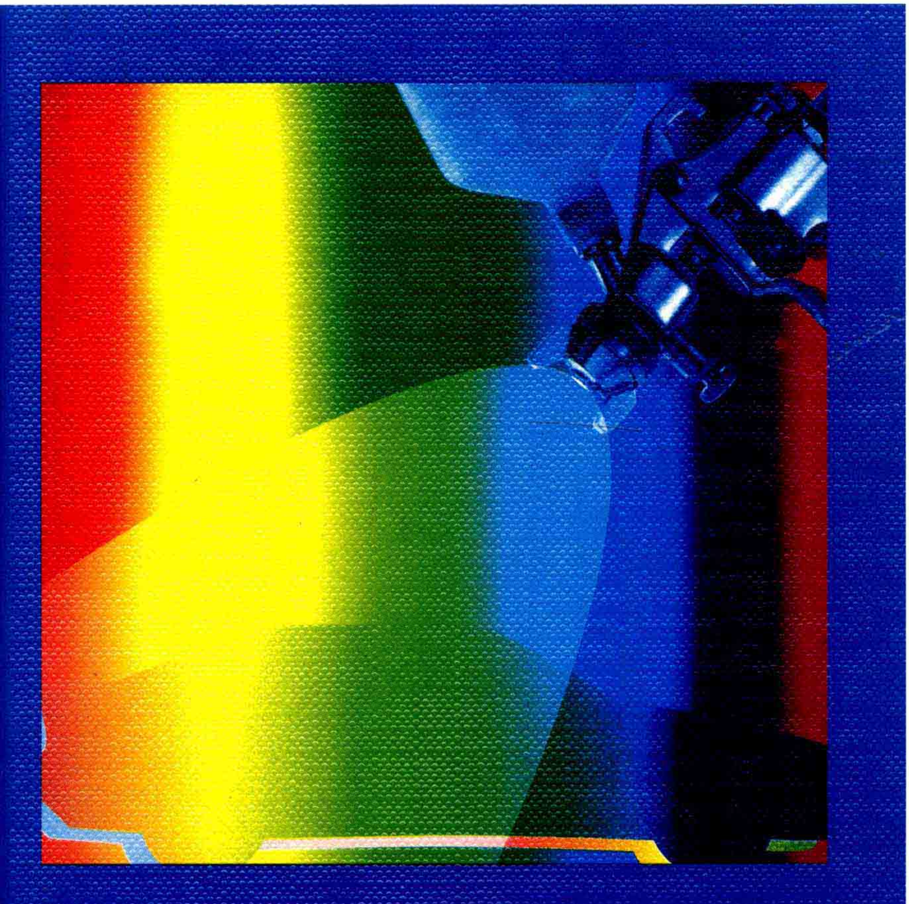
Paints, Coatings and Solvents

Edited by Dieter Stoye



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Paints, Coatings and Solvents

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Preface

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

Paints, coating materials, and with some restrictions lacquers are synonymous terms. They are normally liquid compositions which dry to form well-adhering films when applied in a thin layer on surfaces. Lacquers dry primarily by solvent evaporation. The composition of a paint determines whether a high-gloss film or a flat (matt) surface is formed. Coating is often used as a more general term that denotes any material that is applied to a surface in a thin continuous layer. Paint has been traditionally employed to denote opaque pigmented materials as opposed to clear films (varnishes).

Definitions given in ISO 4618/1 are as follows:

Paint. A product, in liquid or powder form, containing pigment(s), which, when applied to a substrate forms an opaque film having protective, decorative, or specific technical properties.

Varnish. A product, which, when applied to a substrate, forms a solid, transparent film having protective, decorative, or specific technical properties.

1.1. Historical Development

Coating materials were already used in prehistoric times as is witnessed by the cave paintings from ca. 15000 B.C. discovered in the South of France and the North of Spain. The paints used in the Stone Age were composed of substances such as animal fat, colored earths, and carbon black. Although they do not correspond to our notion of a modern coating, they were based on the same principle: they contained a binding agent (e.g., lard) and a pigment (e.g., ochre).

The oldest lacquered works from China dating back to 2000 B.C. are much younger than the cave paintings of the Stone Age. Their smooth, glossy surfaces correspond more closely to modern coatings than the cave paintings. The invention of coatings technology is therefore attributed to the Chinese. Instead of animal fats they used the milky sap of the Chinese lacquer tree *(Rhus vernicifera)* as the binder material. The films resulted from application of this optionally pigmented plant product on wood, fabric, or other substrates.

In the sixteenth century, coated articles were increasingly exported to Europe. The growing demand for lacquered goods in Europe and the fact that the lacquer tree sap was not stable enough to be transported over long distances initiated the development of coatings from readily available domestic raw materials. Combinations of vegetable oils and tree resins (as mentioned in 1000 A.D. by the monk RODGERUS VON HELMERSHAUSEN) were continuously improved and modified.

Vegetable products remained the most important raw materials for coatings manufacture until the beginning of the twentieth century. Faster production techniques and the need for higher quality coatings required the development of novel paints. Cellulose nitrate and synthetic phenolic and alkyd resins were the first "modern" binders. Today a wide range of materials obtained from the petrochemical industry is available to satisfy the needs of the consumer. Vegetable oils and resins are no longer used in their natural form; they are still used as binder components, however, in chemically modified form.

Animal products have never acquired significant importance as coating materials although the word "lacquer" is derived from the Sanskrit expression "laksha" which is associated with shellac, a resin that is secreted by an Indian insect.

Today coating raw materials are mainly produced in the chemical industry and supplied to the highly specialized enterprises of the coatings industry. This was not the case in the past. Up to the end of the nineteenth century artists and professional painters "cooked" their paints themselves. The recipes were developed empirically on the basis of practical experience. As the European coatings industry grew, this approach did not change significantly until the late 1940s. Properties and functions of particular components in complex "paint" systems were then investigated on a scientific basis. As a result enormous improvements have been made in the coatings field, especially since the early 1960s.

Up to the early 1930s paints were applied by hand, mostly with a brush. This technique is still used today for applying conventional architectural paints. Modern methods of industrial paint application are much more efficient (see Chap. 8). Automatic plants are used to coat articles of all sizes rapidly and evenly by spraying, dipping, or roller coating. Many industrial coating methods (e.g., electrodeposition or fluidized-bed powder application) need special coating materials which cannot be applied manually.

Initially paint was used primarily for decoration or identification purposes. Since the middle of the nineteenth century its protective function has become increasingly important. Today, coatings on buildings, industrial plants, ships, automobiles, and many other objects are used both for decoration and protection. In most technical applications protection is of prime importance.

The coatings industry involves raw material producers, paint manufacturers, and equipment suppliers. Wide ranges of coating materials and application techniques are used. This important branch of industry employs a large number of people. In the western part of the Federal Republic of Germany, for example, 1.55×10^6 t of paints were produced in 1991. This quantity is sufficient to coat an area of ca. 12000 km^2 and represents a market value of DM 7.6×10^9 (\$$4.75 \times 10^9$). Compared to 1990, total production increased by 8.3% but the average growth rate for non- and low-polluting systems (e.g., waterborne paints, powder coatings, and high solids) is ca. 20%. In 1991 this allowed savings of 110000 t of solvents compared to 1982. Statistically, 1% of the value of an article is generally accounted for by its coating. The annual per capita consumption of paints in the western part of the Federal Republic of Germany in recent years was >20 kg and was above the average for Western Europe as a whole.

1.2. Composition of Paints

A coating can only conserve an article if it is durable itself. Furthermore, the coating film must not become detached from the substrate to be protected if lasting protection is to be obtained. Since the coating always has to adhere closely to the substrate, the coated area may be regarded as a composite material. Careful coordination of the coating and the substrate is equally as important as appropriate preparation of the surface prior to application. Contamination of the interface between the workpiece and coating with foreign substances may cause failure of the material under mechanical loads or under attack by environmental influences.

No single coating is able to satisfy all requirements. The main objective of applying coatings is to prepare protective, durable, decorative films in an economical way on wood, metals, plastics, or mineral building materials; this needs numerous different systems for its implementation. The consistency and film properties of each paint are developed for a limited field of application and a particular coating process.

The large variety of coatings allows many ways of classification. They can be divided according to use (e.g., can coatings, automotive paints), according to the application method (spray paint, dipping paint), according to the processing state (e.g., low in solvent, water-based), according to the drying behavior (e.g., air drying, cold curing), or according to the chemical nature of the binder (alkyd resin, polyurethane). Several of these features are needed for unequivocal characterization of a coating. The specification of the binder enables the expert to draw conclusions about the working properties of the coating material and the performance of the films.

Coatings generally contain numerous ingredients which can be divided into the following groups:

Volatile components	solvents			
	coalescing agents			
Nonvolatile components	film-forming substances	binders	varnishes	paints
	resins			
	plasticizers			
	additives			
	dyes			
	pigments			
	extender pigments			

Condensation products that are formed after chemical curing of certain binders and released to the atmosphere are also classified as volatile components.

All constituents fulfil special functions in the liquid paint as well as in the resulting solid film. Solvents, binders, and pigments are generally present in much higher amounts than the additives. Low additive concentrations often produce marked effects on, for example, gloss or speed of drying. Solvents and pigments are not always necessary for the coating formulation; solvent-free paints and varnishes (the latter, by definition, do not contain pigments) are common. The crucial component of every coating material is the binder which determines the processability, the curing schedule, and the final utility value of the film. According to ISO 4618/1 the binder is defined as the nonvolatile part of the medium which forms the film and binds the pigment.

1.2.1. Basic Components

Film-forming substances can either be macromolecular products or low molecular mass compounds that react to form macromolecules on curing. Film formers of the first group are represented by cellulose nitrate (Section 2.2.1) or vinyl chloride copolymers (Section 2.4). The second group includes polyurethanes (Section 2.9) or epoxy resins (Section 2.10). Increasing molecular mass of the polymer film formers results in improved mechanical properties of the film until a limiting value is reached. The viscosity of polymer solutions also increases continuously with molecular mass but does not reach a plateau. Good mechanical properties of the film are required on the one hand, but on the other hand, low viscosities and low solvent contents are needed to facilitate processing and to meet environmental requirements. Compromises are therefore often inevitable. A molecular mass range must be chosen that allows satisfactory film performance and acceptable solution viscosities.

These restrictions do not apply to liquid mixtures of low molecular mass compounds which build up the film-forming polymer during the curing reaction. High-grade films can therefore be generated from paints that are low in solvents or even solvent-free if the binder is based on polymerizable mixtures. Since special curing conditions are required, however, such paints can only be used industrially, for example, in the mass production of furniture, appliances, and food cans.

Resins. Most of the film-forming raw materials are resins (e.g., alkyd resins, epoxy resins). Correctly speaking, the term resin denotes that the material is a vitreous–amorphous solid without a defined melting point. However, paint technologists also use the term resin to denote a certain group of natural or synthetic film formers with resinous consistency. The most important natural resin used in paints is rosin (colophony) produced by coniferous trees. Harder products can be obtained by chemical modifications of rosin. Numerous synthetic resins are also employed.

Resins are readily soluble in either organic solvents or water but not both. They increase the solids content of paints and improve the gloss and adhesion of coating films. Their most essential function is to increase hardness and reduce the drying time in oxidative curing systems. This effect was especially important in oil paints and is the reason for the historical importance of resins.

Plasticizers are normally organic liquids of oily consistency and low volatility. Esters of poly acids (e.g., dioctyl phthalate) are typical examples. Plasticizers have the opposite effect to resins; they lower the softening temperature range of the binder, resulting in a lower film-formation temperature, improved flow, and increased flexibility. They act physically and do not react with binder components.

Too much resin in the binder produces hard, brittle coats whereas too much plasticizer produces soft, sometimes tacky films. Since only small amounts of resins and plasticizers are used, they also may be classified as paint additives.

Pigments and extender pigments (Chap. 4) are responsible for coloring, hiding power, and in certain cases for improved resistance of the coating films (e.g., against corrosion). They consist of finely ground, crystalline solids that are dispersed in the paint and film. Metals, inorganic, organic, and organometallic compounds are used as pigments. The hiding power and the tinting strength of a paint depend on the particle size of the pigment. The aspired fineness of 0.1 – 2.0 μm causes a high surface energy that can result in numerous disadvantageous effects in the paints and coating films. Paint technologists strive to overcome these undesirable interactions by adopting suitable measures during paint production and by using special additives (see Section 1.2.2). Nevertheless, no one pigment can be combined with all binding agents.

The intense hiding power of many white and colored pigments enables the paint technologist to partially replace these expensive materials with cheaper extender pigments such as barytes, chalk, or kaolin. These extenders have the same particle size as the pigments. Due to their lower refractive index, they contribute less to the hiding power of coating films than pigments but they do not change the hue.

The degree of pigmentation is described by the pigment volume concentration (*PVC*). This is the ratio of the volume of the pigments and extender pigments to the total volume of the nonvolatile ingredients (ISO 4618/1). Every system has a critical pigment volume concentration at which the binder just fills the cavities between the pigment particles. If the pigment content exceeds this limit, even by a slight margin, many coating properties deteriorate erratically.

1.2.2. Additives

The term additives denotes auxiliary products that, even in small concentrations, significantly improve the technological properties of paints or coating films. They are classified according to their effects (see Chap. 5).

Driers catalyze the decomposition of peroxides and hydroperoxides formed by the action of atmospheric oxygen on binders like alkyd resins. This promotes the formation of radicals, and polymerization of the binders is thus initiated and accelerated. Metallic soaps (e.g., cobalt naphthenate or lead octoate) that are soluble in most binders are efficient driers.

Antiskinning agents are mostly antioxidants that counteract the tendency of drier-containing paints to form an insoluble surface skin on contact with atmospheric oxygen. In the film they promote uniform drying and thus hinder wrinkling. Anti-