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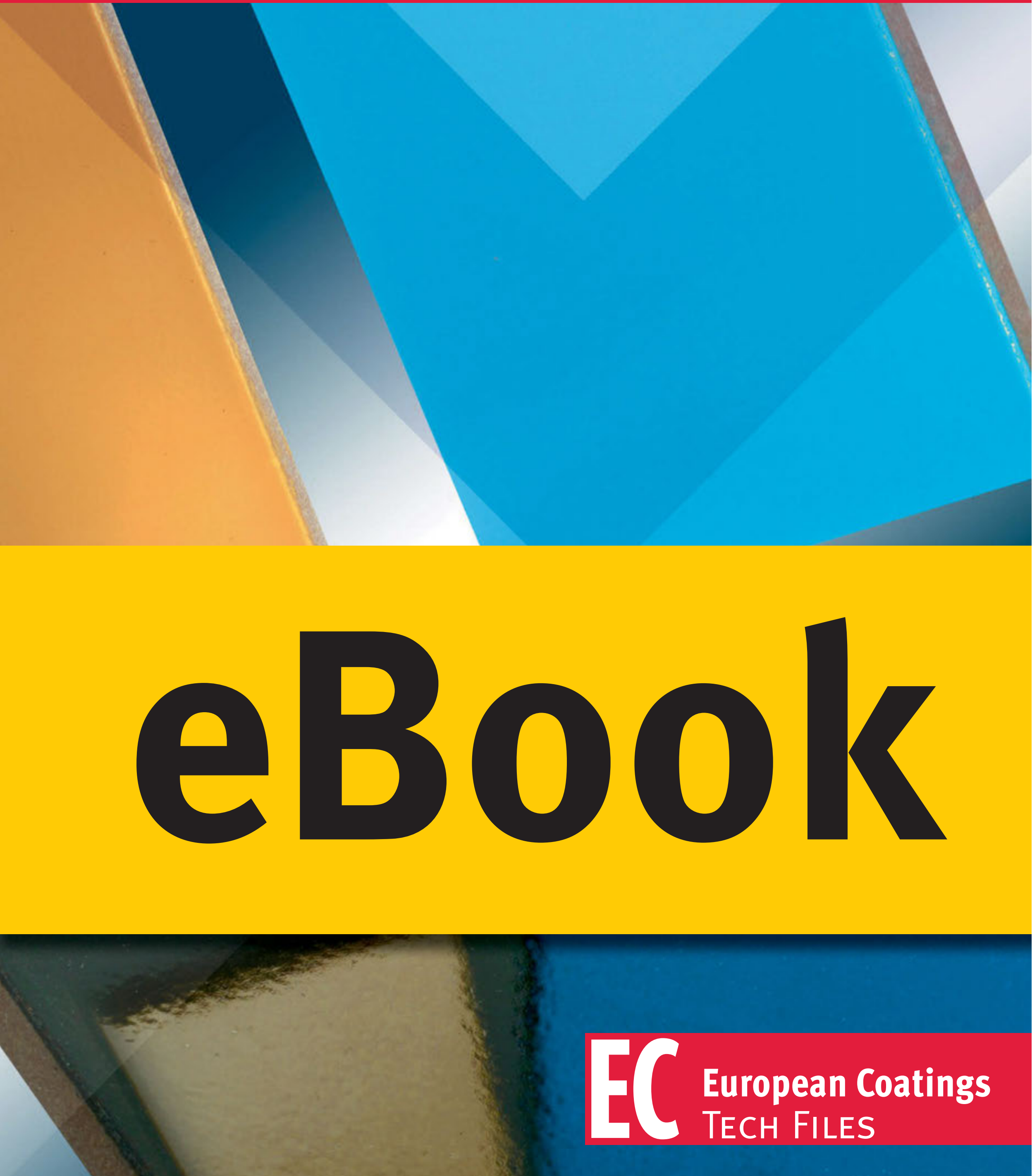
Emmanouil Spyrou

Powder Coatings Chemistry and Technology

3rd, Revised Edition



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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 3rd 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

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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 primer-surfacers 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.

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 marketing data the world-wide market for powder coatings was 290 kt in 1990, 900 kt in 2001 [22], and about **2000 kt in 2010** [23] as shown in *Figure 1.1*, representing a total value

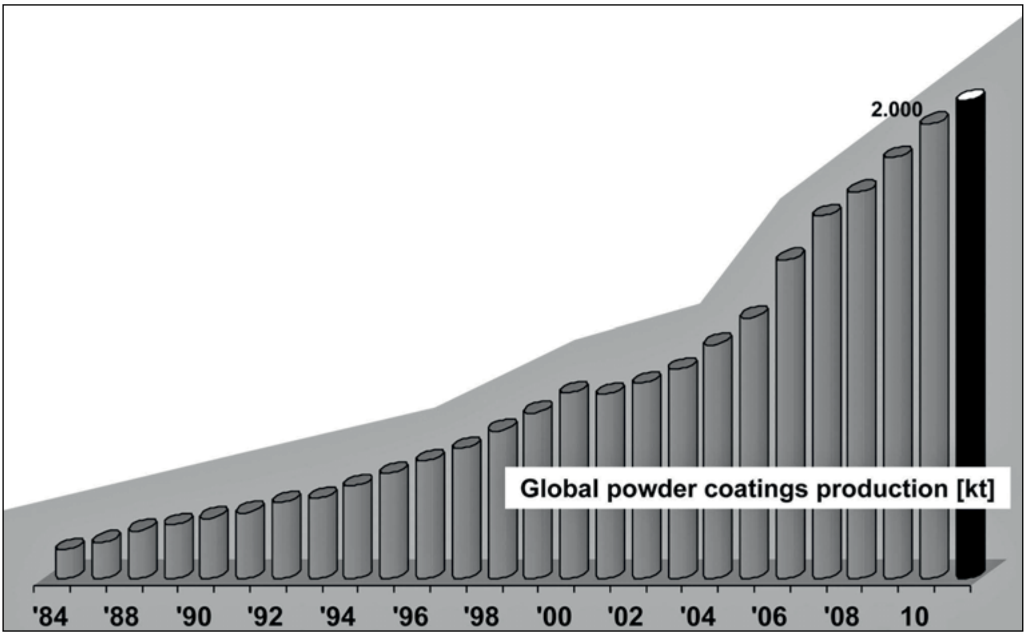

Figure 1.1: Global powder coating production since 1984 [23]

source: Evonik Industries

of roughly 8 billion € ($ 10 billion). The annual growth rate, which showed double digits (more than 10 %) up to 1991, has been decreased in recent years to 4.5 to 10 % (varying by region), due to an economic recession in the nineties and a serious financial crisis in 2009.

Western Europe, where the powder coatings were invented, shows the lowest annual growth rate in the last 10 years, but the highest market share in industrial coatings (18 %), when compared to North America (15 %) and Japan (15 %) [24]. Inefficient production sides are recently rationalized and eliminated in Western Europe and reopened in lower-cost emerging regions like **China**. *Table 1.1* based on data of SRI Consulting [24] gives an indication of the production of powder coatings in different geographical areas. China accounts for 700 kt in 2007, but it is believed that only half of it meets western quality (and price!) standards. The Chinese impetus is not restricted on production volumes. 2004 only 12 % of the patent applications in the field of powder coatings were filed in Chinese, 33 % in English and 30 % in Japanese. This picture is reversed in 2011: Now China is the formal innovation leader with 37 % patent applications, followed by English (27 %) and Japanese (18 %). It has to be mentioned, though, that similar to the powder coatings not all of the Chinese patents meet the high western standard, yet.

The various types of powder coatings commonly used in different **geographical locations** differ considerably. For example the three major market areas in the world, Europe, USA and Asia, have developed completely different systems for exterior use. In Europe, systems based upon carboxyl functional polyester resins/ß-hydroxy alkylamides (HAA) – which have replaced TGIC almost totally in the last couple of years – are the most popular, in the USA polyurethanes with aliphatic polyisocyanates as crosslinkers have dominated for many years, but ever since 1998 they are competing with the polyester/TGIC/HAA/PT910 (TGIC alternatives) types, while in Japan powder coatings with glycidyl functional acrylic resins as binders and dibasic acids as crosslinkers and polyurethanes are market leaders. TGIC systems are not at all used in Japan [25]. For coatings for indoor applications the so-called hybrids, based on carboxylated polyesters and epoxy resins, are the most popular, both in Europe and the USA. *Table 1.2* presents average figures for the **market shares** of five types of powder coatings [23]. The different regional consumption of these competitive powder coating systems are accounted to historical reasons, differences in prices and availability of resins, toxicological issues, governmental regulations and an unequal intensity of sunlight which the coatings are exposed to [24].

More than **1000 powder coating producers** are active world-wide, most of them serving a limited geographical area. The three largest are responsible for 30 % of the global market if China is excluded. These three multinationals are AkzoNobel, DuPont and Rohm and Haas. In China there are about 600 powder coating formulators, but the majority of them are very small.

Table 1.1: The world market for powder coatings by region for 2000 and 2007 [24]

	2000		2007	
	Kilo tons	**%**	**Kilo tons**	**%**
Western Europe	335	41	377	23
North America	175	22	189	11
China	96	12	700	43
Rest of Asia/Pacific	119	15	183	11
Rest of World	85	10	196	12
Total	**810**	**100**	**1645**	**100**

Table 1.2: Market shares (in %) of different types of powder coatings [23]

	W-Europe	N-America	Asia	ROW	World
Epoxy	6	13	13	9	10
Epoxy-polyester (hybrid)	52	32	52	51	50
PES-TGIC + Derivatives	11	29	26	24	22
PES-ß-Hydroxyalkylamide	28	4	7	15	13
Polyurethane	2	17	2	1	4
Acrylic	1	5	0	0	1

The **metal furniture** industry was one of the first areas invaded by powder coatings, and it is steel that is the important substrate. Hybrids are the main type used for this purpose, while for outdoor furniture (garden furniture for example) polyester/TGIC (and its alternatives) or polyurethanes are the common systems.

The industry of **domestic appliances** is an important consumer of powder coatings. Appliance applications in total represent about 14 % of the market for powder coatings world-wide [26]. More than half of this market is located in Asia Pacific, since the appliance production itself has been shifted largely in this region. In Europe hybrids are the main type used since a mild orange peel effect is acceptable. In the U.S. a smooth finish is preferred and therefore polyurethanes are much more common. Typical products of this industry that are coated with powder coatings are food freezers and refrigerators, water heaters, toasters, washing machine lids, domestic cookers, electric and gas heaters, etc.

Architectural application is still the most important market for powder coatings, holding a market share of 36 %. Aluminum plays a special role in this field. Powder coatings show a penetration of roughly 30 %, whereas anodizing accounts for 55 %. In 2007 45 % of the powder coated architectural aluminum has been located in Europe, 34 % in Asia Pacific and only 3 % in North America. In U.S. coil coating panels are used predominantly, due to cost reasons [24].

The **automotive market** accounts for one third of all powder coating applications. The major part of this is claimed by primer-surfacer, a coating to protect the electrocoat primer and to provide a smooth surface for the basecoat. Primer-surfacer resins are usually made by acrylic/styrene/methyl methacrylate mixtures and cured by dodecanoic diacid (DDDA). But ß-hydroxyalkylamide (HAA) based systems and polyurethanes are used, too, due to superior chip resistance. The system, that has been chosen by all car producers, for automotive topcoats is a blend of an epoxy functional acrylic copolymer containing glycidyl methacrylate (GMA) as co-monomer, and DDDA or its (poly)anhydride as crosslinker. Very positive experiences are reported with such acrylic clear topcoats [27]. In 2007 almost half of the powder world market for automotive has been located in Europe, one third in North America [24].

The market growth of **exterior powder coatings** has continued to expand due to the wide acceptance of polyester/HAA systems in Europe and polyurethanes in the USA. Exterior coatings held a market share of 9 % of all powder coatings in 2008 [26].

Another market for powder coatings is in corrosion resistant types for e.g. **pipes and reinforcement bars** (rebars) holding a share o about 6 %. One third of this amount was produced in China, one fourth in the rest of Asia Pacific in 2007 [24]. This is the area where pure ("fusion-bonded") epoxies dominate. In Europe the rebar market has been largely ignored, but its importance from a technical point of view has been recognized and this is an area where a considerable growth can be expected.

When powder coatings economics is compared with the other VOC (volatile organic compound) compliance coating options, one has to take into account all of the expenses connected with the coating process. On-line operating advantages reported for powder coatings compared with other environmental friendly systems are an application utilization of the material from 95 % up to 99 %; 30 % less energy consumption (than with conventional low-solids enamels), combined with a reduction of labor expenses of 40 to 50 %; reduction of waste material accounts for almost 90 % and there are approximately four to six times fewer rejects due to surface defects [28].

Figures with respect to the **economy of the powder** coatings process have been published by the PCI [28] in 1999. The major cost factor for powder coating formulations is raw materials which make up for two thirds of the total costs. In powder coating applications of medium sized job shops the powder coating itself attributes only for 20 % of total costs, the main factor is labor (40 %) [24].

Recent developments in application equipment that make the clean – out of the line easier and the change of the color faster and the trend in developing powders with lower curing temperatures and higher reactivity, which allows higher line speeds thus saving energy, make the economics concerning powder coatings even more attractive. The “Four E’s” – excellence of finish, ecology, economy and energy – are attributes the powder coatings future can certainly rely upon.

1.3 REACH

No chemical legislation ever before has influenced the research, the production and the sales of coating raw materials as fundamentally as REACH – The chemicals legislation of the European Community. Therefore a short description of REACH will follow in this chapter.

REACH (Regulation EC (No) 1907/2006) is the chemicals legislation of the European Community (EC) which came into force in 2007. REACH consists of three main legislative processes: registration, evaluation and authorization of chemicals.

Registration process

All substances which are produced within the EC in quantities of at least 1 metric ton per year have to be registered by the EC manufacturer. Furthermore all substances which have to be imported in quantities of at least 1 metric ton have to be registered by the EC importer. These substances are either imported as pure substances, as substances in mixtures or as monomers covalently bound in imported polymers. A registration is also needed for certain substances contained in imported articles. For registration a Technical Dossier has to be submitted to the European Chemicals Agency (ECHA). The Technical Dossier contains information regarding substance identity, uses of the substance and information about physicochemical, toxicological and eco-toxicological properties. For this purpose available studies should be used, either own studies or studies that have to be shared between the registrants after receipt of a Letter of Access from the study owner. If no study or other alternative data (e.g. read across, qualitative or quantitative structure-activity relationships) are available, physicochemical, toxicological and eco-toxicological studies have to be conducted. With regard to animal welfare, multiple testing of a substance has to be avoided, i.e. studies with vertebrates shall be conducted only once. The registration costs can rise up to several hundred thousands of Euros depending on the substance properties, the annual quantity of the substance, data availability and number of registrants.

Furthermore a Chemical Safety Report has to be submitted to ECHA for substances registered in quantities of at least 10 metric tons per year and per registrant. The Chemical Safety Report consists of an exposure assessment and a risk assessment, which has to be conducted for hazardous substances based on their physicochemical, toxicological and eco-toxicological properties.

A simplified registration is allowed for intermediates which are produced and used under strictly controlled conditions.

Transition periods are granted, if the substance is pre-registered by the potential registrant. Within the transition periods the potential registrant can produce or import the pre-registered substances without registration. The transition period for substances produced or imported in quantities of at least 1000 metric tons per year as well as for substances with carcinogenic, mutagenic or reprotoxic properties (≥1 ton/year) and for substances that are dangerous to the environment (R 50/53 substances ≥100 tons/year) expired in 2010. The transition period for substances produced or imported in quantities of at least 100 metric tons per year ends in 2013 and for substances produced or imported in quantities of at least 1 metric ton per year the transition period ends in 2018.

There are substances that are exempted from REACH registration. Whereas article 2 of the REACH regulation lists substances that are regulated by other legislations, annexes IV and V of the regulation include substances that are exempted from registration (e.g. natural substance such as glucose, carbon dioxide, nitrogen, crude oil).

Polymers are exempted from registration as well but the monomers that are used to manufacture the polymer have to be registered either by the producer of the monomer, by the EC importer of the monomer or by the EC importer of the polymer. Since powder coating raw materials are often polymers, **powder coating have a natural advantage** over other environmentally compliant coatings systems, e.g. UV-curing formulations.

Substances produced or imported for product and process orientated research and development (PPORD) are exempted from registration for at least five years. However the manufacturer or importer has to notify the substance to ECHA.

Evaluation process

The evaluation process will be conducted by ECHA and the national competent authorities of the Member States. Within the dossier evaluation process, ECHA checks the registration documents for compliance and evaluates the testing proposals that are included in the Technical Dossier. The substance information and the chemical safety assessment are evaluated by ECHA in cooperation with the competent authorities of the different Member States.

Authorization process

The authorization process aims to control risks from Substances of Very High Concern (SVHC) and to replace the substances by suitable alternatives substances or to develop alternative technologies. Therefore, the uses of these substances have to be authorized by the European Commission.

The following categories of substances are considered to be Substances of Very High Concern:

- carcinogenic, mutagenic and reprotoxic substances
- persistent, bioaccumulative and toxic substances (PBT substances)
- very persistent, very bioaccumulative substances (vPvB substances)
- substances of equivalent concern (e.g. endocrine disruptors)

Substances of the mentioned categories will be listed in Annex XIV. If a substance is listed in this annex, it can be used only, if an authorization dossier was submitted and approved by the European Commission.

More detailed information about REACH and current activities of ECHA is available at the ECHA homepage (http://echa.europa.eu).

1.4 References

[1] *Gemmer, E.*, Industrie-Anzeiger, 75, 1095 (1953)
[2] *Harris, S.T.*, The Technology of Powder Coatings, Portcullis Press Ltd., Redhill, England, 1976
[3] Scado BV, US Pat. 3.624.232, 1970
[4] UCB SA, DE Pat. 2.352.467, 1972
[5] *Hüneke von H.*, Metalloberfläche, 24, (9), 315, 1970
[6] Unilever N.V., DE Pat. 2.163.962, 1971
[7] *Bodnar, E.*, Product Finishing, August 1988, p.22
[8] *Meiyden, B. van der*, in Thermoset Powder Coatings, Ed. John Ward, FMJ International Publications Ltd, Redhill, 1989, p.54
[9] *Maguire, G.*, Product Finishing, October 1988, p.66
[10] *Misev, A.T., Binda, P.H.G., Hardeman, G.*, to Stamicarbon BV, NL Pat. 8.800.640, 1988
[11] *Misev, A.T., Binda, P.H.G.*, to Stamicarbon B.V., NL Pat 8.802.913, 1988
[12] *Binda, P.H.G., Misev, A.T.*, to Stamicarbon B.V., NL Pat. 8.802.748, 1988
[13] Hoechst AG, EP 315 082, 1987; Hoechst AG, EP 315 083, 1987; Hoechst EP 315 084, 1987
[14] *Floyd, R.*, Polymers Paint Colour Journal, 179, (4236), 270, (1989)
[15] *Miller and Kerr*, Proceed. Powder Coating '92 (1992) p. 79
[16] FARBE&LACK, 102, 8, (1996) p. 16
[17] *Harris, S.T.*, Focus on Powder Coatings, Nov. 2000, p. 3
[18] *Cole, G.*, Industr. Paint & Powder, 69, (12), 24 (1993)
[19] *Bailey, J.*, Industr. Paint & Powder, 70, (7), 12 (1994)
[20] Modern Paint and Coatings, 91, (2), 13 (Feb. 2001)
[21] *Bocchi, G.J.*, Modern Paints and Coatings, 76, 44, (1986)
[22] *Harris, S.T.*, Focus on Powder Coatings, Oct. 2002, p. 8
[23] *Grenda, W., Spyrou, E.*, Congress Papers European Coatings Congress (ECS), Nuremberg, 113, 2011
[24] *Linak, E., Kishi, A., Yang, V.*, Thermosetting Powder Coatings, Specialty Chemicals SRI CONSULTING, 2008
[25] *Rankl, F-J.*, (CEPE), Proc. Pulverlack Kongress, Hamburg, Sep.'96, p. 6, 1996
[26] *Moran, B.*, Market research report, Powder Coatings: Materials, Coatings, Technologies, CHM051A, BCC research, 2009
[27] *Schmidt, H. and Fink, D.*, Surface Coatings International, 2, p. 66, 1996
[28] Powder Coating – The Complete Finisher's Handbook, Edited by the PCI, p. 301–304, 2nd Ed. 1999

2 Thermoplastic powder coatings

The first powder coatings produced were based on thermoplastic polymers which melt at the application temperature, and solidify upon cooling. Several factors such as relatively simple methods of manufacturing and application, no involvement of complicated curing mechanisms, raw materials that in many cases belong to commodity polymers, acceptable properties for many different applications etc. contributed to the popularity of these coatings in the market very soon after their appearance in the beginning of the 1950's. At the same time, however, weaknesses such as high temperature of fusion, low pigmentation level, poor solvent resistance and bad adhesion on metal surfaces necessitating the use of a primer can be listed. These problems inherent to the thermoplastic powder coatings were successfully overcome later on by the thermosetting powders which very quickly took the largest part (90 %) of the market.

Despite the disadvantages, thermoplastic powder coatings can offer some distinguished properties. Some of them possess excellent solvent resistance (polyolefins), outstanding weathering resistance (polyvinylidene fluoride), exceptional wear resistance (polyamides), a relatively good price/performance ratio (polyvinyl chloride) or high aesthetic appearance (polyesters). These properties combined with the simplicity of the system, created a considerable market share for thermoplastic powder coatings.

Thermoplastic coatings are offered in a variety of performance classes (*Figure 2.1*). Besides the engineering and commodity polymers, which will be discussed in the following chapters, there are high performance polymers, e.g. PEEK (polyether ether ketones).

PEEK is a fully aromatic, semi-crystalline thermoplastic polymer with a maximum crystallinity of 48 %. It is a member of the class of polyaryl ether ketones (PAEK) high performance polymers. PEEK has a glass transition point of 143 °C and a melting range of ca. 340 °C. Characteristics of the polymer include a very high heat resistance and therefore service temperature, high rigidity, low water absorption, high hardness, good strength, low sliding friction, excellent chemical and hydrolysis resistance, low flammability, very low emission of smoke and toxic fumes during burning and its good electrical characteristics. PEEK offers one of the highest resistances against radiation among polymers.

Due to its high price PEEK is normally only used in applications where special properties are needed. Examples include valves, cable insulation, bearings, pump parts and sealings. Evonik Industries offers industrial grade PEEK under the trade name "Vestakeep".

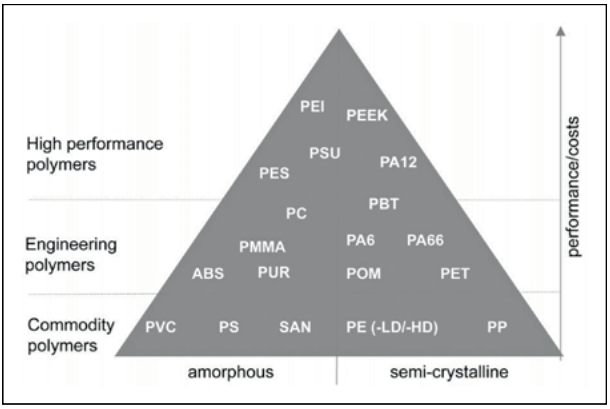

Figure 2.1: Performance/cost ratio of thermoplastics

source: Evonik Industries

Emmanouil Spyrou: Powder Coatings: Chemistry and Technology

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2.1 Vinyl powder coatings

Two binders are used for the manufacture of the so-called vinyl powder coatings; polyvinyl chloride (PVC) and polyvinylidene fluoride (PVDF). On the basis of their polymer nature both powder coatings can be included in the same group, although they differ considerably in their performance. While PVC powder coatings are predominantly intended for indoor application because of their limited outdoor durability, PVDF powder coatings are among the best coating systems with respect to their weathering resistance.

Vinyl polymers belong to a group of resins having a vinyl radical as the basic structural unit. Polyvinyl chloride and copolymers of vinyl chloride are the most significant members of this group being among the first thermoplastics to be applied by powder techniques.

2.1.1 PVC powder coatings

Polyvinyl chloride powder coatings were introduced on the market in the time when the thermosetting powder coatings were in very early stages of development. PVC based coatings offered many advantages over the other thermoplastic materials available as binders for coating production. These coatings have very good resistance to many solvents, which is a rather poor characteristic of the thermoplasts, combined with resistance towards water and acids. They have excellent impact resistance, salt spray resistance, food staining resistance, and good dielectric strength for electrical applications.

Polyvinyl chloride $(-CH_2-CHCl-)_n$ is one of the **cheapest polymers** produced by the industry on a large scale. Its basic properties include chemical and corrosion resistance, good physical strength and good electrical insulation. Polyvinyl chloride (PVC) is by nature a brittle polymer, but the flexibility of the material can be easily adjusted by using an appropriate amount of a suitable plasticizer.

Polymerization of vinyl chloride into PVC homopolymer or its co-polymerization with different co-monomers is carried out by a free radical mechanism. Most PVC resins are produced by emulsion or suspension polymerization of vinyl chloride in an aqueous system containing an emulsifying agent or suspension stabilizer. However, bulk and solution polymerization processes are also carried out on an industrial scale.

Emulsion polymerization of vinyl chloride can be performed in both a batch and continuous way. The reaction temperature is maintained between 40 and 50 °C by cooling the reactor in order to remove the heat developing during the polymerization. The reaction medium is de-ionized water containing enough proper surfactant to obtain a stable emulsion. The initiators used are peroxides soluble in water, such as hydrogen peroxide or different persulphates. Since the monomer itself is a gas at room temperature, the polymerization is performed under pressure in autoclaves. The pressure in the reactor falls as the polymerization proceeds. After reaching conversion of ca. 90 %, the content of the reactor is discharged and the unpolymerized vinyl chloride is recovered.

Suspension polymerization of vinyl chloride is an important process in the commercial manufacture of PVC. In principle it is a batch process, although attempts have been made to develop a continuous technique for suspension polymerization of PVC. The polymerization is carried out by first charging to the reactor the required amount of de-ionized water and adjusting the pH depending on the suspending agent used and then the dispersing agent and the initiator. The monomer is charged after sealing the reactor and evacuating the oxygen. The polymerization reaction is carried out under pressure at 40 to 60 °C, controlling the temperature by appropriate cooling of the reaction mass. Although a great amount of research has been done in this area, it is interesting to note that the compositions of the reaction mass do not differ substantially from those used in the very early days of development of suspension PVC. The differences are mainly limited to the choice of the suspending agent, which is in most cases polyvinyl alcohol obtained by saponification of polyvinyl acetate, gelatin, methyl cellulose and copolymers of vinyl acetate with maleic anhydride. The initiator is water insoluble peroxide, such as lauryl peroxide, or azobisisobutyronitrile.

The type of suspending agent plays a very important role in obtaining primary particles with high porosity. Gelatin normally produces glassy spherical particles which have poor plasticizer absorption characteristics, whereas polyvinyl alcohol gives particles of a porous nature which readily absorb plasticizers to give dry powder blends. Thus, a patent of Air Products and Chemicals, Inc. [1] discloses a process for suspension polymerization of vinyl chloride giving a polymer specially suitable for production of powder coatings. The use of an excessive amount of secondary suspending agent causes two effects necessary for the critical powder coating application. Firstly, it reduces the size of the primary particles within the polyvinyl chloride grain, thus raising the surface to volume ratio and allowing plastication of the primary particles by the plasticizer. Secondly, very high porosity is gained, allowing complete and uniform plasticization of the resin grain in its entirety.

Solution polymerization of vinyl chloride is almost exclusively used for manufacturing copolymers containing vinyl acetate. The co-monomers are dissolved in a suitable solvent such as cyclohexane or n-butane, and the polymerization is carried out at 40 to 60 °C catalyzed by a free radical initiator which is soluble in the reaction mass. The copolymer begins to precipitate after a certain molecular mass is reached, which depends on the co-monomers' ratio, polymerization temperature and type of solvent. The last step of the process includes filtering of the final product and then washing to remove the residual diluent and any traces of organic peroxide which would have a detrimental effect on the heat stability.

The **bulk polymerization** of vinyl chloride has been developed by Pechiney-St. Gobain, and plays an important role in the commercial production of PVC. Although bulk polymerization is associated with a homogeneous system, this is not the case with the bulk polymerization of vinyl chloride; namely, at very early stage of the reaction the polymer formed precipitates from the reaction medium in a form of insoluble material dispersed in the monomer. The system is therefore heterogeneous for a significant portion of the whole conversion. Since the polymer precipitates from the monomer, and there are no solvents present in the system, the concentration of the monomer available for polymerization remain constant with time. Therefore, at constant temperature the average molecular weight of the polymer obtained is apparently independent of the monomer conversion.

Bulk polymerization of vinyl chloride is performed in variants of the original Pechiney two-stage process. Vinyl chloride containing initiator is charged in a reactor and the polymerization is carried out at 50 to 60 °C. Already at 1 % conversion the polymer begins to precipitate. After reaching conversion of about 10 % the entire content of the reactor is discharged in an autoclave where a further quantity of vinyl chloride is added. When the conversion is at about 20 % the material is in the form of a wet powder; at 40 % conversion the residual monomer is completely absorbed by the polymer and the mass takes on the form of a dry powder. The design of the reactor permits further polymerization which usually proceeds up to 90 % conversion. The residual monomer is then removed under vacuum and the polymer is discharged and sieved. Polymer particles with sizes larger than desired undergo additional grinding and sieving.

Polyvinyl chloride is an **amorphous polymer** containing very small amounts of imperfect crystallites. The average molecular weights for the most commercial PVC resins are in the range 50,000 to 120,000. Better physical properties are obtained by PVC having a high molec-

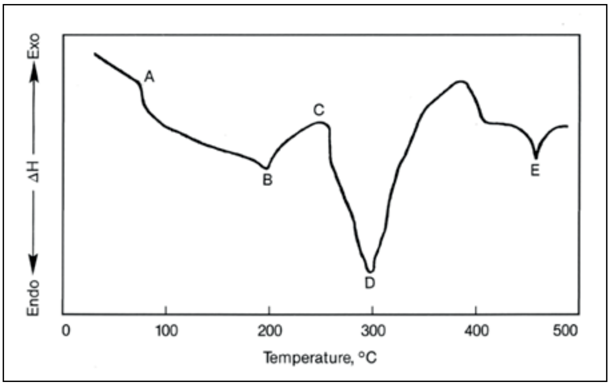


Figure 2.2: Differential thermal analysis curve of unplasticized PVC[3] *source: Federation of Societies for Coatings Technology*

ular weight, but on the other hand, for applications in powder coatings, PVC resins with low molecular weight are more suitable because of lower melt viscosity and lower softening temperatures. Although different glass transition temperatures ranging from 68 to 105 °C are reported, depending on the method of polymerization and especially the temperature at which the polymerization is carried out, the normal commercial grades of PVC have T_g of between 80 and 85 °C.

Figure 2.2 represents the **differential thermal analysis** curve of polyvinyl chloride. Five major regions of different thermal behavior can be noticed above room temperature. *Matlack* and *Metzger*[2] and *Smith* and *Koleske*[3] assign the glass transition temperature to the change of the slope at point A. The endothermic effect between 165 and 210 °C is a result of the melting of the crystallites present in the polymer. At 250 °C they define the point C as a region of oxidative attack, while at 300 °C (point D) the dehydrohalogenation takes place with evolving gaseous hydrogen chloride. Finally, at about 450 °C (point E) the endotherm is attributed to the occurrence of depolymerization.

Polyvinyl chloride is soluble in a wide range of organic solvents. The best solvents for PVC are tetrahydrofuran and cyclohexanone, but it is also easily solubilized by other ketones, halogenated hydrocarbons and nitrated aromatic solvents. However, from the standpoint of a powder coating producer it is important that PVC polymers are not soluble in alcohols and aliphatic hydrocarbons, and powder coatings having PVC as a binder possess considerable **solvent resistance** with respect to the most common solvents used in the industry.

The performance characteristics of the vinyl powder coatings have been compared by *Christensen* and are summarized in *Table 2.1*[4]. Comparisons of this type are always discussible. In this case, the outdoor durability of the vinyl polymers should be reconsidered, keeping in mind new developments particularly those of polyester thermosetting coatings. The table, however, gives a good indication of the characteristics of the vinyl powders with respect to the other thermoplastic materials.

The **main problems** of PVC powder coatings are related to the stability of the binder during processing, and also its brittle nature. These weak points were successfully overcome

Table 2.1: Performance characteristics of various powder coating materials[4]

	Vinyl	Polyester	Epoxy	Nylon	Polyethylene
Exterior durability	+++	++	0	+	0
Salt spray resistance	+++	+	++	++	+
Impact resistance	+++	+	+	+++	0
Flexibility	+++	0	0	++	+++
Food staining	+++	+++	+++	++	+++
Dielectric strength	++	+++	+++	+	+++

+++ = Excellent, ++ = Very good, + = Good, 0 = Fair

due to the enormous amount of work that was done on stabilization and plasticization of polyvinyl chloride. The result was development of a number of heat stabilizers, plasticizers and lubricants permitting problem-free hot compounding of the vinyl resins.

Because it is a rigid material not having sufficient flexibility polyvinyl chloride as such can not be used for powder coating purposes. In fact, only in a few applications can PVC be used without the addition of **plasticizers**. A wide range of high boiling materials has been developed for plasticization of PVC, such as esters of phthalic acid, phosphoric acid and aliphatic diacids. Liquid polymers or oligomers with relatively low glass transition temperatures are also used for the same purpose.

Phthalate esters are the cheapest plasticizers for PVC, proving to be very satisfactory over all properties. Di-2-ethylhexyl phthalate and diisooctyl phthalate have been the most widely used, offering a good price/performance ratio. But recently diisononyl phthalate gained more and more attention and market share due to a lower migration rate. It is also characterized with better oxidation stability and low-temperature flexibility.

Phosphate esters are used to obtain PVC products with **self-extinguishing properties**. Trixylyl phosphate is the most widely used material among the great variety of phosphate esters. The same self-extinguishing effect is obtained by the use of chlorinated paraffins. They in general cannot completely replace the so-called primary plasticizers of phthalate or phosphate type, but they are quite competitive for price reasons. The common chlorinated paraffins used for plasticizing PVC have 42 to 56 % chlorine content and a chain length of C_{15} to C_{25}.

Linear polyesters produced by esterification of dibasic acids with dibasic alcohols are plasticizers that provide good solvent resistance. They are especially suitable for PVC coatings in contact with hydrocarbon fuels or other organic solvents. However, polyvinyl chloride plasticized with polyesters exhibits relatively poor low-temperature flexibility.

The addition of the plasticizer to PVC improves the flexibility and the impact resistance of the polymer, but at the same time reduces the tensile strength, modulus and hardness of the plasticized material. The desired balance between **hardness** and **flexibility** can be achieved by careful choice of the type and amount of plasticizer. Although many efforts have been made to predict the behavior of the plasticized system by systematic approaches to this problem, the desired set of properties is usually achieved by making a series of formulations.

The curve representing **modulus-temperature behavior** of externally plasticized PVC with dioctyl phthalate (DOP) exhibits a typical drop of the modulus at the glass transition temperature at 80 to 90 °C with the rubbery plateau region afterwards in the non-plasticized PVC *(Figure 2.3)* [3]. A further increase of the temperature leads to melting of the crystallites, resulting in an additional drop of the modulus. The addition of DOP shifts the rubbery plateau to lower temperatures, but at the same time decreases the modulus, in this way affecting the hardness of the film.

The type and amount of added plasticizer must be determined in a way that will result not only in a good compromise between flexibility, impact resistance and hardness, but also in a way that will not affect the powder storage stability. Due to a concern over plasticizer leaching into food the market share of PVC has decreased, in particular in the western hemisphere.

Polyvinyl chloride that exhibits good mechanical properties has a molecular weight above 40,000. In pigmented systems, due to such a high molecular weight, there is a considerably more pronounced increase of the **melt viscosity** compared to the thermosetting binders. The melt viscosity of PVC pigmented with TiO_2 shows an asymptotic increase at concentrations of the pigment between 15 and 25 % (by weight). This is almost four times lower than the concentration of the alkyd resins [3].

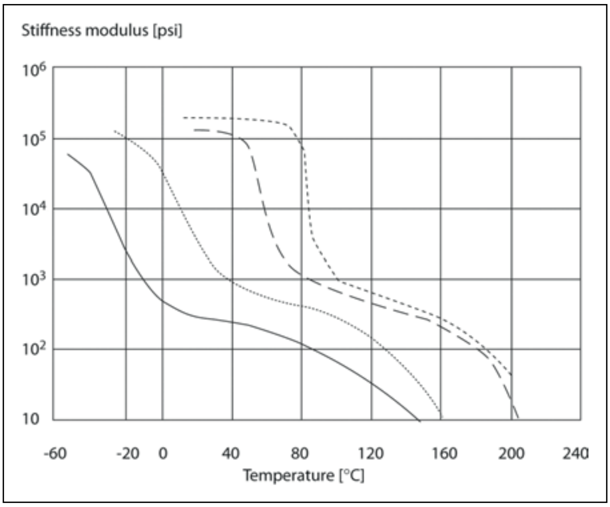
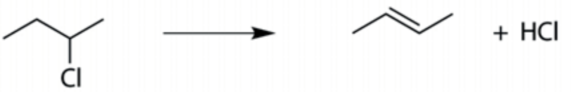


Figure 2.3: Modulus temperature behavior of externally plasticized PVC [3] source: Federation of Societies for Coatings Technology

High melt viscosity of the pigmented PVC powder coatings is one of the reasons for their application in thick films in order to obtain good flow. Very often the low price of PVC powder coatings is compensated by the thick film application, losing in this way the advantage of having cheap and good quality protection. *Smith* and *Koleske* have suggested, that for film thickness below 50 μm, the melt viscosity during cure should be in the range between 50 and 500 Pa · s [3]. This corresponds to a weight averaged molecular mass of between 20,000 and 40,000 (Mn = 10,000 to 20,000), which is 2 to 4 times lower in value than the commonly used molecular masses.

PVC powder coating with a proper formulation should always contain a suitable **stabilizer**. An enormous amount of work has been done to elucidate the mechanism of thermal degradation of polyvinyl chloride. It is beyond the scope of this book to go into detail about the degradation phenomena of PVC. The overall reaction of decomposition involving hydrogen chloride will be presented simply as an illustration to help explain the role of the stabilizers:

Equation 2.1



The common property of all materials used for stabilization of polyvinyl chloride is the ability to react with hydrogen chloride. It seems rather strange that the stabilizer reacts with the product of degradation, i.e. it is active after the degradation has happened. Therefore, it can be assumed that the stabilizer decreases the rate of degradation, lowering the concentration of hydrogen chloride that may act as a catalyst for the degradation process. This can be accepted for some simple stabilizers such as the metal stearates. The experiments with labeled stabilizers of a metal soap nature or dialkyl tin dicarboxylates showed, however, that the soap or carboxylate moieties are retained to a greater extent than the metal or the alkyl groups. This indicates that the stabilizer is involved in some coordinate complex with the polymer chain, and that its action is not limited to a simple scavenging action of the evolved hydrogen chloride only.

A wide variety of materials has been developed for thermal stabilization of PVC. Such materials include mixed salts of calcium and zinc with rather inferior stabilizing properties, barium-cadmium soaps, lead sulfates, tin mercaptides, dibutyltin derivatives, di(n-octyl) tin maleate, amino crotonic esters, epoxy compounds, etc., though lead- and cadmium compounds are now forbidden in many countries for their toxicity.

A typical vinyl powder coating formulation containing a plasticizer and stabilizer is given in *Table 2.2* [5].

Table 2.2: Vinyl powder coating formulation [5]

source: Communication Channels Inc.

Ingredient	Parts by weight
Bakelite vinyl resin QYNJ (1)	100.3
Bakelite vinyl resin QYJV (1)	9.3
Flexol plasticizer EP-8 (1)	6.0
Flexol plasticizer 10-10 (1)	36.0
Mark C (2)	2.0
Thermolite 31, PVC stabilizer (3)	6.0
TiO_2-rutile	20.0

(1) Union Carbide Corp.; (2) Argus Chemical Corp.; (3) M&T Chemicals, Inc.

Additives known as **lubricants** are often used in the powder coating formulation. They influence both the behavior during processing and the properties of the finished product. The primary requirements of the lubricants are to improve the flow properties of the fused compound, and to help the movement of the material through the extruder during the production of the powder coating by lubricating the interface between the PVC and the metal surface.

Two grades of lubricants are usually used for this purpose. The internal types which are compatible with PVC reduce the melt viscosity of the compound, improve the flow properties and reduce the friction in the processing equipment. The external lubricants which are not compatible with PVC act in this case only as a lubricating layer on the surface of the PVC where it comes into contact with the metal surface of the processing equipment.

Representatives of internal lubricants are long-chain fatty acids, calcium stearate, alkylated fatty acids and long-chain alkyl amines. External lubricants include fatty acid esters, high molecular weight alcohols, synthetic waxes, and low-molecular weight polyethylene.

PVC powder coatings applied by the **fluidized bed** method have been the most widely used materials for coating wire goods in thick layers. In this application they offer a good compromise between price and performance. They are characterized by uniformity of the coating, no sagging and good edge coverage. The usual thickness of the PVC powder coatings applied by the fluidized bed method is between 200 and 400 µm. To achieve good uniformity of the coating in thinner layers, the electrostatic spray technique is required.

Typical products coated with PVC powders are appliances and dishwasher racks. In the latter case, PVC coated materials can withstand the normal testing conditions of total vapor and water immersion at 80 to 100 °C without blistering. Detergent resistance and resistance to food stains are excellent. This is combined with the important characteristic of allowing the water to run off from the coated products. PVC powder coatings provide another important characteristic to dish racks by acting as sound dampers, thus preventing the development of noise during filling or discharging of the racks. Chemical and detergent resistance makes them suitable for protection of dishwasher tubes.

The non-toxic nature of the PVC powder coatings allows them to be used for refrigerator racks, freezers and shelves. The stain resistance and low odor of PVC powder coatings are appreciated characteristics in coatings for shelves made of wire, expanded metal or sheets. For the same reasons they are used as metal furniture coatings.

Good dielectric properties of PVC powder coatings are among the pre-requisites they fulfill for application in the electric and electronic industries. The soft touch feeling makes them suitable for covering various types of handles, automotive seat belt anchors, bus bars, tools etc.

Outdoor durability is not a strong point of PVC powder coatings. The main reason is the sensitivity of the binder to the ultraviolet spectrum below 350 nm. The development of effective UV stabilizers has opened up new possibilities for outdoor use of PVC powders.