ~50% of its original gloss after ~2 years of Florida exposure, a super durable polyester cured with TGIC will last at least four times as long until the same loss of gloss occurs. Figure 2 is a plot of % gloss retained vs. original level, measured on a 60° gloss meter, comparing super durable polyesters with several other types of powder coatings. Super durable polyesters are generally inferior in flexibility and impact resistance but recent advances have shown significant improvements in this regard (57).

TGIC cured coating powders have gained a significant market share position in the exterior durable market in both Europe and North America. Many buildings coated with TGIC powders in various European locations from the early 1970s and later are still in good condition, exhibiting minimal corrosion and good retention of gloss and color. In the past 10 years, some concerns have developed over health and safety issues related to TGIC, especially with regard to mutagenic characteristics. In the United States, it is generally believed the hazards are adequately addressed by the Occupational Safety and Health Administration (OSHA) Hazard Communication Standard and the low exposure level of 0.05 mg/m<sup>3</sup> established (58). However, in Europe, the European Union (EU) ruled that the symbol T (Toxic, symbolized by a skull and crossbones) accompanied by the relevant Risk Phase, R46, relating to substances considered to cause heritable genetic damage, is to be used in labeling any product containing TGIC. This requirement went into effect in June 1998 and had the result of powder manufacturers replacing TGIC in their products. Since that time the market share of TGIC cured polyester coating powders has decreased significantly in Europe, being largely replaced by hydroxyalkylamide cured powders (59). Other glycidyl compounds such as a mixture of diglycidyl terphthalate [7195-44-0] and triglycidyl trimellitate [7237-83-4] (60) as well as tris (beta-methyl glycidyl) isocyanurate [26147-73-3] (61) are being evaluated as TGIC replacements as well.

**3.6. Polyester—Hydroxyalkylamide Cured.** HAA curatives were developed in the late 1970s and early 1980s (62). Evaluation as a curative in coating powders was described in early 1991 (63). The primary commercial product is bis (*N,N*-dihydroxyethyl) adipamide [6334-25-4] sold under the tradename Primid XL 552 by EMS Chemie. It reacts with acid functional polyester resins by esterification and the elimination of water. The toxicological profile of this curative is benign and it does not fall under the provisions of any current health and safety or environmental regulations. It has been shown that the ester linkage formed with Primid XL 552 and polyester resins has essentially the same characteristics as the TGIC/polyester bond (64). Practical experience has



confirmed that polyester coating powders cured with Primid are essentially equivalent in weatherability and other properties to TGIC cured powders (65). Because the functionality of the HAA curative is  $\sim 4$ , the functionality of the polyester resins used with them has to be designed accordingly (66).

**3.7. Urethane Polyesters.** In the United States, the search for exterior durable coating powders led to technology based on hydroxyl functional polyester resins. The earliest curing agents evaluated were based on melamine-formaldehyde resins, such as hexa(methoxymethyl) melamine (HMMM) [68002-20-0], which are widely utilized as curing agents in conventional paint systems (see AMINO RESINS). Coating powders based on this chemistry suffer limitations: the melamine resin depresses the  $T_g$  of the coating powder to the point where the powder sinters during storage, especially at elevated temperatures; and the methanol generated during the curing process becomes trapped in the film, especially at thicknesses above  $\sim 50\ \mu\text{m}$ , resulting in a frosty or visually nonuniform surface. An amino resin, specifically developed for use in coating powders, tetramethoxymethyl glycouril [17464-88-9] (TMMGU), overcomes many of these disadvantages, but still requires the use of higher  $T_g$  resins and special acid catalysts (67). Coating powders based on this chemistry have not achieved a high level of commercial acceptance for general purpose use; however, with selected catalysts, attractive wrinkle finishes are produced (68,69) that find use in special applications. Curing agents based on polyisocyanates blocked with caprolactam [0105-60-2] (qv) give an excellent combination of properties in the final film. Because the unblocking reaction does not start to occur until  $\sim 160^\circ\text{C}$ , the powder has a chance to flow out and give a smooth uniform film prior to any substantial cross-linking. Not all of the caprolactam evolves during the curing process and some remains in the film acting as a plasticizer. Thus, urethane polyesters yield a smoother, more orange peel free film than the TGIC polyesters and are more preferred in the United States and Japan than Europe (see Table 5).

The hydroxyl functional polyester resins used in this technology are similar in monomer composition to the acid functional polyesters and are based primarily on terephthalic acid [100-21-0],  $\text{C}_8\text{H}_6\text{O}_4$ , isophthalic acid [121-91-5],  $\text{C}_8\text{H}_6\text{O}_4$ , and neopentylglycol [126-30-7],  $\text{C}_5\text{H}_{12}\text{O}_2$ . These resins branched using trimellitic anhydride or trimethylol propane [77-99-6]. A variety of other polyols and dibasic acids are used to modify specific resin properties such as  $T_g$ , melt viscosity, curing characteristics, and others (70,71). Resins ranging in OH number from 30–300, equivalent weight of  $\sim 190$ –1870, are used in the formulation of urethane coating powders. Since the blocked isocyanate curatives are three to four times the cost of the polyester resin, the lower OH number resins are preferred for general purpose formulations, with a 50 OH number resin providing a good balance between raw material cost, physical properties and appearance. While the higher OH number resins require higher levels of curative, the final coatings have outstanding hardness and chemical resistance. Blends of high and low OH number resins and the stoichiometric level of curative form the basis of low gloss coatings. Hydroxyl functional super durable resins, similar in monomer composition to the acid functional resins cured with TGIC, are also available. When cured with isophorone diisocyanate (IPDI) based isocyanates, they possess exterior durability equal to that of the super durable/TGIC based coatings (see Fig. 2). The most commonly used curing agents are trimerized

IPDI,  $C_{12}H_{18}N_2O_2$ , [4098-71-9] blocked with caprolactam and the trimethylol propane adduct of IPDI blocked with caprolactam. Blocking agents, which unblock at lower temperatures, provide the basis for urethane powders that cure at lower temperatures (72). New curatives have been developed that do not rely on blocking agents to mask the reactivity of the isocyanate group. Most are based on the uretdione structure, a four-membered ring formed by the reaction of isocyanate groups with each other (73). While uretdione-based curatives have been available for many years, they have high melt viscosities and require higher temperatures for curing than the blocked isocyanates. Newer versions have overcome these problems to some extent (74).

Urethane polyesters have not received widespread commercial acceptance in Europe primarily because of the caprolactam (or other blocking agents) emitted during curing. Despite the development and commercial availability of the uretdione based curatives, which do not give off volatiles during cure, the European market for exterior grade polyester powders is still based primarily on acid functional resins (see Table 6).

**3.8. Unsaturated Polyester Powders.** A special class of coating powders is based on unsaturated polyester resins. They are utilized in matched metal die molding operations such as those based on sheet molding compounds (SMC) and bulk molding compounds (BMC) where the mold is coated with the powder prior to placing the resin charge in the mold (see POLYESTERS, UNSATURATED). The powder melts and flows on the mold surface, and when the mold is closed, the powder reacts with the molding compound forming a coating on the molded part. This process is known as inmold coating. Unsaturated polyester resin powder coatings can provide a colored and finished exterior molded surface or a finish ready for painting. Normally, a primer/sealer must be applied to molded articles prior to painting. In addition to the unsaturated polyester resin, multifunctional resins prepared from unsaturated monomers such as triallyl cyanurate [101-37-1] or diallyl phthalate [131-17-9], suitable peroxide initiators (qv) or mixtures thereof, and mold release agents (qv), are used to formulate the coating powder (75).

**3.9. Acrylic Powders.** Coating powders based on acrylic resins have been available in Europe, the United States, and Japan since the early 1970s but have not achieved significant commercial success until recently. However, since 1997 BMW has been applying an acrylic clear-coat powder to several models and currently (2000) is powder coating over 1000 cars/day (16). Acrylic-based

Table 6. 1999 World Thermoset Powder Coatings  
Production<sup>a</sup>

Region	Metric tons	%
Europe—West and East	329,100	45.3
Far East	161,585	22.2
North America	175,600	24.2
South America	29,950	4.1
Rest of World	30,865	4.2
<i>Total</i>	<i>727,100</i>	<i>100.0</i>

<sup>a</sup> Ref. 118.

powders are also used in exterior trim (pigmented) and wheels (clear). The majority of clear coatings are based on a glycidyl functional methacrylic resin (GMA) cured with dodecanedioic acid [693-23-2] or a polyacid/anhydride polymer (76). Acrylic powders based on GMA resins have poor compatibility with epoxy- and polyester-based powders. If cross-contamination occurs, surface defects in the form of pinholes, craters, and excessive orange peel are common.

The GMA clear coatings have outstanding exterior durability, hence their acceptance in the automotive sector (see Fig. 2). Pigmented GMA acrylic powders have not found widespread use in market areas other than automotive, eg, architectural applications. Hydroxyl functional acrylic resins cured with blocked isocyanates or uretdione-based curatives have also found use in automotive applications and their exterior durability is only somewhat less than the GMA acrylic powders (77). Carboxyl functional acrylic resins are also commercially available. They can be cured with TGIC for exterior applications or with bisphenol A epoxy resins. The latter combinations are sometimes called acrylic/epoxy hybrid coating powders and are noted for their excellent hardness, stain, and chemical resistance. They find use primarily in appliance coatings (78).

**3.10. Recent Developments.** As noted, powder coating technology has advanced to the point where powders are now routinely applied in critical automotive applications. Another market area where intense work is in progress is the development of powders having low temperature curing capabilities such that they can be used to coat wood, plastics, and other temperature sensitive substrates. A coating powder must have a high enough  $T_g$  and molecular mass so it does not sinter on the one hand while on the other hand a low melting point and melt viscosity is desirable for low temperature application and smoothness. It is a difficult task to balance these diverse requirements. This is especially true in the case of thermally cured powders compared with uv curable powders. In the latter case, the flow and leveling of the coating are separate from the curing reaction while with heat curable powders, cross-linking occurs even as melting and flow are in progress.

One technique for dealing with this low temperature cure/reactivity dilemma is to use a two component powder system. The resin and other binder components comprise one component and the curative and other nonreactive binder ingredients comprise, the other (79). In the case of uv curable powders, an unsaturated polyester resin is one of the major binder components but more reactive binder components such as oligomers with high allyl functionality (80) or vinyl ether/ester groups (81) must also be present. Crystalline resins with reactive methacrylyl groups have also been disclosed (82). A review of photoinitiators, additives, and other components of uv curable powders are given in (83,84).

## 4. Manufacture

The vast majority of thermosetting coating powders are prepared by melt mixing. Some thermoplastic powders are also produced by this method but most are manufactured by the dry blend process as shown in Figure 1. Production methods based on spray drying from solution (85) and precipitation from solution (86)

have been evaluated but never achieved commercial success because of difficulties in solvent and/or water removal from the powders. Many types of coating powders are still manufactured in small batches, eg, 50–1500 kg due to differences in color or chemistry, where chemical processes are not economical.

**4.1. Melt-Mixing.** Dry ingredients, resins, curatives, additives, pigments, etc, are weighed into a batch mixer such as high speed impeller mixers, container mixers, horizontal plow mixers, or tumble mixers where they are thoroughly blended. High-speed impeller mixers such as the Henschel give the best distributive mixing and the cycle time is relatively short, eg, 1–2 min. However, these mixers have relatively small capacity, eg, 100–300 kg and many individual batches must be prepared for longer production runs. Horizontal plow mixers require a slightly longer mix cycle but have a larger capacity, 500–1000 kg. They also provide good distributive mixing but require longer cleaning times. Tumble mixers have a high capacity and are adequate for general purpose powders, but mixing cycles are long, 30–60 min, and distribution of ingredients is sometimes marginal. With container mixing systems, only one mixer is required and generally satisfactory distributive mixing is obtained. However, many mixing containers, which become the hopper for feeding the extruder, are required as well as a mixer for each size of mixing container (see MIXING AND BLENDING). The premix is then melt compounded in a high shear extruder where the ingredients are compacted, the resin(s) melt, and individual components are thoroughly dispersed in the molten resin. These compounding machines generate sufficient heat through mechanical shear so that after start-up, little external heat needs to be supplied. Both single screw machines, with a reciprocating screw that intermeshes with fixed baffles in the barrel, such as the Buss Ko-Kneader and twin screw extruders, primarily corotating, intermeshing types as supplied by Krupp Werner Pfleider, Baker Perkins, and others are used (see PLASTICS PROCESSING). Residence time in the extruder is short, usually <1 min and melt temperatures is low, typically 90–120°C, slightly above the melting points of the resinous components. Because of these processing conditions, very little reaction between the thermosetting components occurs. In a study carried out based on epoxy resin compositions, it was determined that 6–11% of the epoxy groups initially present reacted during extrusion (87). Significant improvements have been made in both single and twin screw extruders and for a given size machine throughput rates have increased by a factor of 3–4 over the last 10 years or so. Product quality is more consistent as a result of improved process control (88). The molten compound is cooled rapidly by passing it through water-cooled nip rolls and subsequently onto a watercooled continuous stainless steel belt or drum. The cooled compound is broken into small chips, ~10–12 mm, suitable for fine grinding. Thermosetting resins are quite friable and are usually ground to final particle size in an air classifying mill. In this grinder, a blower generates an air stream through the mill in which the product is entrained and which also serves to remove the heat of grinding. A variable speed separator controls airflow in the grinding chamber so that only the particles with the desired particle size escape. The fine powder is separated from the air stream with a cyclone separator or bag house. Powders with a finer average particle size produce smoother coatings than powders with a larger particle size. While the addition of a colloidal silica or alumina to the powder, (either to the chips prior to grinding or to the ground

powder), significantly improves the dry flow, handling, and transport characteristics (89), the presence of high levels of superfine particles adversely affects these same characteristics. Recent advances in grinding equipment include in-line air classifiers and baffles in the cyclone separators, which allow the production of powders with a narrower particle size distribution (90). This results in powders with a finer average particle size but without a significant increase in superfine particles, ie, those below  $\sim 8\text{--}10\text{ }\mu\text{m}$ .

**4.2. Dry Blending.** Most plasticized PVC powders are prepared by a dry-blend process in which the plasticizers, stabilizers, pigments, and additives are absorbed on the porous PVC particles at elevated temperatures while they are being agitated in a high speed mixer (6). Other thermoplastic powders are pigmented in this fashion. Attempts to prepare thermosetting powders by a dry blend process have proven to be unsatisfactory because of the poor wetting and dispersion of pigments and the poor appearance of the subsequent coatings.

**4.3. Recent Developments.** A completely new process for the manufacture of coating powders has been recently developed by the Ferro Corp. It involves solvating resinous components in supercritical gas, typically carbon dioxide ( $\text{CO}_2$ ), and dispersing the pigments and other solid ingredients with an impeller or dispersion blade. After dispersion is completed, the material is hydraulically atomized into a second vessel at a lower pressure. The  $\text{CO}_2$  vaporizes and a combination of particles or easily grindable solid is obtained (91). A similar process for preparing coating powders is described in Ref. 92. The main advantage of these processes over conventional extrusion and grinding technology is that processing temperatures are lower, eg,  $40\text{--}70^\circ\text{C}$ , and it is possible to form powders directly. At present, there are no powders commercially available prepared by these methods.

Another recent development is the successful application of powders from aqueous dispersions. This process is being used to apply both primer surfacers and powder clear coats to the Mercedes A Class automobiles (93). An advantage of this process is that a very fine particle size powder can be used,  $100\% < 10\text{ }\mu\text{m}$ , (94) and it can be applied using conventional wet spray equipment. The concept of applying powders by aqueous dispersion is not new (95) but this is the first time it has been commercially successful. Now that there are large volume applications for powder coating in the automotive sector as primer surfacers and clear coats, it is anticipated that novel methods for preparing either powders or powder dispersions utilizing efficient chemical processing methods will be developed.

## 5. Application Methods

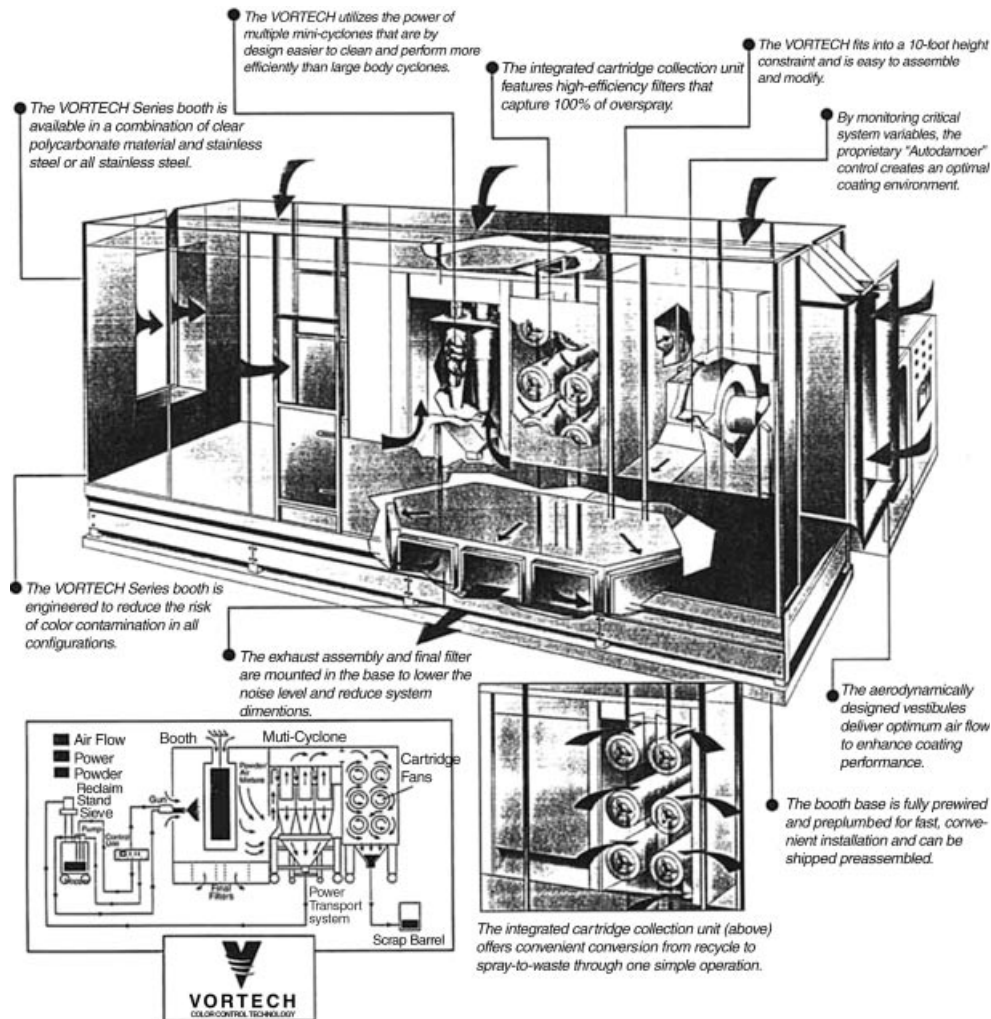
**5.1. Fluidized-Bed Coating.** Fluidized-bed coating, the first significant commercial process for applying powdered polymeric materials to a substrate to form a uniform coating, is the method of choice for many applications where a heavy functional coating is required. The process is relatively simple. The main variables are the temperature of the part as it enters the fluidized bed, the mass of the part being coated, dip time, and postheat temperature. Other variables, such as motion of the part in the bed and the density and temperature of the powder in the bed, also affect the quality of the coating. The process is

especially useful in coating objects having a high surface/mass ratio such as fabricated wire goods and expanded metal. Sharp edges and intersections are well covered because of the heavy film thickness, eg, 250–500  $\mu\text{m}$  (10–20 mils) applied. The size of parts that can be coated is limited because the fluidized bed container must be large enough to readily accommodate them.

**5.2. Electrostatic Fluidized-Bed Coating.** In an electrostatic fluidized bed, the fluidizing container and the porous plate must be constructed of a non-conductive material, usually plastic. Ionized air is used to fluidize and charge the powder. The parts to be coated are passed over the bed and charged powder is attracted to the grounded substrate. The rate of powder deposition varies significantly depending on the distance of the part from the fluidizing powder. Therefore, this process is usually utilized only when the object to be coated is essentially planar or symmetrical and can be rotated above the charged powder. Electrostatic fluidized-bed coating is an ideal method for continuously coating webs, wires, fencing, and other articles that are normally fabricated in continuous lengths and are essentially two dimensional. In a variation of this process, two electrostatic fluid beds are arranged back to back and the continuous web of material is passed between them, coating both sides simultaneously. Millions of lineal meters of window screen have been coated using this technique (96).

**5.3. Electrostatic Spray Coating.** Electrostatic spray coating is the most widely utilized method for the application of powder coatings (see COATING PROCESSES, SPRAY COATINGS). In a typical high voltage system, powder is maintained in a fluidized-bed reservoir, injected into an air stream, and carried to the gun where it is charged by passing through a corona discharge field. The charged powder is transported to the grounded part to be coated through a combination of electrostatic and aerodynamic forces. Ideally, the powder should be projected toward the substrate by aerodynamic forces so as to bring the powder particles close to the substrate where electrostatic forces then predominate and cause the particles to be deposited. The powder is held by electrostatic forces to the surface of the substrate that is subsequently heated in an oven where the particles fuse and form a continuous film. The processes involved are powder charging, powder transport, adhesion mechanisms, back ionization, and self-limitation. As charged powder particles and free ions generated by the high voltage corona discharge approach the powder layer already deposited, the point is reached where the charge on the layer increases until electrostatic discharge occurs. At this point, any oncoming powder is rejected and loosely adhering powder on the surface falls off. It has been demonstrated that some imperfections in the final coating are a result of defects in the powder layer (97).

The characteristic of the electrostatic spray process to form self-limiting films enables operators to apply satisfactory coatings after only brief training and instruction. It is almost impossible to create runs, drips, or sags characteristic of spray-applied liquid finishes. Furthermore, the practical design of automatic spray installations is possible. Multiple electrostatic guns mounted on reciprocators are positioned in opposition to each other in an enclosed spray booth and parts to be coated are moved between the two banks of guns where a uniform coating of powder is applied. Oversprayed powder is captured in the reclaim system and reused. Powder coating booths have been designed with interchangeable filter units to facilitate change from one powder type of color to



**Fig. 3.** Schematic diagram of an electrostatic powder spray system. Courtesy of ITW Gema.

another. A state-of-the-art automatic powder spray system using a combination of cyclone separators to reclaim the majority of over-spray powder and cartridge filters to capture the remaining powder is shown in Figure 3. The cyclone units are designed for quick cleaning and are much easier to clean than a bank of cartridge filters; quick color changes are facilitated. For very short runs, the cyclone separators can be removed and over-sprayed powder is not recovered.

One disadvantage of the electrostatic powder spray process using corona discharge guns is that a high voltage field is set up between the gun and the parts to be coated. Parts having deep angles or recesses are sometimes difficult to coat because of the Faraday cage effect. One method of overcoming the Faraday cage effect is by the use of triboelectric guns in which powder charging occurs by the frictional contact of the powder particles and the interior surface of the

gun. Electrons are separated from the powder particles, which become positively charged and attracted to the substrate. Because there is no electrostatic field between the gun and the article being coated, a Faraday cage is not developed and particles are more readily able to penetrate into recessed areas of the substrate. There are a number of commercial powder coating systems using triboelectric charging technology, but this number is quite small compared to those based on the more conventional corona guns. The powder application rate of triboelectric guns is lower than for corona guns; additionally, whereas powders based on a wide variety of resins and formula types charge and apply readily with corona guns, only certain resin systems charge well in triboelectric guns. However, additives have been developed that improve the tribocharging characteristics of powders (98).

While the basic principles of the electrostatic powder spray process have not changed, many advances in the equipment and process design have been made to improve process efficiency and the quality of the finish (99). Significant improvements have been made in reducing the time to change types of powders or make color changes. Much effort has gone into improving the first pass transfer efficiency, ie, the ratio of powder deposited on parts to that sprayed (100). High transfer efficiencies mean less overspray to reclaim. Less powder to reclaim means the recovery system can be reduced in size and requires less air volume and energy to operate. Some of the means to improve transfer efficiency include: programmable logic controls to adjust the motion of the guns and spray patterns for the specific parts being coated and to recognize the parts passing through the booth, shutting off powder flow when a vacancy in the line occurs or the line stops (101); sensors that detect the amount of powder in the air and modulate the air flow according (102), and non conductive spray booths and filter belts to facilitate powder reclaim (103). In the ideal case of 100% transfer efficiency, a powder reclaim system would be unnecessary and no clean up required between color changes.

Improvements have also been made in materials. Stricter control of particle size distribution improves powder handling and transport characteristics, spray patterns, and transfer efficiency (104,105). Reduction of the superfine fraction, ie, particles below  $\sim 8\text{--}10\text{ }\mu\text{m}$  also results in less fines in the overspray powder and less load on the reclaim system (106). More spherical powders charge more efficiently and show improved spraying characteristics (107).

**5.4. Recent Developments.** A recent major development is the commercial application of powders to auto bodies as primer surfacers and clear coatings. Also, specialized coating lines have been developed for the application of powders to metal blanks and coil. In the case of blank coating, sheet stock is cut and punched and coated on a flat line, using either standard or tribocharging guns. Powders are applied at a lower thickness ( $\sim 25\text{--}40\text{ }\mu\text{m}$ ) and must cure rapidly, eg, 1–2 min, to accommodate the relatively high line speeds (108). Coated blanks are shipped to the manufacturer flat, and assembled there into the final shape, eg, a refrigerator box. This eliminates an in-house coating line.

The continuous powder coating of steel coils is being carried out at a number of locations in Europe and the United States (109). Lines are now operating on coils 60 in. (1.52 m) wide at line speeds of 250–300 ft/min (76–91 m/min) (110) and developments are in progress in which line speeds of up to 1000 ft/min (305 m/min)



are expected (111). Many special finishes, such as textures, hammertones, and wrinkles, are possible with powder while smooth finishes are only possible with liquid coatings. Because of the high line speeds and volume of powder applied, a novel powder charging and application system was developed (112).

Specialized application equipment has also been designed to coat the interior of can bodies (113). Powders having a finer particle size are required as well (114). A significant new powder application method has been developed utilizing photocopying and laser printing technology. Designated electro-magnetic brush (EMB) technology, it is possible to apply very thin powder coatings continuously on flat stock, either metallic or nonmetallic. By using a clear uv curable powder on a 17-in. wide EMB machine, rolls of wallpaper were coated at a thickness of 5–7  $\mu\text{m}$  (0.2–0.3 mils) at a line speed of 60 m/min (197 ft/min) (115).

**5.5. Hot Flocking.** Several nonfluidized-bed coating methods are based on contacting a preheated substrate with powder to form a coating. Although these techniques are not widely used, for certain parts they are the preferred method of application. For example, the coating of motor stators using a thermo-setting powder provides primary insulation between the core and windings. The part is preheated to  $\sim 200^\circ\text{C}$  and the powder is directed from a fluidized bed using an air venturi pump, similar to those used to supply powder from the reservoir to electrostatic guns, through flexible tubes and directed at the preheated part that is rotating on a mandrel. Multiple tubes, usually in pairs in opposition to each other, are normally used. In a similar fashion, the inside diameter (ID) of the pipe can be coated by entraining powder in an airstream and blowing it through a preheated section of pipe (116). Very uniform coatings in the range of 200–300  $\mu\text{m}$  can be applied by this process to provide corrosion protection for drill pipe, and water injection and gathering pipe in diameters up to  $\sim 50$  cm.

**5.6. Metal Cleaning and Preparation.** As in any finishing operation, the surface of the object to be coated must be clean, dry, and free from rust, mill scale, grease, oil, drawing compounds, rust inhibitors, or any soil that might prevent good wetting of the surface by the coating powder. Steel should be sandblasted or centrifugally blast-cleaned to give a near white finish (see METAL SURFACE TREATMENTS). Phosphate coatings are normally a pretreatment for most fabricated steel parts while nonchrome and organometallic conversion coatings are used on aluminum (117).

## 6. Economic Aspects

The worldwide market for coating powders increased at an annualized growth rate (AGR) of almost 10% during the 1990s in North America compared with a 12–13% AGR during the 1980s. Even though the rate of growth has decreased somewhat, it is estimated that powder coating represents only  $\sim 4$ –5% of the industrial paint market in North America. Globally, the penetration of powder coatings in the industrial paints sector is 6% with Europe leading at  $\sim 9$ %. By 2010, global penetration of powder coatings is expected to reach the 10% level (109).

While the primary driving force for growth during the 1980s was environmental regulations, growth during the 1990s has been driven additionally by

superior performance and application economies. Powder coating is seen as an environmentally friendly technology because no solvents are present; volatile organic compounds (VOCs), are absent, for the most part, venting, filtering, and solvent recovery systems are not necessary; process air is recycled; and there is little waste since most overspray powder can be collected and reused. Further, any waste generated is not classified as a hazardous waste under current regulations (see HAZARDOUS WASTE TREATMENT). Permits required for new coating facilities or additions to existing lines are much easier to obtain when the installation utilizes powder coating processes. Future growth will largely depend on advances in both coating materials and application technology in comparison with advances in other environmentally friendly coating methods.

The worldwide production of coating powders in 1999 was estimated at 727,100 mt having a value of \$803,861,000, a 6.9% increase over the quantity sold in 1998 (118) (see Table 5). This compares with a production of 236,000 mt in 1989, a growth rate of over 12%/year. Europe is still the largest market, accounting for almost half, followed by North America and the Far East, each with 20%+ market share.

An indication of the growth of the powder coating in North America is reflected in the membership statistics of the Powder Coating Institute, a trade organization representing the industry. From 1987 to 2000, the number of members who manufacture coating powders increased from 5 to 28; suppliers of powder application equipment from 3 to 8; custom powder coaters from 1 to 200; and raw material suppliers from 5 to 114 (118).

Thermoset decorative coatings are by far the largest segment of coating powder production accounting for >90% of the pounds produced. Other market segments are thermoplastic powders, essentially all of which are used in fluidized-bed coating and functional thermoset powders that find use in the pipe coating, rebar, and electrical insulation markets.

The distribution of coating powder production by resin type for several geographical areas is given in Table 6. The epoxy-polyester hybrid powder coatings account for the largest resin type in both Europe and North America. Increasing market share is mostly at the expense of the 100% epoxy-based powders, as a result of more favorable economics. In Europe, weatherable carboxyl polyesters cured with TGIC are being replaced with carboxyl functional polyesters cured with HAA, other glycidyl curatives and, to some extent, urethane polyesters. While the hydroxyl functional polyester resins cured with blocked isocyanates or uretdione curatives, ie, urethane polyesters, have a significant market share in the North American market, they are still a relatively small part of the market in Europe.

The vast majority of acrylic powders in both Europe and North America find use in the automotive industry, as clear coats for wheels and bodies and as pigmented coatings in exterior trim, "blackout" coatings, and primer surfacers.

The automotive market is the largest and fastest growing segment of the powder coating market in North America accounting for over 16% market share, followed by appliance coatings at 15%, architectural at 3%, lawn and garden at 7%, and general metal finishing at 58% (118).

## 7. Analytical Methods

Methods for evaluating the performance of powder coatings are the same as those used for conventional coatings. Test methods for coating powders include particle size distribution, powder free flow, sintering, fluidization characteristics, and others. They have been reviewed in detail and reported in the literature (120,121). In addition, the American Society for Testing and Materials (ASTM) has issued a comprehensive standard that covers the most important test methods for the evaluation and characterization of powder coatings (122).

## 8. Environmental and Energy Considerations

A significant factor contributing to the growth of powder coating processes has been the proliferation of federal, state, and local environmental regulations. Starting with the Clean Air Act of 1970, which defined Hazardous Air Pollutants (HAPs), VOCs, and set standards for nationwide air quality, many additional regulations have since been enacted. In nonattainment areas, localities where pollution levels persistently exceed National Ambient Air Quality Standards, the Best Available Control Technology (BACT) or Maximum Available Control Technology (MACT) may be necessary to reduce the level of pollutants to that required. Powder coating installations are generally accepted as meeting these levels of control technology. States are charged with the job of achieving compliance. Permits are required by states where new finishing operations are being added or in existing facilities. The presence or absence of VOCs and HAPs in coating materials has become a significant factor in the economic analysis in planning new finishing operations.

Since coating powders are 100% solid materials, they are essentially free of VOCs and HAPs, with the exception of trace quantities of monomers or, in some cases, solvents used in the manufacture of the raw materials (123). Caprolactam and other compounds used as blocking agents in blocked isocyanate curatives are emitted during curing. Typical levels in formulated urethane coating powders are in the range of 4–6%. While caprolactam is considered a VOC, it is not classified as an HAP. Powder coating remains the process of choice where VOCs must be reduced to the lowest possible levels, as in many OEM and automotive coating operations. Permits for additions to existing paint lines or installation of new systems are much easier to justify and obtain than when most liquid coatings are specified. In addition to the environmental advantages, the low volatile emissions of powder coatings during the baking operation has economic and energy saving advantages. Fewer air changes per hour in the baking oven are required for powder coatings than for solvent-based coatings, which saves fuel. Further, in the coating operation almost all powder is recovered and reused, resulting in higher material utilization, and waste minimization. The air used in the coating booths during application is filtered and returned to the workplace atmosphere, reducing heating and cooling demands. Additionally, because of the need for more sophisticated devices to control emission of VOCs in liquid systems, the capital investment to install a new powder coating line is becoming

increasingly more economically favorable. The savings in material and energy costs of powder coating systems has been documented in a number of studies. An economic analysis worksheet for comparing the cost of operating a powder coating line compared with alternate systems can be found in Technical Brief No. 21 in Ref. 121.

The only components in a coating powder that might cause the waste to be classified as hazardous are certain heavy-metal pigments sometimes used as colorants. Lead (qv) and cadmium-based pigments (qv) are seldom used, however, and other potentially hazardous elements such as barium, nickel, and chromium are usually in the form of highly insoluble materials that seldom cause the spent powder to be characterized as a hazardous waste (124).

## 9. Health and Safety Factors

Any finely divided organic material can form ignitable mixtures when dispersed in air at certain concentrations. The most significant hazard in the manufacture and application of coating powders is the potential of a dust explosion (see POWDERS, HANDLING). The severity of a dust explosion is related to the material involved, its particle size, and concentration in air at time of ignition. The lower explosive limit (LEL) is the lowest concentration of a material dispersed in air that explodes in a confined space when ignited. The LEL for a number of epoxy and polyester powders was measured and found to be in the range of 0.039–0.085 oz/ft<sup>3</sup> (39–85 g/m<sup>3</sup>) (125). In powder coating installations, the design of the spray booth and duct work, if any, should be such that the powder concentration in air is always kept below the LEL employing a wide margin of safety. General safety considerations are detailed in Ref. 126. The use of flame detection systems in all automatic powder coating installations is required. These devices must respond within 0.5 s or less to arrest all powder flow in the system. If powder ignition should occur, flame detection sensors shut down the power to the system, halting powder spraying and air flow circulation. Another element of safety for a powder coating system is the design of the booth recovery equipment. Some recovery designs utilized today, such as illustrated in Figure 3, are configured so no external venting is required. However, when traditional cyclones or dust collectors, isolated by ducting, are utilized in the coating system, a pressure relief system is necessary. If these units are not located outside the building or properly vented, explosion suppression may also be required (see POLLUTION CONTROL METHODS). Furthermore, cyclones and dust collectors located inside the building should be near an outside wall and ductwork from the pressure relief vents should be directed through short runs, not exceeding 3 m when possible. Required explosion vent areas and other design considerations can be found in the literature (127). The spray guns, spray booth, duct work, dust collection, and powder reclaim system, as well as the work piece, must be properly grounded (128,129).

The health hazards and risk associated with the use of powder coatings must also be considered (see HAZARD ANALYSIS AND RISK ASSESSMENT). Practical methods to reduce employee exposure to powder such as the use of long sleeved shirts and gloves to prevent skin contact should be observed. Furthermore, exposure

can be minimized by good maintenance procedures to monitor and confirm that the spray booth and dust collection systems are operating as designed. Ovens should be properly vented and operated under negative pressure so that any volatiles released during curing, eg, caprolactam, do not enter the workplace atmosphere.

In general, the raw materials used in the manufacture of powder coatings are relatively low in degree of hazard. None of the epoxy, polyester, or acrylic resins normally used in the manufacture of thermoset powder coatings are defined as hazardous materials by the OSHA Hazard Communication Standard. Most pigments and fillers used in powder coatings generally have no hazards other than those associated with particulates. Some epoxy curing agents are skin irritants; however, most of these characteristics are greatly diminished when these materials are compounded into the powder coating. In addition to being diluted, the materials are dispersed in a resinous matrix having a low degree of water solubility that appears to make them less biologically accessible. For example, anhydrides and anhydride adducts generally elicit a strong respiratory or eye irritant response. However, when powder coatings containing anhydride-based curing agents were tested in animal exposures, the coatings were found to be nonirritating to the skin, eye, and respiratory tract (130,131). Similarly, TGIC is a skin irritant, but formulated powders containing TGIC were not (132). Regulations in Europe require cautionary labeling of powders containing TGIC (see Sections under Thermosetting Coating Powders, and Polyester, TGIC Cured).

Although coating powders do not appear to pose significant hazards to personnel working with them, worker exposure should nevertheless be minimized. Coating powders should be treated as Particulates Not Otherwise Classified (PNOC) having a Threshold Limit Value–Time Weighted Average (TLV–TWA) of 10 mg/m<sup>3</sup> for total particulates (133). The TLV should be maintained primarily through environmental controls. Hoods and proper ventilation should be provided during handling and application of powders. When environmental control of dust cannot be maintained below the TLV, protective equipment such as dust and fume masks or externally supplied air respirators should be used (134).

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DOUGLAS S. RICHART  
D.S. Richart Associates