

Dieter Stoye, Werner Freitag (Editors)

Paints, Coatings and Solvents

Second, Completely Revised Edition

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Paints, Coatings and Solvents

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Preface to the Second Edition

The work at hand offers a wealth of information about coating materials and coating processes in a form that is clearly laid out. The swift pace of developments in the past few years has made a revised edition seem appropriate. The organization and structure of the work have been maintained, but changes and additions to content have been made where necessary. In particular, attention has been paid to updating economic data and information on standards, laws, and regulations. Commercially available products and their producers have also been subject to clearly recognizable changes, and these changes have been in part caused by the growing tendency of companies to merge and concentrate on their core businesses.

Among products and processes, the trend to environmentally friendly alternatives has also increased, even though the share of solvent-containing coating materials still dominates the market. Therefore, the article on solvents will remain indispensable for some time to come. The second edition will serve to confirm the book in its role as a standard reference for anyone working with coatings.

Marl, April 1998

WERNER FREITAG

Preface to the 1st edition

Paints and coatings are used to protect substrates against mechanical, chemical, and atmospheric influences. At the same time, they serve to decorate and color buildings, industrial plants, and utensils.

Coatings are of high economic importance because they provide protection against corrosive and atmospheric attack. It is therefore understandable that in industrialized countries such as the European Community, the United States, and Japan the annual consumption per capita is high and is continuing to rise.

There are numerous paint systems, production and process technologies due to the many demands made on quality, processibility, and economical importance. These have been fully discussed in this book, which presents the articles "Paints and Coatings" and "Solvents" as published in the 5th Edition of Ullmann's Encyclopedia of Industrial Chemistry.

Comprehensive information on all paint systems and binders, pigments, fillers, and additives has been given in individual chapters. Modern, low-emission paints such as high-solids paints, water-borne paints, powder paints, and radiation-curing systems are also discussed in detail.

There are special sections which deal with different production and processing technologies. Recommendations for each target application of a coating system are provided. Finally, special treatment of state-of-the-art paint testing, analysis, environmental protection, recycling, and toxicology is offered.

Although the paint industry has made great efforts to substitute volatile and organic solvents for environmental reasons, the majority of paints today still contain these solvents since they are useful processing agents. A knowledge of their physical data, their toxicological and environmental properties as well as the interaction between solvent and binder forms the basis for practice-oriented paint development. The inclusion of the chapter on Solvents is an ideal addition to this presentation of coating systems.

The special value of this book is that it provides a concise, up-to-date overview of all the properties of paints and coatings, their production and processing technologies, and applications for a wide readership. The book is generously illustrated with numerous figures that aid further understanding, and the extensive literature references serve to deepen one's knowledge of the topics described.

The publisher has successfully gathered together authors of international renown. Undoubtedly, the book will become a standard work for all producers of raw materials, paints and coatings, for users of paints and coatings, as well as for institutes and public authorities.

August 1993

Dieter Stoye

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1. Introduction

1.1. Fundamental Concepts

Paints or coatings are liquid, paste, or powder products which are applied to surfaces by various methods and equipment in layers of given thickness. These form adherent films on the surface of the substrate.

Film formation can occur physically or chemically. Physical film formation from liquid coatings is known as drying, whereas for powder coatings, it is melting process. Drying is always associated with evaporation of organic solvents or water. Physical film formation is only possible if the coating components remaining on the substrate are solid and nontacky. Chemical film formation is necessary if the coating components are liquid, tacky, or pasty; conversion to a solid nontacky film takes place by chemical reaction between the components. The reactive components can be constituents of the coating, and the reaction can be initiated by energy (heat or radiation) after application of the coating. However, it is also possible to add a reaction partner while applying the coating (multipack paints). A special case of chemical film formation is the oxidation of coating component(s) by atmospheric oxygen (air drying). Physical and chemical film formation are often combined, e.g., in solvent-containing stoving paints, where the first stage is solvent evaporation, after which the film is cured by stoving. The properties of a paint are determined by its qualitative and quantitative composition, suitable choice of which enables the viscosity, electrical conductivity, and drying behavior to be matched to the application conditions. **Also**, the properties of the coating film (luster, elasticity, scratch resistance, hardness, adhesion, and surface structure) are determined by the paint properties. However, the condition of the substrate surface (cleanliness and freedom from dust and grease) is also important.

Coatings must fulfill many requirements. They protect the substrate against corrosion, weathering, and mechanical damage; have a decorative function (automotive coatings, household appliances, furniture); provide information (traffic signs, information signs, advertising); or have other specific properties.

“Coating” is a general term denoting a material that is applied to a surface. “Paint” indicates a pigmented material, while “varnish” refers to a clear lacquer (ISO 4618/1; DIN 55945).

1.2. Historical Development

The earliest evidence of well-preserved prehistoric paintings, dating from the 16th millennium B.C. can be found in caves in Southern France (Font-de-Gaume, Niaux, Lascaux), Spain (Altamira), and South Africa. The colors used were pure oil paints prepared from animal fat mixed with mineral pigments such as ocher, manganese ore (manganese dioxide), iron oxide, and chalk. The oldest rock paintings from North Africa (Sahara, Tassili n'Ajjer) date from between the 5th and the 7th millennium B.C. Many examples of paintings from Babylon, Egypt, Greece, and Italy dating from the 1st and 2nd millennium B.C. are also known.

The first painted objects come from China. Furniture and utensils were covered with a layer of paint in an artistic design. The oldest tradition work dates from around 200 B.C. The lacquer used was the milky juice from the bark of the lacquer tree (*Rhus vernicifera*). This was colored black or red with minerals, and later also with gold dust or gold leaf.

The oldest recipe for a lacquer, from linseed oil and the natural resin sandarac, dates from 1100 A.D. and was due to the monk ROGERUS VON HELMERSHAUSEN. Natural products such as vegetable oils and wood resins remained the most important raw materials for paint production, into the early 1900s. Only the introduction of faster production equipment such as belt conveyors made the development of new paints necessary. Initially, the rapid-drying binder used was nitrocellulose, which after World War I could be manufactured on a large scale in existing guncotton plants. Phenolic resins were the first synthetic binders (ca. 1920), followed by the alkyd resins (1930). The large number of synthetic binders and resins now available are tailored for each application method and area of use. These paint raw materials are based on petrochemical primary products. Vegetable and animal oils and resins are now seldom used in their natural form, but only after chemical modification. The tendency to use such "renewable" raw materials is increasing. Consumer demand has led to a marked renaissance of natural products ("biopaints").

The use of organic solvents in paint technology was linked to the development of modern rapid-drying binders. Whereas the liquid components previously used in coatings were vegetable oils or water and possibly ethanol, it now became necessary to use solvent mixtures to give accelerated drying and optimized paint-application properties. Production of a wide range of solvents began worldwide in the chemical industry in the 1920s.

Methods of applying paints also underwent major changes in the 1900s. Whereas up to this time coatings were applied manually with a brush, even in industry, this technique is today only used in the handicraft and DIY areas. Modern mechanized and automated application methods are used today for industrial-scale application because of greater efficiency, low material losses, qualitatively better results, and lower labor costs. They include high-pressure spraying using compressed air or electrostatic charging, modern automatic and environmentally friendly dipping and electrophoretic processes, and application by rollers.

Problems of environmental pollution also followed from the introduction of solvents. These were recognized by the late 1960s and became the subject of develop-

ment work. Waterborne coatings, low-solvent coatings, solvent-free powder coatings, and new radiation-curing coating systems with reactive solvents that are bound chemically during the hardening process were developed. These environmentally friendly coating systems have gained a considerable market share. However, in some areas solvent-containing coatings are difficult to replace without affecting quality. For this reason, solvent-recycling and solvent-combustion plants have been developed to recover or incinerate the solvents in the waste air.

1.3. Composition of Paints

Paints are made of numerous components, depending on the method of application, the desired properties, the substrate to be coated, and ecological and economic constraints. Paint components can be classified as volatile or nonvolatile.

Volatile paint components include organic solvents, water, and coalescing agents. Nonvolatile components include binders, resins, plasticizers, paint additives, dyes, pigments, and extenders. In some types of binder, chemical hardening can lead to condensation products such as water, alcohols, and aldehydes or their acetals, which are released into the atmosphere, thus being regarded as volatile components.

All components fulfill special functions in the liquid paint and in the solid coating film. Solvents, binders, and pigments account for most of the material, the proportion of additives being small. Low concentrations of additives produce marked effects such as improved flow behavior, better wetting of the substrate of pigment, and catalytic acceleration of hardening.

Solvents and pigments need not always be present in a coating formulation. Solvent-free paints and pigment-free varnishes are also available.

The most important component of a paint formulation is the binder. Binders essentially determine the application method, drying and hardening behavior, adhesion to the substrate, mechanical properties, chemical resistance, and resistance to weathering.

1.3.1. Binders and Resins

Binders are macromolecular products with a molecular mass between 500 and ca. 30000. The higher molecular mass products include cellulose nitrate and polyacrylate and vinyl chloride copolymers, which are suitable for physical film formation. The low molecular mass products include alkyd resins, phenolic resins, polyisocyanates, and epoxy resins. To produce acceptable films, these binders must be chemically hardened after application to the substrate to produce high molecular mass cross-linked macromolecules.

Increasing relative molecular mass of the binder in the polymer film improves properties such as elasticity, hardness, and impact deformation, but also leads to higher solution viscosity of the binder. While the usefulness of a coating is enhanced by good mechanical film properties, low viscosity combined with low solvent content are also desirable for ease of application and for environmental reasons. Therefore, a compromise is necessary.

The low molecular mass binders have low solution viscosity and allow low-emission paints with high solids contents or even solvent-free paints to be produced. Here, the binder consists of a mixture of several reactive components, and film formation takes place by chemical drying after application of the paint. If chemical hardening occurs even at room temperature, the binder components must be mixed together shortly before or even during application (two- and multicomponent systems).

Today, most binders are synthetic resins such as alkyd or epoxy resins.

The natural resin most commonly used as a binder today is rosin, which is often tailored by chemical modification to suit specific applications. **Also**, many synthetic hard resins mainly based on cyclohexanone, acetophenone, or aldehydes, are used in the paints industry. Hard resin binders increase the solids content, accelerate drying, and improve surface hardness, luster, and adhesion.

Most synthetic binders are softer and more flexible than hard resins. Consequently, they impart good elasticity, impact resistance, and improved adhesion, even to critical undercoats, as well as offering adequate resistance to weathering and chemicals. These binders are produced with a property profile tailored to suit particular application methods and to comply with a range of technical requirements, including environmental protection, low toxicity, and suitability for recycling and disposal.

1.3.2. Plasticizers

Plasticizers are organic liquids of high viscosity and low volatility. The esters of dicarboxylic acids (e.g., dioctyl phthalate) are well-known examples. Plasticizers lower the softening and film-forming temperatures of the binders. They also improve flow, flexibility, and adhesion properties. Chemically, plasticizers are largely inert and do not react with the binder components. Most binders used today are inherently flexible and can be regarded as "internally plasticized" resins. For this reason, use of plasticizers has declined.

1.3.3. Pigments and Extenders

Pigments and extenders in coatings are responsible for their color and covering power, and in some cases give the coating film improved anticorrosion properties.

Pigments and extenders are finely ground crystalline solids that are dispersed in the paint. They are divided into inorganic, organic, organometallic, and metallic pigments. By far the most commonly used pigment is titanium dioxide. As a rule, mixtures of pigments are used for technical and economic reasons. The hiding power and tinting strength of a paint depend on the particle size of the pigment. The usual size range aimed at is $0.1 - 2.0 \mu\text{m}$, which means that the pigment has a high surface area that must be wetted as effectively as possible by the binder components to give the coating film good stability, weathering resistance, and luster. This is achieved by bringing the pigment and binder into intimate contact under the influence of high shear forces. The high hiding power of some pigments enables them to be partially replaced by the cheaper extenders such as barium sulfate, calcium carbonate, or kaolin. Extenders have a particle size distribution similar to that of the pigments and are incorporated into the coating in the same way. The concentration of pigment in coating films is expressed by the pigment volume concentration (PVC). This is the ratio of the volume of pigments and extenders to the total volume of the nonvolatile components. Each coating system has a critical pigment volume concentration (CPVC) at which the binder just fills the free space between the close-packed pigment particles. At higher pigment concentrations, the pigment particles in the coating film are no longer fully wetted by the binder, leading to a marked deterioration in coating film properties such as luster, stability, strength, and anticorrosion properties.

1.3.4. Paint Additives

Paint additives are auxiliary products that are added to coatings, usually in small amounts, to improve particular technical properties of the paints or coating films. Paint additives are named in accordance with their mode of action.

Leveling agents promote formation of a smooth, uniform surface on drying of the paint. Suitable materials include certain high-boiling solvents such as butyl ethers of ethylene glycol, propylene glycol and diglycols, as well as cyclohexanone and alkylated cyclohexanones, and in some cases aromatic and aliphatic hydrocarbons. Low molecular mass resins (e.g., some polyacrylates and silicones) are also used. Solid leveling agents, such as special low molecular mass resins, are also useful for improving the surface properties of films produced from powder coatings. Flow agents act by reducing the paint viscosity during drying. The effectiveness of a particular flow agent depends on the type of binder and the drying or hardening temperature.

Film-formation promoters, which are closely related to flow agents, reduce the film-forming temperature for film formation from dispersions, leading to a surface that is as pore-free and uniform as possible. Certain high-boiling glycol ethers and glycol ether esters are used, often in combination with hydrocarbons.

Wetting Agents, Dispersants, and *Antisetting* Agents. Wetting agents from one of the largest groups of coating additives. These are surfactants which aid wetting of the pigments by the binders and prevent flocculation of the pigment particles. This leads to the formation of a uniform, haze-free color and a uniformly high luster of the

coating film. This group also includes the dispersants, which give good pigment wetting and hence optimum dispersion of the pigments in the paint, thereby preventing sedimentation particularly of high-density pigments. As well as good wetting properties, some pseudoplasticity is also necessary. Antisetting agents have similar characteristics to dispersants.

Antifoaming agents are used to prevent foaming during paint manufacture and application and to promote release of air from the coating film during drying. Various products are used, including fatty acid esters, metallic soaps, mineral oils, waxes, silicon oils, and siloxanes, sometimes combined with emulsifiers and hydrophobic silicas.

Catalysts are added to paints to accelerate drying and hardening. They include drying agents (driers, siccatives), which, in the case of the air-drying binders (including some alkyd resins or unsaturated oils), accelerate decomposition of the peroxides and hydroperoxides that form during the drying process, thereby enabling radical polymerization of the binders to take place. The driers used are mainly metallic soaps such as cobalt naphthenate; manganese, calcium, zinc, and barium salts; and zirconium compounds.

Various products are used to catalyze the cross-linking of binder systems at room temperature. For acid-catalyzed systems such as polyester – melamine resin systems, free acids, their ammonium salts, or labile esters are suitable. While for base-catalyzed systems such as polyester – isocyanate, tertiary amines or dibutyltin dilaurate are used. The amount of catalyst used must be such that the pot life is not impaired.

Antifloating and antiflooding agents prevent horizontal and vertical segregation of pigments with different densities and surface properties. This prevents differences in the color and luster of the surface of the film, which can lead to a blotchy appearance.

Antiskinning agents are added to air-drying paints to prevent surface skin formation caused by contact with atmospheric oxygen. In the film, they produce uniform drying and prevent shrinkage (wrinkling). Chemically, these materials are antioxidants such as oximes, which evaporate with the solvents during the drying process.

Matting agents are used to produce coatings with a matt, semi-matt, or silk finish. They include natural mineral products such as talc or diatomites and synthetic materials such as pyrogenic silicas or polyolefin waxes. Matting can also be obtained by special formulations that exploit the incompatibility between binder components and their cross-linked structures.

Neutralizing agents are used in waterborne paints to neutralize binders and stabilize the product. Ammonia and various alkylated aminoalcohols are used, depending on the type of binder and method of application. On hardening, the amines mainly evaporate along with the water.

Thickening agents control the rheological properties of paints of various types. They include inorganic (mainly silicates), organometallic (titanium and zirconium chelates), naturally occurring organic (mainly cellulose ethers) and synthetic organic products (polyacrylates, polyvinylpyrrolidone, polyurethanes).

Preservatives (biocides, fungicides) prevent the attack of paint systems, principally water-based, by microorganisms.

Corrosion inhibitors are used to prevent the formation of corrosion products when waterborne paints are applied to metallic substrates (flash rust). They include oxidiz-

ing salts such as chromates, metaborates, nitrites, and nitrates; organic amines or sulfur-containing products; and organic salts (benzoates, naphthenates, octoates).

1.3.5. Solvents

Solvents are compounds that are normally liquid at room temperature. Those most commonly used in coatings technology are aromatic and aliphatic hydrocarbons, esters of acetic acid, glycol ethers, alcohols, and some ketones. Solvents dissolve solid and highly viscous binder components. They enable incompatibility between paint components to be overcome, improve pigment wetting and dispersion, and control storage stability and viscosity of the coating. They promote the release of included air from the liquid coating film, control the drying behavior of the coating, and optimize flow properties and luster. Organic solvents are used in most liquid coatings systems, including, waterborne coatings, in which they perform important functions.

After paint application, the solvents should evaporate as quickly as possible, leaving the film. If no special precautions are taken, the solvents enter the atmosphere as pollutants. To protect operating personnel from the toxic effects of evaporating solvents, safety measures such as ventilation and air exhaust are necessary. To protect the environment, incineration and sometimes solvent-recovery plant is installed to prevent solvents entering the atmosphere. Other measures for the protection of the workplace and the environment from solvent vapors include the development and use of new low-solvent or solvent-free coatings, e.g., high-solids paints, waterborne coatings, and powder coatings.

1.4. Paint Application

Paint application can be performed manually, for example with brushes or rollers, or by mechanical methods such as spraying, atomization by rotating disks or cones, dipping, pouring, rotating drums and tumbling equipment, and automated application by rollers. Powder coatings are applied by electrostatic spraying or by dipping components into the powders. Multicomponent coatings are applied with multicomponent spraying equipment.

1.5. Drying and Film Formation

As the paint dries on the substrate, a firmly bonded film is formed. The properties of this film are determined both by the substrate and its pretreatment (cleaning, degreasing) and by the composition of the coating and the application method used.

Drying of the paint on the substrate takes place physically (1 - 3) or chemically (4):

- 1) Evaporation of the organic solvents from solvent-containing paints
- 2) Evaporation of water from waterborne paints
- 3) Cooling of the polymer melts (powder coatings)
- 4) Reaction of low molecular mass products with other low or medium molecular mass binder components (polymerization or cross-linking) to form macromolecules

Physical Drying. Physical drying takes place mainly for paints with high molecular mass polymer binders such as cellulose nitrate, cellulose esters, chlorinated rubber, vinyl resins, polyacrylates, styrene copolymers, thermoplastic polyesters and polyamide and polyolefin copolymers. These materials give good flexibility and stability because of their high molecular mass. Their glass transition temperature should be above room temperature to ensure adequate hardness and scratch resistance. With these polymers, film formation can also take place from solutions or dispersions in organic solvents or water, from which the solvent or water evaporates, leaving behind the chemically unchanged polymer film.

Film formation can be accelerated by drying at elevated temperatures (forced drying). Physically drying solvent-containing paints have a low solids content because the molecular mass of the binder is relatively high. Higher solids contents are obtained by dispersing the binder in water (dispersions, emulsions) or in organic solvents (nonaqueous dispersion or NAD systems). Films formed from physically drying paints, especially those formed from solutions, are sensitive to solvents (dissolution or swelling). The physically drying coatings also include many powder coatings that contain thermoplastic binders. Film formation takes place by heating the powder that has been applied to the substrate above its melting point. This ensures that a sealed film of polymer is formed.

Plastisols and organosols are a special case of physically drying coatings systems in which the binders consist of finely dispersed poly(vinyl chloride) or thermoplastic poly(meth)acrylates suspended in plasticizers. Organosols also contain some solvent. On drying at elevated temperatures, the polymer particles are swollen by the plasticizer, a process known as gelation.

Chemical Drying. Chemically drying paints contain binder components that react together on drying to form cross-linked macromolecules. These binder components have a relatively low molecular mass, so that their solutions can have a high solids content and a low viscosity. In some cases, solvent-free liquid paints are possible. Chemical drying can occur by polymerization, polyaddition, or polycondensation.

When polymerization is used as the hardening principle, reactive components combine to form the binder, e.g., unsaturated polyesters with styrene or acrylate monomers. Here, one component often behaves as a reactive solvent for the other, and low-emission coating systems are the result. Cross-linking can be carried out at room temperature (cold curing) or by radiation curing.

In drying by polyaddition, low molecular mass reactive polymers such as alkyd resins, saturated polyesters, or polyacrylates react with polyisocyanates or epoxy resins to form cross-linked macromolecules. Because this reaction can take place at room temperature, the binder components must be mixed shortly before application. The period of time during which a coating of this type remains usable after mixing of the components is known as the pot life. These are known as two-pack coatings, differing from the one-pack systems, which can be stored for months or even years.

Chemically blocking one of the polyaddition binder components (e.g., the polyisocyanate) gives a coating system stable at room temperature. Heat is required to deblock the component and enable cross-linking to occur. Stoving paints of this type are used in industry and in powder coatings.

Polycondensation drying requires the addition of catalysts or the use of higher temperatures. Acid-catalyzed coatings are well-known cold-curing paint systems used in the furniture industry, while heat-curing and stoving paints are used as industrial and automotive coatings. The binding agents used are functional alkyd resins, saturated polyesters, or polyacrylates in combination with urea resins, melamine resins, or phenolic resins. On cross-linking, water, low molecular mass alcohols, aldehydes, acetals, and other volatile compounds are released.

In practice drying of coatings and paints does not take place by one method alone. With solvent-containing and waterborne heat-curing coatings, physical drying by solvent evaporation always precedes chemical drying. Depending on the composition of the binder system, physical and chemical drying can take place simultaneously, and the various mechanisms of chemical drying can proceed concurrently or consecutively, depending on the nature of the binder. A knowledge of binder composition is important in order to assess the drying of a coating and able to accelerate it by heat, radiation, and addition of catalysts.

1.6. Multicoat Systems

Because dried coating films are not always pore-free, optimal protection of the substrate is not always ensured by one coat. A single coat can seldom fulfill all requirements such as good adhesion, corrosion protection, elasticity, hardness, decorative effect, coloration, and resistance to weathering and chemicals. Coatings with different compositions and functions are therefore often applied in succession. For example, primers provide good adhesion to the substrate and maximum corrosion protection, whereas color stability, gloss, and resistance to weathering are better provided by a top coat which is specially designed for this purpose but may not have particularly good corrosion resistance.

Intermediate coatings between the top coat and the primer are also applied if the highest quality is required, e.g., in the automobile industry. These have the task of providing adhesion between the primer and the top coat, and they also smooth out irregularities on the substrate, thereby indirectly helping to ensure good flow of the top coat and a high gloss with no defects.

1.7. Economic Aspects

In the industrialized countries of Europa and in North America, annual paint consumption of coatings per capita is $> 20 \text{ kg}$, and high growth rates can be expected in the less industrialized countries of Eastern Europe, Asia, and South East Asia. The volume of coatings produced in Western Europa in 1994 was ca. $5.4 \times 10^6 \text{ t}$, and in the United States, $6.2 \times 10^6 \text{ t}$. The annual growth rates of solvent-containing conventional coatings are estimated to be $1-2 \text{ Y}_o$, and, of environmentally friendly coatings (high solids, water-based, powder coatings, etc.), ca. 5 Y_o .

1.8. Future Outlook

In the past, the development of coatings was mainly based on technical, quality, and economic considerations. These factors are just as important today from a business point of view and will continue to be so in the future. However, other considerations are now very much in the foreground, i.e., environmental protection, toxicology, environmentally friendly disposal of paint residues and coated articles at the end of their life cycle, the recycling of coated articles, and the conservation of raw materials and energy.

Thus, numerous low-emission paints have been developed, including high-solids paints, waterborne paints, aqueous dispersions for industrial use, powder coatings, and radiation-curing coatings. At the forefront in adopting these environmentally friendly products is heavy industry, in particular the automobile and household appliance industries. Medium-sized and smaller businesses will profit from this experience, adapting it for their own needs.

To conserve raw materials based on mineral oil, renewable raw materials derived from natural oils and resins will be investigated and assessed for potential use in paints.

Nevertheless, the principal development goal is still to secure further improvements in the quality of paint systems and to prolong the durability of coating films. The longer the renewal of a coated surface can be delayed, the less the environment is polluted, and the smaller are the amounts of waste produced and of raw materials and energy consumed.

The continuous increase in automation and electronic control of paint production and application are equally relevant, enabling products to be manufactured that are consistently of the highest quality.