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Emmanouil Spyrou

Powder Coatings Chemistry and Technology

3rd Revised Edition

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Vincentz Network GmbH & Co KG

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Cover: Evonik Industries AG, Marl/Germany

Bibliographische Information der Deutschen Bibliothek
Die Deutsche Bibliothek verzeichnet diese Publikation in der Deutschen Nationalbibliographie; detaillierte bibliographische Daten sind im Internet über http://dnb.ddb.de abrufbar.

Emmanouil Spyrou, 3rd Revised Edition
Based on
Pieter G. de Lange's, 2nd Edition, Vincentz Network, 2004, and
Tosko A. Misev's, 1st Edition, John Wiley and Sons, 1991
Powder Coatings: Chemistry and Technology
Hanover: Vincentz Network, 2012
European Coatings Tech Files

ISBN 978-3-86630-824-4

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Layout: Vincentz Network, Hanover, Germany

ISBN 978-3-86630-824-4

eBook-Herstellung und Auslieferung:
readbox publishing, Dortmund
www.readbox.net

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Preface

“If I have seen a little further, it is by standing on the shoulders of giants.” (Isaac Newton, 1676) The excellent original book “Powder Coatings, Chemistry and Technology” written by Tosko Aleksandar Misev and later updated by Peter Gillis de Lange has served for my generation as a sort of bible on its sector. Therefore, it has been a great honor while at the same time a tremendous challenge to write a third edition of this book. Due to this respect the original text is maintained where possible, but altered and extended if recent scientific findings made it necessary.

The Stone Age did not end due to a lack of stones. New technologies replace the old ones; novel developments change the look of the world, sometimes at an incredibly fast speed. Just to name a few recent incidents since the last print of the book: The rise of China, severe worldwide financial crises, the changed way of communicating (e.g. smart phones, social media) and radical governmental regulations (e.g. REACH). Of course, these developments had influences on the world of powder coatings, too. Consolidation, relocation and customization are some of the effects. Replacement of toxic ingredients (e.g. TGIC), use of energy saving curing methods and the extension of powder coatings into new application fields are the interconnected technological changes that are covered in this book.

This book is directed to anybody who is involved in developing, producing, testing and marketing of powder coatings, raw materials or application equipment.

What is new compared to the second edition? More than 5,000 recent articles and patents concerning powder coatings have been evaluated and 250 of those have been referenced in this book to ensure that it illustrates the current state-of-the-art. Highlighted core terms and a significant extended index should help finding the desired topic in a shorter time. A list of powder coating related web addresses will enable the reader to locate additional relevant information at the push of a button. Product and company names have been updated as much as possible. Plus more than 30 new photos, diagrams and drawings complete this revised and updated third edition.

I would like to thank Werner Grenda for valuable discussions, Dr. Corey King for corrections of the manuscript and Dr. Michael Ringel for his contribution regarding REACH. Many thanks to the two dozens companies for the excellent additional photos they provided for the 3_{rd} edition of this book.

Emmanouil Spyrou

Marl, Germany, Mai 2012

Contents

1 Introduction

1.1 Historical background

Two thousand five hundred years ago the great Greek philosopher Thales of Miletus (624 to 556 BC), who was dubbed as the “father of science”, was the first to discover that amber stone when rubbed attract other objects. The Greek word for amber, ελεκτρον (electron), is the origin of electrostatic forces, which are used nowadays for almost 90% of all powder coating applications.

The appearance of powder coatings is often associated with the ecological and energy related events of the late 1960’s and early 1970’s. The famous **Rule 66** which was brought in by The Town Council of Los Angeles in 1966 was the first legislative act regulating the environmental aspects of the coatings. Later on similar regulations were introduced in most of the industrially developed countries.

Although the history of powder coatings has been strongly influenced by environmental aspects, first developments in the field began in the 1940’s with a simple flame spray application process. Early in 1950’s powdered PVC was successfully applied by *Gemmer* in a fluidized bed process on a preheated metal surface [1]. A patent application for *Gemmer’s* invention was filed in Germany in 1953 and the patent was issued in 1955. Very soon the fluidized bed technique for application of thermoplastic powders including polyethylene and nylon powder coatings was well established in the USA.

In the late 1950’s the first thermosetting powder coatings appeared on the market, mainly as a result of the research work done by Shell Chemicals. The target was development of superior protective (“functional”) organic coatings for the company’s own underground natural gas and oil pipelines. The first systems were relatively simple physical **dry blends** of epoxy resins, hardeners and pigments dispersed by ball milling techniques. Due to a considerable degree of heterogeneity, the application results were rather inconsistent.

The hot melt mixing methods of the present day for production of powder coatings were preceded by a technique that employed liquid epoxy resins and hardeners. The homogeneous liquid binder/crosslinker blend was prereacted until partially cured (“B stage”) solid material was obtained, which was finely ground in the next step. The completely cured “C stage” was obtained by stoving the “B stage” powders at high temperatures. A drawback of this technique was the lack of reproducibility and difficult control of the process [2].

Hot melt compounding on a heated twin roller mill or in a heated **Z-blade mixer** was already a step forward in the development of thermosetting powder coatings, but the immense cleaning problems, created by the fast(er) curing powder coatings, have almost completely excluded the Z-blade mixer and of course the twin roller mill from the machines (extruders) used to produce contemporary powder coatings. However, Z-blade mixers are still used for batch-wise production of thermoplastic powder coatings, where chemical reactivity does not play a role.

Extrusion methods for production of thermosetting powder coatings, which are in current use, were developed in the Shell Chemical Laboratories in England and The Netherlands in the period 1962 to 1964. In 1962 the first decorative epoxy/dicyandiamide (DICY) powder coatings, produced by Wagemakers (now DuPont) in Breda, and soon followed by Libert in Ghent and Van Couwenberghe in Le Havre, appeared on the European market. Also in 1962 SAMES in France developed the first equipment for **electrostatic spraying** of organic powder coatings. This made a considerable contribution to the success of decorative thermosetting powder paint, since for the first time coatings with an acceptable “thin” layer thickness could be applied.

One serious drawback of epoxy/DICY thermosetting powder coatings is their sensitivity to attack by UV light. Exposed to sun they chalk and deteriorate rapidly. This, followed by poor yellowing resistance restricted their use mainly to protective coatings or decorative coatings for interior use where resistance towards yellowing was not a prime target.

Attempts to overcome these problems led to polyester/melamine systems which were introduced in 1970 by Scado BV and UCB in The Netherlands and Belgium [3, 4]. Almost at the same time *Hüneke* reported that the gloss retention and yellowing resistance of powder coatings based on blends of epoxy and polyester resins is considerably improved compared to pure epoxy powders [5].

The real breakthrough in the area was made in 1971 by Scado BV in The Netherlands. It was discovered that coatings with exceptionally good decorative properties can be obtained by hot melt compounding of carboxyl functional polyester resins and epoxy compounds in the form of bisphenol A resins (polyester/epoxy hybrids) or triglycidyl isocyanurate (TGIC systems) [6]. Shortly after, in 1972 a **weathering resistant** powder coating system produced by VP-Landshut in Germany was used for protection of aluminum extrusions and claddings in outdoor architecture in Switzerland [7].

At the same time in 1971 Bayer AG and BASF AG in Germany each offered thermosetting acrylic powder coatings to the market. Although later on attempts to commercialize the acrylic systems failed in Europe and the USA, they were widely accepted in Japan for outdoor use.

In the 1980’s polyurethane powder coatings established a solid position in the American market and in Japan with a marginal market share in Europe.

Other developments in the area include a wider acceptance of PVDF powder coatings [8] mainly used for monumental architectural objects and ethylene chlorotrifluoroethylene (ECTFE) powders for protective purposes [9].

The development of new powder coating systems was quickly followed by improvements in the production and application equipment. Although the melt extrusion method, “borrowed” in the1960’s from the plastic industry, remained almost the only process used for powder production, contemporary plants are changing substantially and very often use a continuous concept of powder paint production.

Developments in the application equipment led to the introduction of so-called frictional **tribo guns**. The frictional method of electrical charging of powder coatings has reduced considerably the *Faraday* cage effect, improving the penetration of powder coatings into recessed areas during spraying. These developments were followed by corresponding efforts to overcome the inefficient tribo chargeability of polyester (including hybrid) powder coatings, which at this moment dominate the market [10–13].

Reclaiming of powder during application is an advantage that leads to almost **100 % utilization** of the material. This creates, however, serious problems with respect to the color change in the spraying booths. The producers of application equipment have made considerable efforts to speed up the color change. This resulted in the development of systems that allow color change up to 5 minutes which is quite close to the liquid systems [14]. But modern equipment suppliers have their doubts and say, that the shortest possible time for color changing is 10 to 15 minutes.

The **automotive market** is one of the most demanding concerning the protective and decorative characteristics of the coating. The lack of good flow was an inborn weakness of powder systems and the orange peel effect was one of the major concerns. Other problems encountered when powder paints were used as automotive body coatings were inconsistent transfer efficiency, color change time, color contamination, difficulties to reach areas around the doors, and under the hood and trunk areas. Together with relatively high curing temperatures these were the main reasons for powder coatings not being successful competitors to the wet paints for car body finishing. Therefore, for a long time all applications have been limited to underbody and interior trim components and later on to exterior trim parts and steel and aluminum car wheels and the car manufacturers remained reluctant to use powder as a full-body coating.

However, Honda in Japan began in the 1980’s with the application of a powder coating **primer-surfacer** on the car bodies, followed by Fiat in Italy. The car manufacturers in the USA were more careful, regarding the speed of introduction of full-body primer-surfacers. General Motors began in 1982 with a powder primer-surfacer on small pick-up trucks and built up experience and know-how, which was implemented in the early 1990’s to passenger cars. *Miller and Kerr* [15] summarize the qualities and advantages provided by powder primer-surfacers as follows: overall surface smoothness (improving the appearance of the succeeding layers), no VOC emission, chip and corrosion resistance for the entire vehicle body, almost 100 % utilization and no waste disposal problems.

Especially the combination of the high utilization rate and the elimination of paint sludge, collected in the spraying booths, make powder primer-surfacers very interesting paints from an economical point of view, and can be considered as one of the major driving forces for a “revolution” in the automotive industry. The following examples may illustrate it: In the period 1991 to 1995 General Motors and Chrysler introduced full-body powder primersurfacers in more than 10 production sites for passenger cars. Some years later Eurostar Works in Austria (a joint-venture of Chrysler and Steyer-Daimler-Puch) introduced powder primer-surfacers as full-body anti-chip coatings for their passenger cars [16]. These developments in the 1990’s secured and consolidated the position of the powder primer-surfacer at the automotive producers in the USA. This is confirmed by the fact, that in 2000 more than 10,000 car bodies were coated daily with powder primer-surfacers at both GM and Daimler-Chrysler [17]. This trend is now followed in Europe.

The automotive clear **topcoat** was considered for years as a too difficult field for powder coatings to enter in. But the ecological and economical advantages offered by powder coatings, and, last but not least, the proven success with the powder primer-surfacer, initiated extensive research work at both coating producers and car manufacturers. General Motors, Ford and Chrysler have formed the so-called Low-Emission Paint Consortium (LEPC) to jointly develop new technologies for application of powder clear topcoats on automotive bodies [18, 19]. BMW, Volvo, Audi and Renault are or were among the European car manufacturers, experimenting with powder clear topcoats over metallic base coats.

BMW is the first car manufacturer in the world to use powder clear topcoat in standard production. Up to the end of 2000 powder clear topcoats has been commercially utilized in BMW's German plant for over 500,000 cars [20]. Since 2007 the main supplier of powder clear coats, PPG and BASF, delivered 800 t to BMW each year.

1.2 Market situation and powder economics

The different powder coating systems that have been developed in the last 40 years employ most of the polymers used in the conventional solventborne coatings. At the same time the continuing market growth considerably lowered production costs. Combined with sharp price increases of solvents after the "oil shock" in the 1970's this resulted in powder coating prices comparable with those of the wet coatings. Therefore powder coatings today are recognized not only as environmentally friendly systems, but also as materials that can compete successfully in price with the solvent and waterborne coatings.

Next to environmental and price aspects, quality is an even more important element, especially in high-tech areas of use, where powder coatings are commonly used. In this respect, powder coatings satisfy many of the most stringent requirements by the end users, failing only in cases where an extremely good flow of the coating is expected. Therefore the answer to the question *"why powder?"* contains the popular "**Four E**'s" introduced 1986 by *Bocchi* [21]:

- Ecology
- Excellence of finish
- Economy
- Energy

Even a fifth E could be added for efficiency: no need get rid of a solvent to cure. Comparing the relative importance of these factors, it can be said, that at the moment, the high quality and the economic aspects perhaps contribute more to the acceptance of powder coatings by industrial users, than the regulatory compliances alone.

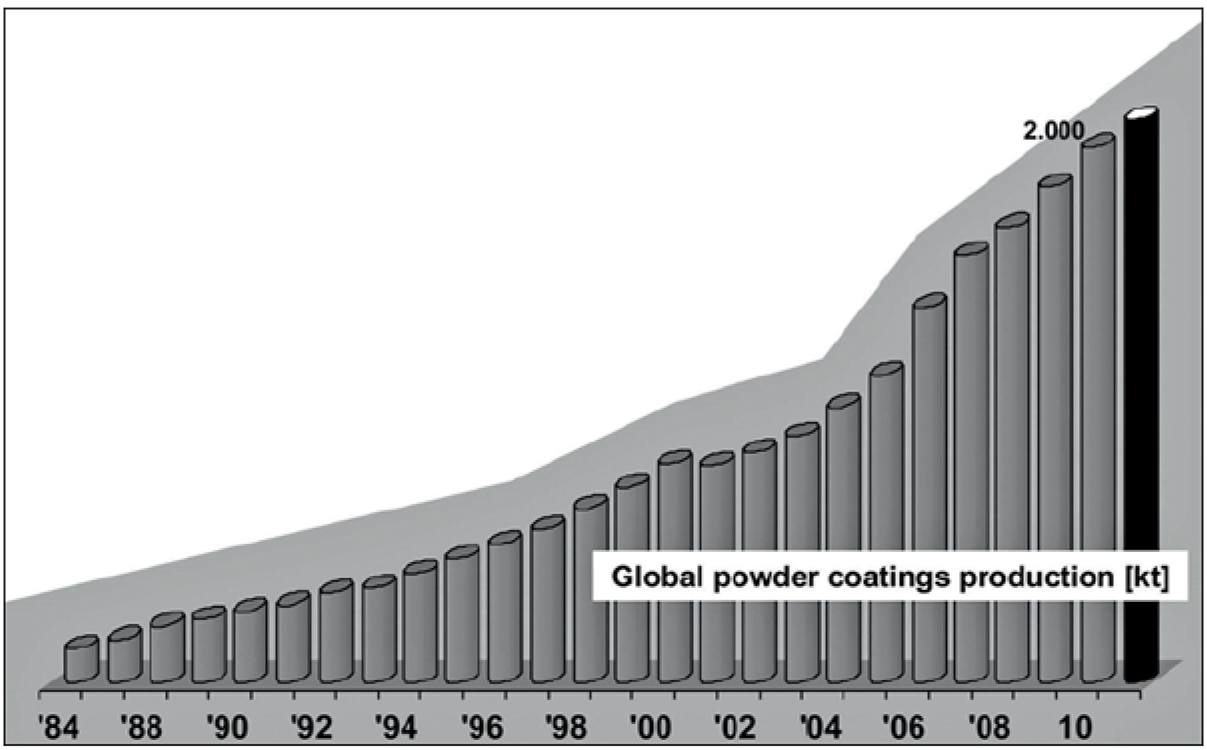

Figure 1.1: Global powder coating production since 1984 [23]

source: Evonik Industries

The market shares of powder coatings compared to other types of coating materials are not yet large. However, in a relatively mature field like the paint industry, powder coatings are among the few still enjoying a considerable growth in volume per year. According to available

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