VINCENTZ

Bodo Müller | Ulrich Poth

Coatings Formulation

2nd Revised Edition
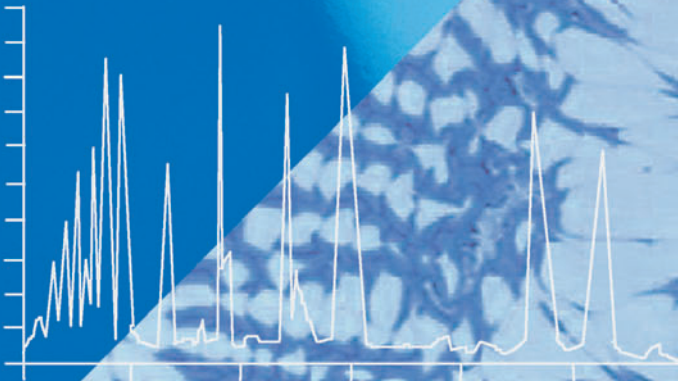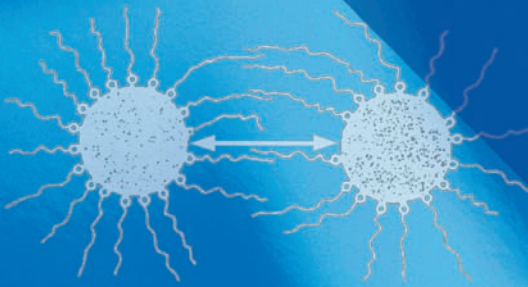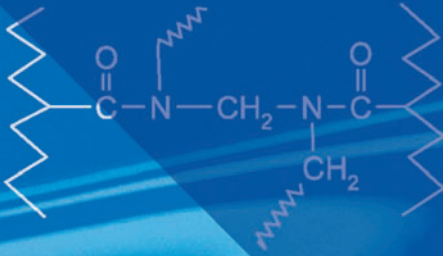
Cover: Dr. Iwona Löhrke

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Coatings Formulation

An international textbook

2nd revised edition

Preface

The authors were not surprised by the success of the first edition, as there had been no comparable reference book on the market that provided detailed explanations of recipes and formulations. Although guide formulations abound, meaningful and informed selections accompanied by notes and evaluations are in short supply. The authors have therefore gladly taken on the task of revising and updating the first edition. To this end, they have replaced outdated guide formulations, eliminated errors and added several new figures.

Developing paint recipes or paint formulations is an important part of paint and coatings technology. Unfortunately, paint recipes are listed in very few publications because they are closely guarded secrets of the paint and coatings industry. While starting formulations are available from the manufacturers of raw materials, they cannot be used for a textbook without careful selection and revision beforehand.

This book will teach paint formulation in two steps. Each chapter will first describe the chemical composition of and, especially, the binders for the type of paint presented. This will then be followed by formulation advice and an analysis of existing recipes (e.g. starting formulations). This analysis consists in calculating the important characteristic values of coatings, such as the pigment/binder ratio, pigment volume concentration and, as necessary, the hardener addition level. Finally, examples of how to develop a real-life paint formulation are provided in the case of the most important types of coatings. All calculations based on recipes and formulations are worked through step by step and should therefore be intelligible to beginners, as well.

The skills acquired in dealing with these recipes can also be employed in other applications, such as adhesives and sealants. This book focuses on the paint formulation itself, and how to arrive at it.

Of the many various paint and coating systems available, the selection provided in this textbook features the most important types. The formulations have been developed mostly from starting formulations or patent examples and cannot be used to produce paints without further ado. Patent restrictions or registered trade marks (™ or ®) are not mentioned explicitly. Furthermore, it should be noted that product and trade names may change as a result of mergers and acquisitions. Nonetheless, most of the raw materials described herein or their equivalents should be available worldwide.

This textbook seeks to familiarize laboratory assistants, engineers and chemists with the practice of formulating paints. It presupposes a basic knowledge of chemistry, binders, pigments and additives. It will also serve as a reference work for all readers interested in paints and coatings.

Our thanks to Dr. Jürgen Kraut for kindly providing scanning electron micrographs for use herein, and to Ray Brown for polishing the text.

Esslingen and Münster, Germany in February 2011

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Exclusion of liability

It should be noted that this book reflect the authors' personal views, based upon their own knowledge. This does not absolve readers of the responsibility of performing their own tests with respect to the uses and applications of various processes or products described herein, and/or of obtaining additional advices regarding the same. Any liability of the authors is excluded to the extent permitted by law, subject to all legal interpretations.

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Part I   Basics

Part I   Basics

1   Introduction

1.1   Preliminary remarks

Paints are semifinished products (intermediates); the end products are the coated objects. Paints are used in a wide variety of applications (Figure I-1.1).
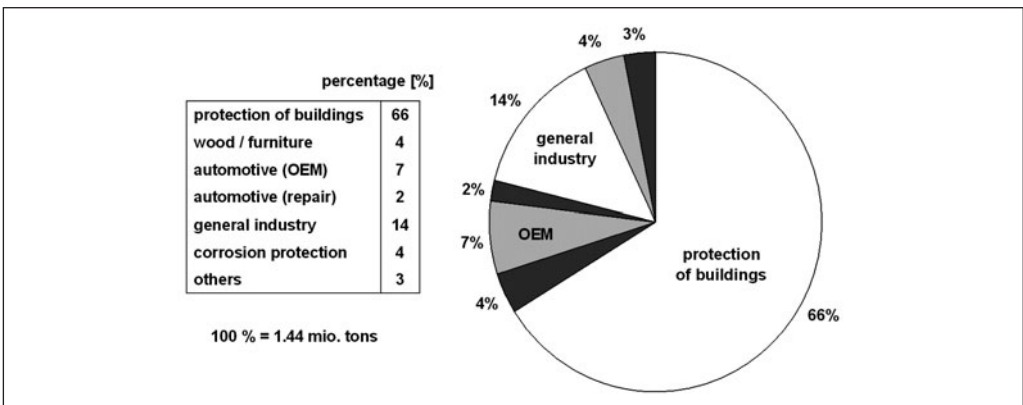
Figure I-1.1: Analysis of paint consumption in Germany in 2009   Source: www.lackindustrie.de

Figure I-1.1 shows that protective paints for buildings accounted for the largest proportion, followed by paints for general industry and other applications. All these different paint systems will be described in this textbook, especially with regard to problems of paint formulation.

1.2   Comments on environmental protection

The general public unfortunately has a negative image of paints because organic solvents are emitted into the atmosphere when solvent-borne paints are applied. In the past, most decorative or protective paints were solvent-borne. In this chapter, we would like to redress this negative image by describing the emissions-lowering measures that have been taken to improve the environmental safety performance of coatings.

In Germany, emissions into the atmosphere are regulated by "TA Luft", which limits the level of organic solvents that may be emitted during paint application. This legislation therefore actively contributes to environmental protection. There are three ways to lower the level of organic solvents emitted from paint formulations:

1. Use high-solids paints (paints with a high content of non-volatile matter and therefore low content of organic solvents)

2. Replace organic solvents by water
• Water-borne paints
• Latex paints

3. Use solvent-free systems
• Two-component systems
• Radiation-curing coatings
• Powder coatings

All these low-emission, ecologically beneficial paints will be described in this book.

For the sake of clarity, the solids contents of paints are classified in Table I-1.1.

The level of organic solvents emitted can also be lowered by certain application methods, e.g. those which have a high transfer efficiency, such as electrostatic spraying, and those which adsorb the solvent as the paint is being applied.

The reduction in the levels of organic solvents emitted during automotive painting (OEM) is shown in Figure I-1.2 [1]; there has been much progress in this regard over the last two decades.

Table I-1.1: Classification of solvent-borne (pigmented) paints

paint type	nonvolatile matter [wt.%]
low-solids	< 30
normal-solids	30 to 60
medium-solids	60 to 70
high-solids	> 70 (sometimes > 80)
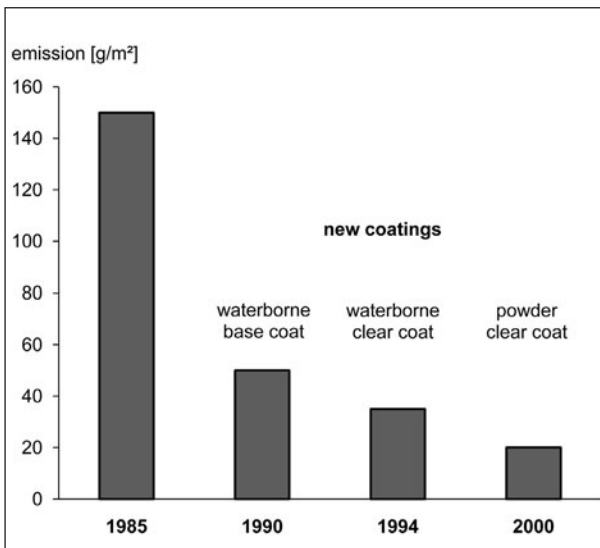
Figure I-1.2: Total emissions (g) of organic solvents during painting of vehicles (OEM), expressed in terms of surface area (m²) of the vehicle bodies (average values; years may vary with vehicle producer)

Corrosion protection as a means of protecting the environment

The second measure taken to protect the environment is not immediately apparent and will be illustrated with the example of iron corrosion (unalloyed steel; Figure I-1.3).

Thermodynamically, the atmospheric corrosion of iron or unalloyed steel (formation of rust: $Fe_2O_3 \cdot H_2O$) is the opposite of its production. The production of iron (in a blast furnace) uses iron ore (e.g. Fe_2O_3) and coal or coke (C) and generates the greenhouse gas, carbon dioxide (CO_2; Figure I-1.3). Corrosion protection extends the working life of corrodible metallic materials (e.g. steel). This means that raw materials and energy

are conserved and there is less of a burden placed on the environment. Besides preserving value, any corrosion protection measure, e.g. coating, therefore also serves to protect the environment. For example, only 15 to 25 kg paint is required for coating a 1,000 kg vehicle; but this coating greatly extends the working life.

Integrated view of paints and coatings

Figure I-1.4 is an integrated view of paints and coatings, ranging from the recovery of resources (e.g. oil production) to the manufacture of raw materials and paints. It also includes the disposal of coated objects when their working life is over[2].

Any assessment of the ecological impact of a paint system must consider all the production steps shown in Figure I-1.4.
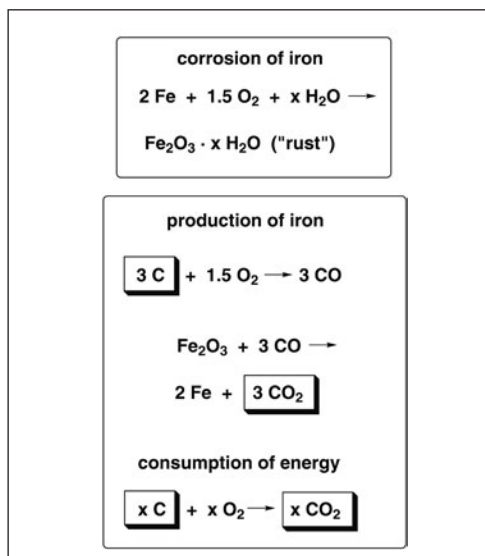
Figure I-1.3: Corrosion protection as a means of protecting the environment (highly simplified equations)

1.3 Paints and coatings as high-tech products

As already mentioned in chapter 1.2, paints often have a negative image because of solvent emissions. Measures that lower levels of solvent emissions, such as the introduction of water-borne paints and powder coatings (Figure I-1.2), are not reported in the mass media. On the other hand, there is much public debate about so-called future or key technologies, especially information technology and biotechnology. More recently, nanotechnology has been mentioned in this context. Unlike coatings technology, terms such as "technology of the future" and "key technology" have a positive image in this public debate.

A sub-area of nanotechnology is that of nanoparticles, which are particles with diameters of 100nm or less[3, 4]. Coatings experts prick up their ears since many disperse pigments and fillers are nothing other than nanoparticles. Long-established paint raw materials, such as carbon blacks and pyrogenic (fumed) silica (see Table I-2.3), are now considered as nanoparticles[3].

In addition, nanostructures have generated further innovative ideas in coatings technol-
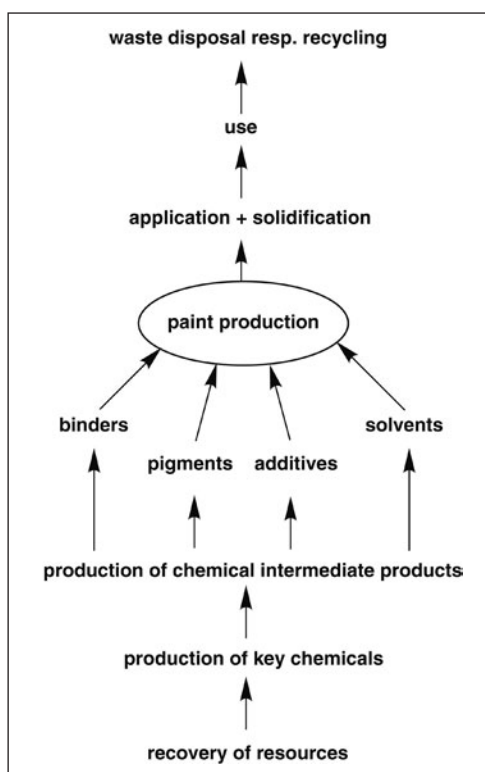
Figure I-1.4: Integrated view of paints and coatings. By recovery of resources is meant, e.g., oil recovery. Key chemicals are, e.g., ethylene, propylene. Examples of chemical intermediates are acrylic acid, epichlorohydrin.

ogy. Recent examples are the chemical incorporation of nanoscale silica into paint resins [5] and the pretreatment of metals by nanostructured layers of silica [6]; both nanostructures are made by sol-gel processes [7]. A current review of nanomaterial technology applications in coatings is presented in [25]. In conclusion, there are many links between nanotechnology (with its positive public image) and coatings technology (and its negative public image) that have gone unnoticed in the past. Paints and coatings are high-tech products and their public image should benefit from a greater general awareness of these considerations.

1.4   Definitions

The following necessary definitions and abbreviations are mostly in accordance with DIN and EN [8, 9].

Coating material is the generic term for liquid-to-pasty or powdery materials which consist of binders and, if necessary, additionally of pigments, other colourants, fillers, solvents and additives.

Coating materials can be subdivided as follows:
- Paints
- Coating materials for plasters
- Knifing fillers
- Special coating materials (e.g. for floors)

The paints or coating materials described in this book can be further subdivided as follows:
- Dilutability (solvent-borne or water-borne, solvent-free)
- Position in multi-coat systems (e.g. primer or topcoat)
- Application (e.g. for industrial products or buildings)
- Properties (e.g. anticorrosion or effect coating, clear coat)

The **binder** is the non-volatile matter of a coating material without pigments and fillers but including plasticizers, driers and other non-volatile additives. The binder bonds the pigment particles to each other and to the substrate.

To simplify matters, driers and other non-volatile additives may be neglected in calculations of characteristic coating values of coatings (Chapter 3.1), without risk of major error.

Colourant is the generic term for all colour-bearing substances; they may be further subdivided as shown in Figure I-1.5.

Pigments are particles which are virtually insoluble in the paint or coating composition. Pigments are used decoratively as colourants or functionally as anticorrosion or magnetic pigments.

Synthetic inorganic pigments (Figure I-1.5) can be subdivided into white, black, coloured and lustre pigments. Anisometric lustre pigments are, e.g., metal effect and pearlescent pigments.

Fillers (extenders) are powdery materials (particles) which are virtually insoluble in the paint or coating composition. They are mostly used to extend the volume (lower the price), to confer or to improve technical properties (e.g. abrasion or stone-chip resistance) and/or to influence optical properties.

It should be mentioned that fillers have only minor colour-bearing properties; in some cases, (e.g. latex paints, see Chapter III-2), they are used like white pigments to increase hiding power (see Figure I-1.5). Mostly, fillers are inorganic substances.

The **solvent** is a liquid that mostly consists of several components and dissolves binders without chemical reaction. Solvents must be volatile when solidification of the paint (film formation) takes place. If the binder is not dissolved but dispersed, the liquid phase (often water) is called the dispersion medium (see Chapter 1, Part III).
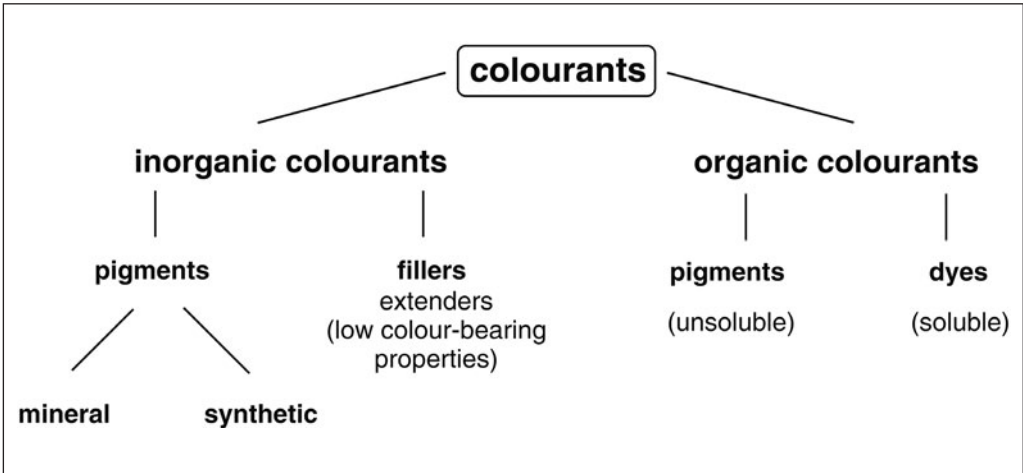
Figure I-1.5: Colourants

Additives are substances added in small proportions to coating compositions to modify or improve properties of the liquid paint (e.g. rheology) or of the solid coating (e.g. gloss).

The following helpful abbreviations for describing the binders of coatings will be used in this book (Table I-1.2).

1.5   Coatings

1.5.1   Solidification of paints

Solidification (also called film formation) is the transition of an applied paint from the liquid to the solid state. A distinction is made between (physical) drying and (chemical) curing, and they can take place simultaneously or one after another. Solidification transforms the intermediate paint product into the final product, which is the solid coating adhering on the substrate.

Physical drying

Physical drying of an applied paint is the transition from the liquid to the solid state by evaporation of solvents (including water).

The dissolved binder molecules first form polymer coils flooded by solvents (solvates) which are mobile in a phase of free solvent (Figure I-1.6). The bound and free solvents are in equilibrium. The vapour pressure of a solvent in a binder solution is lower than that of the pure solvent. On account of its vapour pressure of a solvent in a binder solution is lower than that of

Table I-1.2: Abbreviations for some binders

letter symbol	binder (paint resin)
AK	alkyd resin
SP	saturated polyester
UP	unsaturated polyester
AY	acrylic resin
CAB	cellulose acetobutyrate
CN	cellulose nitrate
EP	epoxy resin
EPE	epoxy ester resin
MF	melamine resin
PF	phenolic resin
UF	urea resin
PUR	polyurethane
PVAC	polyvinyl acetate
PVB	polyvinyl butyrale
PVC	polyvinyl chloride
RUC	chlorinated rubber
RUI	cyclized rubber
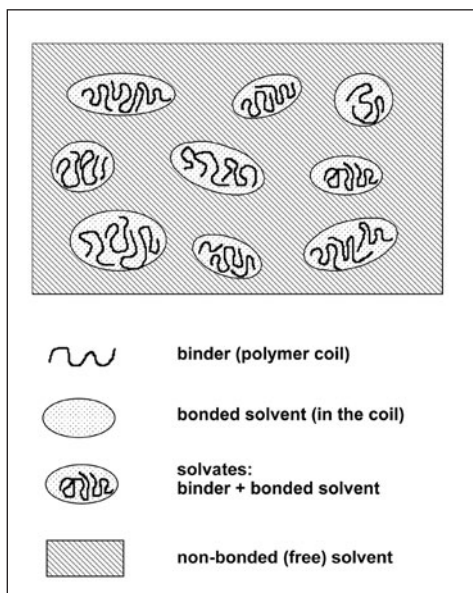
Figure I-1.6: Simplified diagram of a diluted binder solution

the pure solvent. On account of its vapour pressure, the solvent (the free solvent initially) will always evaporate far below its boiling point if an adequate volume of air prevents the establishment of an equilibrium vapour pressure in the gas phase above the paint film. For complete physical drying, adequate ventilation is necessary.

Because some of the solvent evaporates, the polymer coils (binder) approach each other; simultaneously there is a decrease in the level of bound solvent. Finally, the solvates come into close contact. At this stage, there are no longer any boundaries between the solvates and the first stage of solidification is reached. Further solvent evaporation becomes progressively slower. The film shrinks and further solidification occurs. Small fractions of solvent may remain in the film for a long time, even in stoving coatings; this phenomenon is called solvent retention.

In **organosols** [dispersions of binders in organic solvents (NAD or non-aqueous dispersion)], most of the solvent used as dispersion medium evaporates first of all. Ultimately, the polymer dispersion turns into a solution, namely in that part of those solvents which evaporate slowly and are good solvents for the polymer.

Plastisols (dispersions of polymers in plasticizers) solidify by gelation at higher temperatures; i.e. the polymers dissolve in the plasticizers (or vice versa), which become a solid film on cooling.

Physical drying of aqueous polymer dispersions (latices) is a special case and is described in Chapter III-1.

Another type of physical solidification is the cooling of melted thermoplastic powder coatings (see Chapter IV-3.4.1).

Chemical curing

Chemical curing of an applied paint is the transition from the liquid to the solid state accompanied by an increase in molar mass and crosslinking. Therefore, "oxidative drying" of alkyd resins should be called "oxidative curing" [8].

A basic requirement for any chemical reaction (including curing) is adequate mobility of the reacting molecules. This is the case in gases and liquids, but in solids it occurs only at the interfaces.

For this reason, liquid binders (see Chapter IV-1) and melts (see Chapter IV-3) solidify well by means of chemical reactions.

Binder solutions are particularly advantageous. In solution, binder molecules that would otherwise be solids are capable of reacting with each other. The first precondition is that the binder molecules be dispersed by the solvent and form solvates as described above. These solvates should be mobile in the free solvent. Second, the binder molecules must even be mobile when curing takes place in order that reactive functional groups may react chemically with each other.

In curing paints, mostly two different types of binders (or binder and crosslinking agent) have to be made to react with each other. A basic requirement for homogeneous chemical reactions between two different oligomers or polymers is compatibility.

Binders or binder and crosslinking agent are compatible when they contain similar structural parts or at least structural parts of similar polarity or solubility. If binders of inadequate compatibility have to be combined, the mixture of the two can be pre-reacted. In most cases, this is effected by chemical reactions at elevated temperatures. Typical pre-reactions are pre-condensation of saturated polyesters with either urea or silicone resins.

The various molecules come together and react with each other by means of diffusion processes which should be sufficiently rapid. High-molecular, immobile molecules crosslink less effectively than low-molecular, mobile ones.

Curing (crosslinking) is employed especially in industrial paint applications because it can be accelerated to yield ready-to-use coatings within a relatively short time. Industrial cycle times determine the paint formulator's choice of crosslinking reactions. On one hand, these must be effective within a given time. On the other, the paints must offer as much storage stability as possible. Consequently, the paint systems used crosslink only at elevated temperatures (stoving paints) or start curing after the addition of crosslinkers, initiators or catalysts (e.g. acid-curing paints). Moreover, it is possible to separate the reactive components in storage (two-components paint systems).

Dispersions can contain very high-molecular binders. This is advantageous if the paints are to undergo physical drying only. Chemical reactions in dispersions are more difficult to effect. Dispersed binders can be cured with added crosslinking agents which can be dissolved or dispersed too. These crosslinking agents must diffuse into the phase boundary and further into the centre of the dispersed binder particles if chemical curing reaction is to take place.

Often, dispersed binders are only crosslinked at the phase boundary. If the dispersed particles consist of a (pre)mixture of binder and crosslinking agent, the binder system can be cured effectively. Another possibility is to combine a polymer dispersion with a dissolved self-crosslinking binder; in this case the dispersed binder phase will not be crosslinked.

Powder coatings are cured effectively only if binder and crosslinking agents are mixed efficiently (polymer melt in the extruder) before the powder is ground (see Chapter IV-3.2).

Organic binders as polymeric materials

At this point, we will now discuss coatings from the point of view of plastics technology and polymer science; this is unusual, but offers interesting insights. Organic binders in coatings are nothing more than polymeric plastic materials and can be classified according to the rules of plastics technology (Figures I-1.7 and I-1.8).
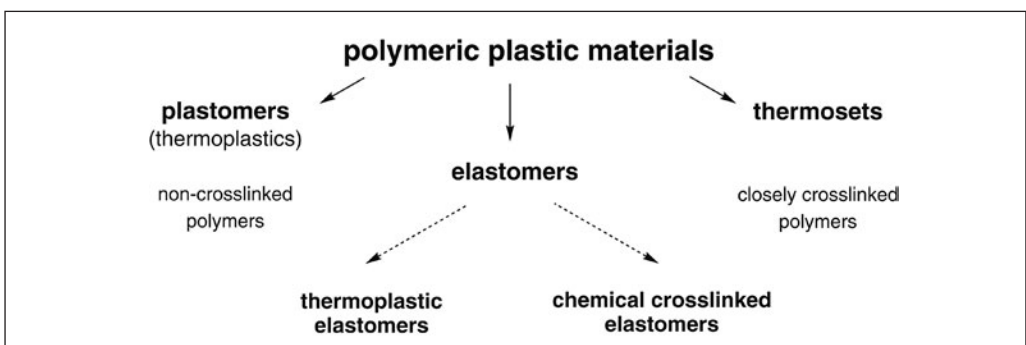
Figure I-1.7: Classification of polymeric plastic materials
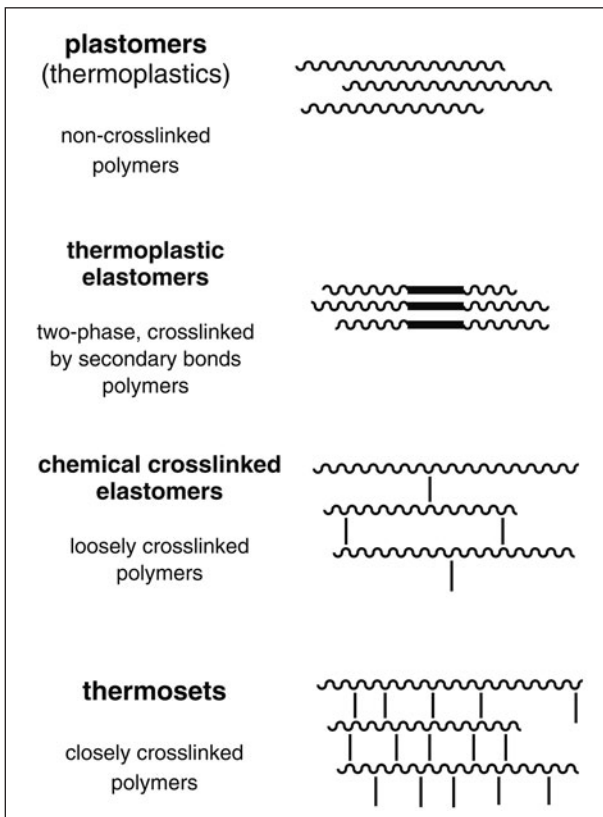
Figure I-1.8: Schematic diagram of polymeric plastic materials

Coatings (films) formed by physical drying are plastomers. Coatings formed by chemical curing reactions are thermosets. Elastomers are not commonly used in coatings technology and can be neglected.

Plastomers are thermoplastic and soluble in suitable solvents. The rate of dissolution of physically dried coatings is usually low because of the low surface area (planimetric surface area); this is advantageous but should not be confused with solubility. Thermosets are unmeltable; at elevated temperatures they decompose by chemical degradation. Moreover, thermosets are insoluble; sometimes cured coatings show some swelling which may lead to (mostly reversible) softening of the coating.

1.5.2 Phase boundaries in coatings

Non-pigmented clear coats may have heterogeneous film structures caused by, e.g. nonuniform crosslinking or separation of binders [10]. The consequence of this heterogeneity could be large inner phase boundaries originating from various binder phases. Furthermore, certain functional groups of the binder (e.g. carboxyl groups) can be oriented towards polar substrates (e.g. metal oxides), and that also causes heterogeneity [10].

Generally, film structures containing pigments and fillers are heterogeneous and have large phase boundaries (so-called phase-boundary-dominated systems).

Coatings exhibit as may as four different phase boundaries (Figure I-1.9).

- The first phase boundary is the binder/substrate interface; this phase boundary is equal to the planimetric surface area of the substrate (may be four times as large because of the roughness of the substrate surface). The function of this interface is adhesion (and, on metal substrates, corrosion protection).
- The second phase boundary is the binder/pigment or filler interface; this phase boundary can be very large because of the large specific surface area of pigments (up to 100 m^2/g; see Chapter I-2). This interface is responsible for the internal cohesion of the coating and may influence its mechanical properties (such as stone-chip resistance). A pigmented coating may therefore be viewed as a (very thin) composite material. Moreover, this interface can influence the corrosion protection properties of the coating [20].
- The third phase boundary is the binder/atmosphere interface (in the case of coatings for hydraulic steel constructions, a binder/water interface). This phase boundary is approximately equal to the planimetric surface area. Of great practical interest is the fact that weathering of coatings takes place at this interface (perhaps also in the layers below).

• Furthermore, there may be binder/binder phase boundaries if the binder consists of different phases (see above).

As a rule, the binder structure at all phase boundaries is different from the polymer structure in the bulk phase, which has been discussed above.

Figure I-1.9: Simplified diagram of coating below the critical pigment volume concentration on a substrate (cross-section)

1.6   Adhesion

Adhesive strength is a measure of the resistance of a coating to mechanical removal from the substrate; the usual unit of measurement in coatings technology is force/area (N/mm^2; MPa).

Permanent adhesion (under wet conditions, too) of the coating on the substrate and in a multicoat system is a basic prerequisite for the protective effect (e.g. corrosion protection).

One exception is strippable coatings, which are temporary coatings for protecting goods during transport.

1.6.1   Wetting of substrates

A necessary (but not sufficient) prerequisite for good adhesion is adequate wetting of the substrate by the liquid paint during application. The substrate/air interface (surface) is converted into a substrate/liquid interface (an interface between two condensed, immiscible phases). During subsequent drying or curing, the film solidifies (Figure I-1.10).

The term wetting is important in coatings technology because pigment particles also have to be wetted (Chapter I-2.3). Thus, wetting needs to be discussed in more detail.

Surface and interfacial tension

In a liquid such as water, all molecules in the bulk phase are uniformly surrounded by their neighbouring molecules. Thus, the attractive forces acting on these molecules extend equally in all directions in space and cancel each other out (Figure I-1.11). At the water/air
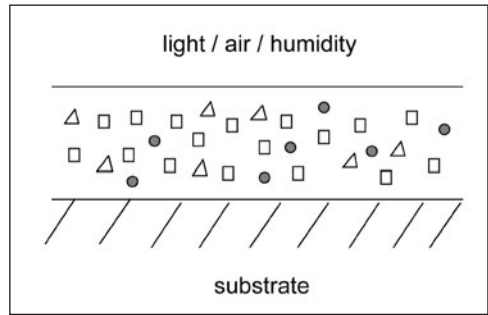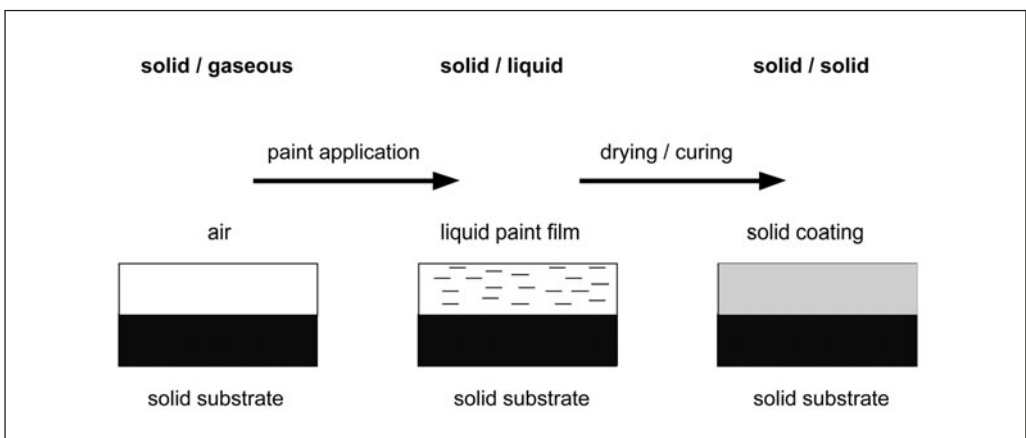

Figure I-1.10: Interfaces on solid substrates (diagram not true to scale)
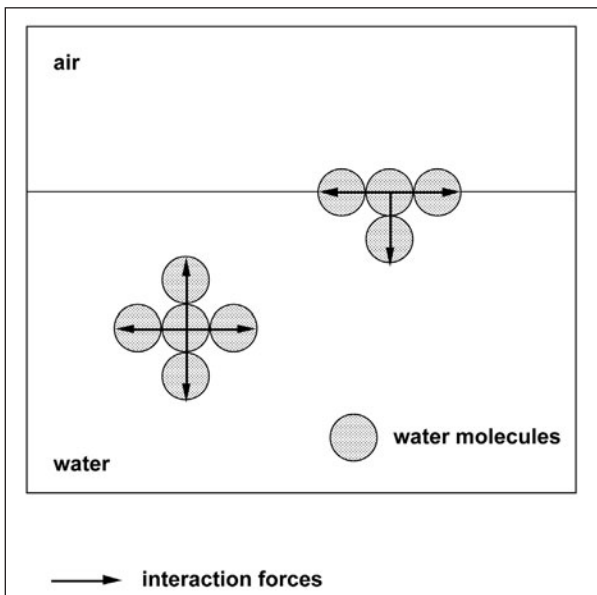
Figure I-1.11: Force diagram to explain surface tension

interface, things change dramatically because there a water molecule is surrounded by other water molecules only at the interface and in the direction of the bulk phase. Thus, the forces of attraction do not cancel each other; a force acts on the water molecule in the direction of the inner phase of the liquid (Figure I-1.11). The effect of this force is that the liquid's surface becomes as small as possible. This is why a droplet in gravity-free space is spherical – the sphere has a minimal surface area combined with maximum volume.

This force has to be quantified. The interfacial tension (γ) is the force acting along 1 m of an imaginary boundary between two phases [force/length = N/m; usually quoted as mN/m; obsolete unit: dyn/cm]. If one of the phases is air, the tension is called surface tension.

To enlarge a surface area, molecules have to move from the bulk to the surface. Thus, forces of attraction have to be overcome and work needs to be done or energy expended.

The following mathematical conversion shows that energy/area is equal to force/length. In other words, the surface tension is also a measure of surface energy:

$$\frac{\text{energy}}{\text{area}} \;=\; \frac{J}{m^2} \;=\; \frac{N \cdot m}{m^2} \;=\; \frac{N}{m} \;=\; \frac{\text{force}}{\text{length}} \; ; \text{interfacial or surface tension}$$

Typical surface tensions of liquids are presented in Table I-1.3.

The higher the surface tension, the greater is the cohesion in the respective phase and the stronger are the forces of interaction between the atoms or molecules in that phase. Water molecules are strongly associated with each other by hydrogen bonds, which generate high a level of cohesion and a high surface tension. The water surface behaves like a skin. The less polar the liquids are, the lower is their surface tension.

Wetting

A simplified diagram of the wetting of a solid surface (substrate) by a liquid is presented in Figure I-1.12.

A measure of wetting is the contact angle Θ between the solid substrate and the applied liquid drop (Figure I-1.12). The smaller the contact angle Θ, the better is the wetting.

Wetting is mathematically described by Young's equation:

$\gamma_S = \gamma_{SL} + \gamma_L \cdot \cos \Theta$

Spreading is the complete wetting of a substrate by a liquid: $\Theta = 0°$ and $\cos \Theta = 1$.
For spreading, Young's equation becomes $\gamma_S = \gamma_{SL} + \gamma_L$ and $\gamma_L = \gamma_S - \gamma_{SL}$. If a liquid such as paint has to wet the surface of a solid substrate, the surface tension of the liquid must

be lower than the surface tension of the substrate ($\gamma_L < \gamma_S$). Thus, if a liquid has a higher surface tension than the substrate, there will be no sufficient wetting.

The critical surface tensions of solids (Table I-1.4) can be measured indirectly in wetting experiments[26, 27].

Possible changes in the surfaces of substrates (e.g. oxide layers, mould-release agents) have to be considered because there may be a great effect on the surface tension (see below).

Metal surfaces

If the prerequisite for sufficient wetting is $\gamma_L < \gamma_S$, then water should not spread on metal surfaces (see relatively low surface tensions of solid metals in Table I-1.4). This is borne out by measurements of contact angles of water on various pre-treated aluminium sheets (Table I-1.5); while the water does wet ($\Theta < 90°$), no spreading occurs ($\Theta > 0°$).

Table I-1.3: Surface tensions [mN/m] of liquids

liquid	surface tension [mN/m]	remark
mercury	500	liquid metal
water	73	
epoxy resins	45 to 60	
melamine resins	42 to 58	
alkyd resins	33 to 60	
acrylic resins	32 to 40	
butyl glycol	32	
xylene	29 to 30	
white spirit	26 to 27	
butyl acetate	25	
butanol	23	
white spirit	18 to 22	free of aromatic hydrocarbons
hexane	18	
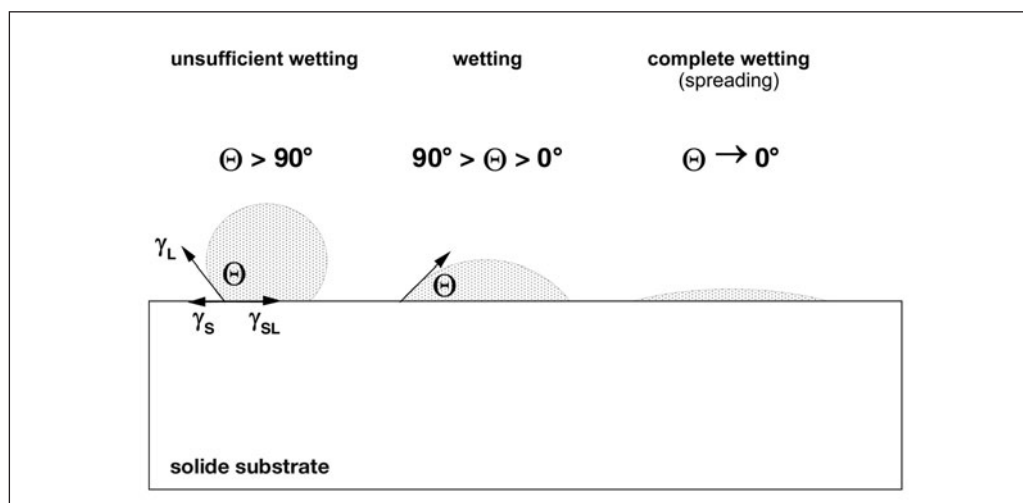
Figure I-1.12: Wetting of a solid substrate by a liquid.
γ_S *Surface tension of the solid substrate* γ_L *Surface tension of the liquid*
γ_{SL} *Interfacial tension between solid substrate and liquid* Θ *Contact angle of the liquid on the substrate*

Figure I-1.13 is a schematic diagram of an aluminium surface [11] that would be better referred to as an aluminium oxide surface; similar considerations apply to all commonly used metals. If the model in Figure I-1.13 fully describes reality, the hydrated aluminium oxide surface would be wetted by water completely; but this is not observed (Table I-1.5). Figure I-1.13 is a simplification of the real situation. ESCA/XPS measurements show that various pre-treated

Table I-1.4: Critical surface tensions [mN/m] of solid substrates

solid substrates	surface tension [m/Nm]
glas	73
phosphated steel	43 to 46
poly(vinyl chloride)	39 to 42
tin-plated steel*	about 35
aluminium*	33 to 35
polyethylene	32 to 39
polypropylene	28 to 29
steel (untreated)*	29
polydimethylsiloxane	19
polytetrafluorethylene	19

* Solid metal (oxide) surfaces! Melted (liquid) metals have much higher surface tensions (see mercury in Table I-1.3)
In different references one may find a slight variation of these values.

Table I-1.5: Contact angle of water on various aluminium surfaces

aluminium surface	contact angle Θ (± 5°)
rolled	63
pickled with a commercial caustic	22
pickled with NaOH	31

aluminium surfaces have, in addition to aluminium and oxygen, a significant amount of carbon. Presumably, the carbon is adsorbed from the atmospere (e.g. carbon dioxide or hydrocarbons) [12]. Thus, while there is still no universal model that describes the structure of metal surfaces, it is certain that metal oxides are present.

Surfaces of plastics

Even more complicated are the structures of surfaces of engineering plastics [11]. The problem here is that the bulk properties of the polymer are different from the surface properties. Theses differences may be caused by the composition of the plastic or by the production or processing conditions. Mostly the surfaces have low energies (low surface tension), which leads to poor wetting.

Composition of plastics

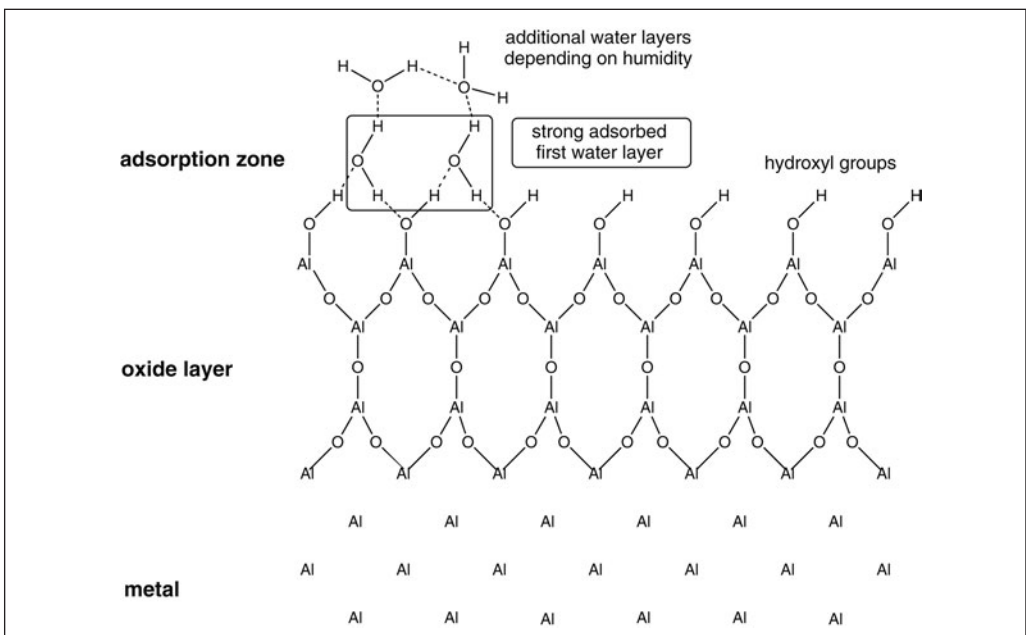Many plastics contain low-molecular components, such as additives

Figure I-1.13: Hydrated aluminium (oxide) surface (very simplified model). Similar considerations apply to the Fe/Fe_2O_3 system

(e.g. stabilizers), residues of solvents and sometimes plasticizers. All these components can impair adhesion if they are on the surface. Many low-molecular components tend to migrate to the surface and accumulate there. Thus, there may be an anti-adhesive layer on the surface of plastics (Figure I-1.14).

Production and processing conditions of plastics

a) Mould-release agents
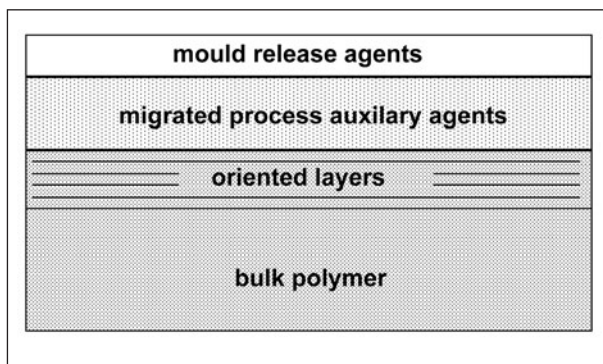   When moulded or compressed plastic parts have to be released

Figure I-1.14: Surface of engineering plastics

from the mould, internal and external mould-release agents are used. Internal mould-release agents are mixed into the plastic pellets and are distributed completely in the plastic material; therefore, there is no point in sanding the plastic surface. Internal mould-release agents generate plastic surfaces that are either unwettable or barely wettable. External mould-release agents are sprayed into the open injection mould; they are based on paraffins, soaps and oils (including silicone oils). Because of the processing conditions, external mould-release agents are found not only in the surface layer, but also in the layers below.

b) Surface properties caused by processing conditions
   Injection moulding or compression creates surface properties that differ from those of the bulk polymer. The dense surface layers of moulded plastic materials are very smooth (oriented layers; Figure I-1.14).

Improvements in wetting

In the case of water-borne paints especially, $\gamma_L > \gamma_S$ and leads to poor wetting. There are two ways to improve wetting:

- Lower the surface tension of the water-borne paint (γ_L) by adding wetting agents (see Chapter I-2.2.3).
- Increase the surface tension of the substrate (γ_S).

The surface tension of metals may be increased, for example, by phosphating (see Table I-1.4).

Oxidation of plastic surfaces (e.g. by flame treatment) generates polar functional groups (e.g. -OH, -COOH) on the surface and increases γ_S. A detailed description of pre-treatment processes for different plastics is presented in [11]. Sometimes sanding or rubbing with emery or cleaning with organic solvents or water-borne cleaners will improve the wettability of plastic surfaces.

Furthermore, adhesion-promoting primers may be applied before the plastics are painted. For example, polyolefins (low surface tensions; Table I-1.4) can be coated with chlorinated polymers, which increase the surface tension.

1.6.2 Adhesion forces and mechanisms

So far, no universal theory of adhesion exists; the theories that exist explain only sub-areas. Nonetheless, a partial theoretical explanation of phenomena related to adhesion is better than none.