Solutions without solvents

Trends, technologies and perspectives in the replacement of wet paints

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The chemistry and areas of application for powder coatings have steadily evolved since their introduction in the 1960s. As a result, their share of the industrial coatings market has continually increased. Their current and future evolution are reviewed. Powders offer many technical advantages, but may have to face major challenges such as reduction of energy use in curing and further enhancing exterior durability.

The use of powder coatings as an industrial coating technology can be traced back more than fifty years to the early 1960s. The main reason for developing this new class of material was to get rid of the sticky wet paint and the processes involved in its industrial application. In those times, dominated by solventbased paints, major problems were solvent fumes, the danger of explosion and sticky coagulated waste wet paint material which had to be disposed of.

Starting with thermoplastic resins (e.g., polyamides) and the process of melting polymer powder onto a hot, usually metal, surface in a fluidised bed of the particulate material, the idea was developed of using a spray gun as for wet paint application and transferring the electrostatically charged powder particles more or less directly to the surface of the object to be painted.
This worked well, and so thermoplastic resins were largely replaced by thermosets (mainly epoxies, polyesters or acrylics crosslinked with hardener), having the advantage of lower curing temperatures as well as lower film builds. This process was an economic success; powder coating production has continued to show a much higher growth than that of the paint market as a whole.

Economy in use creates several niche applications

Powder coatings took over from conventional paints several areas which were difficult to coat with wet paint due to high amounts of overspray, such as open metal con-

Figure 1: Powder coating of aluminium wheels

structions, shelves, aluminium wheels for cars (*Figure 1*) and aluminium panels for facades.
In all these cases it must be considered that despite a high dry film build of typically 60-80 µm compared to 30-40 µm for wet paint application, 1 kg of powder coating material is able to cover a significantly greater surface area due to its inherent application advantages. It is 100 % solids in application and in most cases recirculation of the overspray is simple, as the dry powder material can be mixed back into the original material for further application.
This creates the awareness that in the case of powder coatings the coating material is on the object to be coated (*Figure 2*), whereas in the case of liquid paint materials the loss of solvents and difficulties in overspray collection mean that the original material disappears to a significant extent and can even cause problems in disposal.
Several monographs describe in detail the processes and the materials in use for powder coating of different substrates [1 - 6]. The following sections will deal with the economic and ecological impact of powder coating, referring then to the technical state of the art and future perspectives, challenges involved in the use of powder coatings and future development goals to reduce current drawbacks.

Economic impact and applications of powder coatings

As already mentioned, usage of powder coating is still increasing. On a world-wide basis, powder coatings represented approximately 6 % by value [7] of the overall coatings market in 2008. In Germany, representing a typical European country, this was 3 % on a mass basis in 2008 [8]. The average annual volume growth rate of powder coatings is around 10 % per year, whereas the total coatings market grows on average by around 2.5 % per year [9].
This shows clearly that tremendous changes are still going on in the painting industry and in the major users of powder coatings – general industry. This is notable, as powder coatings are presently limited mainly to industrial use. Thus, huge areas that are coated by craftsmen, such as architectural surfaces or ships' hulls, cannot be powder coated for technical reasons, mainly the necessity for electrostatic application and the relatively high average curing temperature of 160-180 °C to make the powder flow and cure.
Thus, powder coating materials are to some extent underrepresented in the overall coatings use statistics because their use is limited mainly to industrial applications. In the area of general industrial painting, approximately 30 % of the areas to be covered are already powder coated [7].
Major users of powder coatings are, for example, industries producing household appliances such as washing machines, stand-alone refrigerators, radiators or microwave ovens, or (due to the need for high corrosion protection) industrially pre-painted architectural elements such as aluminium profiles, e.g. window frames or façade elements, or paints for metal casings and shelves.

Automotive applications are among the most demanding

In the area of automotive parts, powder coatings are also used widely. Powder coatings were once extensively used in Europe on cast iron engine blocks for cars and light trucks, now mostly substituted by uncoated alumin-

Results at a glance

››› The market share and the areas of use of powder coatings have steadily increased since their industrial introduction in the 1960s.

››› In many respects powder coatings offer considerable advantages: a clean and simple painting process with simple achievement of high film builds. Coatings for different fields of use offer generally good corrosion protection properties, adaptable weathering properties and mechanical robustness of the paint film, all with generally acceptable costs.

››› Due to growing concern with energy consumption, powder coatings will have to take further steps towards reduction of curing temperatures. Other issues for the future include the quest for cost-effective powders with greater exterior durability than "superdurable" polyesters, and the elimination ofsome limitations of the curing agents which have replaced hazardous TGIC.

ium, or for primer or primer and clearcoat systems for aluminium wheels for cars.
Where high mechanical and/or corrosion stability of the coating is necessary, powder coatings are used, and so springs and stabiliser bars, seat frames, window regulators or other critical items in cars, buses or other public transport vehicles are mostly powder coated, as are roof rail systems for estate cars (station wagons) and MPVs.
A technically demanding area is painting and corrosion protection in the automotive car body painting. In the USA, some car bodies are powder coated (primer-surfacer, Chrysler and GM), whereas in Europe the clearcoat lines in three BMW plants were successively changed to the use of acrylic powder.
In economic terms this is not a large market share, but it shows that powder coatings are able to give top performance in respect of combined mechanical and chemical requirements while achieving and preserving the highest optical quality under severe weathering conditions, as the automotive industry requires.
This leads to the appreciation that we are living in a world of powder coated goods, often not knowing that we do so.

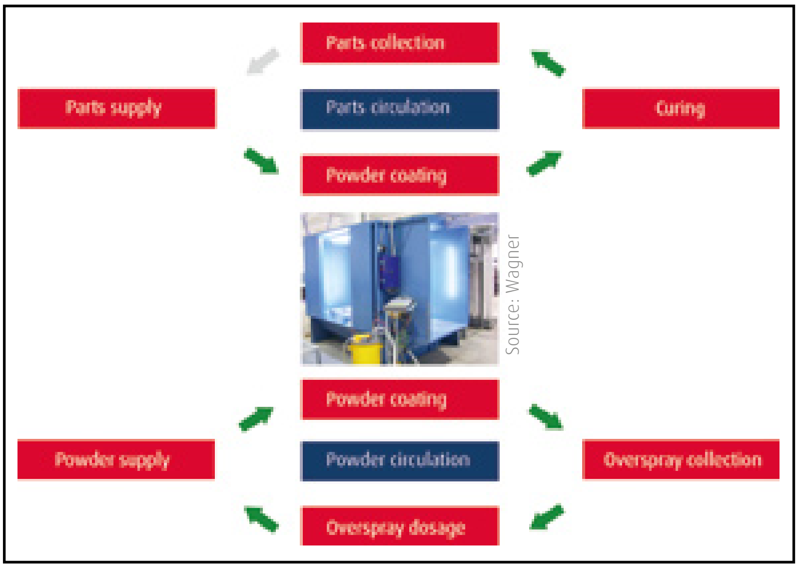

Figure 2: Parts and material circulation in powder coating

Wet and dry manufacturing processes compared

Since paint was first invented, people used materials consisting of solvent and binder, and pigments were added if it had to be coloured (*Figure 3*). The solvent was necessary to wet the pigment with binder, and to transfer the liquid paint to the object to be coated.
The solvent also had to assist in coating film formation, but afterwards it was redundant. In the case of organic solvents, it created problems in terms of flammability, smell and ultimately toxicity of the solvent fumes.
Powder coatings broke with that paradigm, but the trade-off for a solvent-free system was that a certain temperature had to be achieved to melt the powder so as to wet the substrate, give smooth film formation and crosslink the two components in the powder. Thermoset systems are needed to attain a high level of film properties such as mechanical, chemical and weathering stability and corrosion protection, because of the reduced diffusion rates of a crosslinked polymer system.
But first, powder coating materials (*Figure 4*) must be produced, and this is mostly done by pre-mixing and extrusion of the different components such as binder, hardener and pigment. This process leads to melting of the resin which can, in the case of highly reactive components, initiate curing reactions.
After being extruded, the resulting polymer chips are broken, milled to the required size, sieved, filled in packages and stored. All these processes need a certain level of technology, but by dealing mostly with dry products at room temperature, the only hazard is that the resulting fine particles must be taken care of by filtering the exhaust air.

Energy demands raise environmental questions

Storage and transport can be an issue in the case of resins which are too reactive or too sticky (where the molecular weight is too low) at the storage or transport temperature. This basic challenge is not fully resolved, and so far the curing temperatures of commercial high performance resins with perfect levelling and flow are limited to a minimum of 130–140 °C, though most classical resin types still cure within the range of 160–180 °C.
Depending on oven type and the products to be coated, these high curing temperatures may be an issue in the future, when the carbon dioxide footprint will be used as a measuring rod to evaluate the environmental compatibility of painting systems. In the complex case of automotive primer-surfacers and top coatings this issue was investigated in depth [10], with the conclusion that powder concepts are still very valuable for this field in terms of energy costs and applied cost of the processes compared.
Underlying this investigation was the assumption of high energy consumption for spray booth conditioning in the automotive wet painting processes. The newly introduced "dry scrubbing" processes may change the picture in the near future so that the details must be re-examined.
Other situations must be investigated case by case, but nevertheless this new technology leads to the observation that the curing conditions of powder coatings could be a major issue in future.
The processes of powder application are not environmentally critical, in terms of obeying the general technical rules for SHE (safety, health, environment). Powder dust particles should be filtered and overspray should be molten. Certainly, the concept of powder coating is intrinsically less wasteful due to in-line recycling of overspray and has low emissions of volatile components due to the lack of liquid components.

Technical aspects of modern powder coatings

In the 1990s powder coatings could penetrate into markets which were classical fields for wet paint. Many have already been mentioned. Powder coatings make particular sense where two coating layers can be substituted

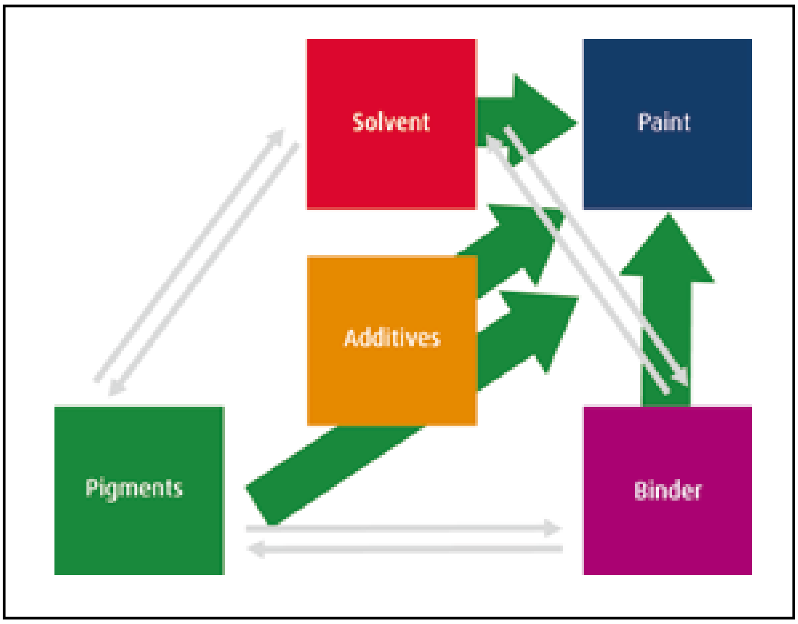

Figure 3: Components of a liquid paint system

by one powder coating layer or for industrial processes where the coating process should be integrated into the part flow. Here, powder coating is a relatively clean technology which is easy for the end user to handle.

An issue for many years was colour change. Several systems are now used in industrial processes, but colour change remains easier when using liquid paints. In-depth analyses using numerical simulation programmes have been carried out for powder coating application [11, 12].

Looking at the top level of coating requirements, powder coating could penetrate the automotive priming process, mainly at Chrysler, Scania and Peugeot. Topcoat processes were installed at BMW for clearcoat in three plants and for the body frame of the smart car in Hambach as a complex multi-layer powder primer/basecoat/clearcoat application, according to the specific requirements (effect or solid colour).

Nevertheless, there has been a change of strategy within BMW; it will change its powder clearcoat line back to wet clearcoat again [13].

In the area of corrosion protection, powder coatings excel due to their high film build and resistance to penetration, especially when appropriate pretreatments are applied. Modern powder coatings are still mainly polyester systems when exterior durability is required or epoxy systems for corrosion protection. What are known as hybrid systems (polyester-epoxy) have emerged as they offer better weather fastness than epoxy and lower cost and better corrosion prevention than pure polyesters.

Acrylates are still used in small amounts in Europe, whereas in Asia their use is much higher. This arises partly from the severe chemical incompatibility of powder coatings of different types, which may even require different production sites for different classes of material. In most cases, the binder type initially chosen is retained.

Application is still mostly by charging the powder by corona charge and using spray guns, whereas in high-end applications rotary bell application is common (eg, BMW powder clearcoat). Tribo charged powders are also in use, but to a minor extent.

To reduce the energy consumption for curing, UV-powders were developed. The current use of these promising products is still minor. New classes of substrates can be coated, but technical development is still required to achieve optimum film properties at a minimum of facility investment and with process control. A challenge, as for all UV processes, is the effect of the pigmentation on curing.

Video interviews on powder coatings: www.european-coatings.com/videos/

The quest for safer crosslinkers

The crosslinkers or hardeners in powder coatings remain an environmental concern. Since the seventies, the crosslinker triglycidyl isocyanurate (TGIC) has been the standard for highly weather resistant polyester powders for architectural, automotive and general industrial applications.

Some years ago, toxicological studies showed it had some evidence of mutagenic potential. Therefore the EU decided that the symbol T (toxic, symbolised by a skull), accompanied by the relevant risk phrase, was to be used for TGIC labelling from May 1998 onwards. In Europe especially, this labelling led raw material producers to develop safer alternatives to TGIC. Over the last two decades, two main market products have become established in Europe:

» Di- or tri-glycidyl esters of terephthalic and isophthalic acid, tetrahydrophthalic acid and trimellitic acid (e.g., "Araldite PT 910" from Huntsman);
» β-hydroxyalkylamide (e.g., "Primid XL-552" from EMS-Chemie).

The crosslinking reaction of the first is a poly-addition with carboxyl functions of the polyester resin similar to TGIC. Although this product is one of the best technical alternatives, powder products with this hardener have to be labelled in the EU with X_i and risk phrases R36/38 and R43 (irritation to eyes and skin, may cause sensitisation by skin contact).

Alternatives based on the second technology crosslink via esterification with the carboxyl functions of the polyester resin. Water is a cleavage product, which may lead to pinholes at higher film builds above 80 µm.

On the other hand, due to their comparatively high performance in terms of appearance, outdoor stability, mechanical and anti-corrosion properties, both crosslinking technologies have, in spite of some specific disadvantages, gained significant market acceptance.

Maximising exterior durability

Polyurethane powder coatings are based on hydroxy-functional polyesters with two main blocking technologies for the crosslinking isocyanate. ε-caprolactam blocked isophorone diisocyanate (IPDI) derivatives are most widely used. With catalysts, the deblocking temperature can be decreased to 140 °C, where ε-caprolactam effects good levelling of the powder film. A disadvantage is the VOC content derived from the blocking agent.

A newer technology without this disadvantage is based on IPDI internally blocked to an uretdione derivative. Combining this hardener with hydroxy-functional poly-

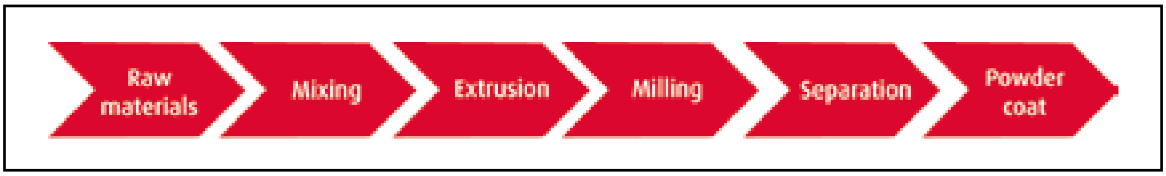

Figure 4: Principle of powder coating production

esters based on isophthalic acid yields powder coatings with excellent weatherability, referred to as superdurable products [14].

The superdurable powder coating market segment is growing faster than the powder market in general, particularly in Europe. Products to be designated superdurable (or according to the GSB International seals of approval "Premium quality") show outstanding weathering characteristics for applications such as architectural coatings.

Powder coatings with GSB-Master and GSB-Premium approved quality labels have to endure Florida weathering conditions with a relative gloss retention of not less than 50 % after 36 months and 30 % after 60 months [15].

As the leading state of the art, powder coatings which give higher outdoor durabilities with a Florida test exposure of ten or more years are based on fluorocarbon polymer chemistry [16]. There is a major economic incentive to "fill the gap" in the durability range between five and ten years' Florida weathering with suitable powder coatings at commercially acceptable costs. This development goal poses a major challenge for both resin and hardener technology.

Further developments and limitations considered

Powder coating materials can now satisfy many demands for colour and effects. Besides high gloss materials and a wide range of colours (with some limitations due to the high curing temperatures) effect coatings and matt appearance are available.

In the field of production optimisation there has been major progress with "one-shot matt" systems for "Primid"-based coatings. This innovative matting technology is based on a 'single extrusion' process, combining a low and a high acid value polyester instead of extruding each resin separately followed by a dry blending process.

The limitations of powder coatings are:

» High curing temperatures;
» High film builds;
» Limitations in appearance;
» Use mainly limited to metal substrates (with some exceptions);
» Necessity of metal surface pretreatment to achieve adhesion under wet conditions;
» Application mainly in industrial processes;
» Challenges with colour changes.

This list shows that there is a limit to the further use of powder coatings, unless the curing temperature can be lowered or other curing mechanisms can be implemented. Low film build systems (40–50 µm) with curing temperatures of 80–100 °C could extend the range of substrates, e.g. to wood or plastics.

This could ultimately be achieved by UV-curing for clearcoats or by implementation of new ideas and pigment types in the case of coloured powder coatings. When this goal can be achieved, a new era of this environmental friendly and technically robust painting technique could emerge 50 years after its first implementation.

Overall, powder coating is a concept widely used in industry. Its technology is robust in both application and in the finished film, when the specific system requirements are complied with. Nevertheless powder coatings have their limitations, especially curing temperatures and film build; both affect the eco-balance. When these issues are solved, which requires both research and engineering development, further market penetration, further market growth and a new future for powder coatings will become viable.

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