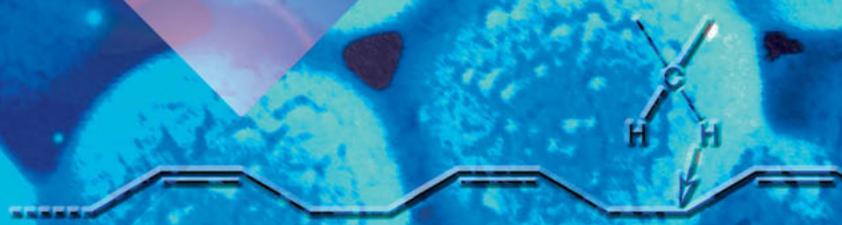
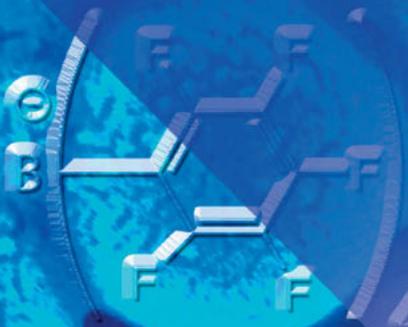


Peter Mischke

# Film Formation



Vincentz Network GmbH & Co KG

Peter Mischke

# **Film Formation in Modern Paint Systems**

Translated by Ray Brown

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**Peter Mischke**

**Film Formation**  
**in Modern Paint Systems**

Translated by Ray Brown

# Foreword

This book is all about how coating materials, especially paints, form films. A student asked me recently: “How is it possible to write a book on a topic like that?” Her question was right on the mark. There can be no doubting that common textbooks on surface coatings devote very few pages to the topic of film formation. And yet, close examination shows that film formation is a theme that surfaces and resurfaces in the expert literature and in technical discussions on coating technology, without ever being specifically addressed. And that leads on to the problems inherent in tackling the topic. These include how to isolate the subject matter from the related areas of application methods, chemistry/formulation, and metrology, and the rest of current coatings literature; the extent to which the latest specialist advances be taken into account. And last but not least: A university teacher in a broad sweep of disciplines ranging from chemical principles to colloid and polymer chemistry through to the science of binders, adhesives and paint chemistry, my purpose in writing this book is to present the basics of film formation in a broad canvas while striking the right balance of topics and not delving too far into other fields. I have drawn on my own expertise and university teaching experience as well as a wealth of information from monographs directly accessible to me and periodicals such as “Farbe und Lack”.

The book commences with a brief explanation of the main coating concepts, before presenting methods of application as the first step towards a finished coating. This is followed by the physical aspects of drying. The middle section of the book deals at length with fundamental polymer and physicochemical aspects. It is intended to enable readers who lack an academic background in chemistry to understand the more specific content of the later chapters, without first having to study a comprehensive textbook on the subject. The second half of the book covers the fundamental film-forming principles and coating systems. A brief overview of test methods used to study film formation is presented in Annex 4.

So who should read this book and why? The intended readership includes:

- third-level students of coating technology wishing to deepen and round out their knowledge of pure paint technology on one hand and pure paint chemistry on the other;
- newcomers and career-changers seeking a readable textbook that is not overloaded with individual facts and/or specialist material
- skilled personnel in paintshops wondering why the various effects they observe as they go about their daily work actually occur and how they might intervene to solve particular problems that arise;
- finally, the book may be particularly instructive to laboratory staff and technicians seeking to gain a deeper understanding of film-forming mechanisms.

My thanks to everyone from the Department of Coatings Technology at Niederrhein University of Applied Sciences who kindly provided thoughtful suggestions, information and hands-on support. I would also like to thank Ilia Korolinskij, a graphics expert, who converted numerous sketches into a print-ready form. Finally, I am forever indebted to my family for sacrificing a great deal of quality time together during the year-and-a-half which I spent writing the book.

Willich/Germany, August 2009

Peter Mischke

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# 1 Introduction

## 1.1 Basic concepts

The act of applying a solid, adhering, organic chemical layer or film to any kind of surface or substrate is called **coating** (note that inorganic coatings, such as distempers, are not the subject of this book) and the outcome is properly called a coating system. Depending on the **coating material** employed, the coating may be decorative, protective or otherwise functional and may be a varnish, an emulsion paint, a floor-coating compound or a filler. Before and immediately after application, the coating material is a liquid, a paste, or a powder (as in coating powders). The transition to finished coating requires the film of coating material to solidify and is called **film formation**, or, from an application point of view, **drying**. These terms and others employed in coating technology are defined in the EN ISO 4618 and also in the German standard DIN 55945 (2007-03).

In order for a coating material to form a film at all, it must contain a substance which is capable of forming a film by itself, i.e. without the presence of other chemical components. Such substances are called **film-forming agents** or **binders**.

Older standards, such as DIN 55945 (1988-12 and earlier), clearly distinguished between the terms “binder” and “film-forming agent”. However, this distinction never really took hold in practice, and seems to have largely been abandoned.

According to DIN 55945 (1999-07),

- the film-forming agent is “the binder which is needed in order that the film may form”

In EN ISO 4618, we find:

- binder is the nonvolatile part of a medium, where medium is defined as all constituents of the liquid phase of a coating material.

In keeping with general parlance, in this book we will use the term “binder” even when, according to the traditional definition, a film-forming agent is meant.

Binders generally, and in this book, are the most important class of substance present in all coating materials. Every coating material contains a binder, which frequently is a mixture of several substances (resins, etc). We can say therefore that:

- the binder determines the fundamental properties of the coating material and the coating.

The job of the binder (or film-forming agent) is to form a more or less solid film and, where other ingredients are present, to embed them or to bind them to each other. Binders are generally organic substances that vary considerably in molecular size. Depending on their composition, degree of dissolution/dilution or manufacturing process, they are called either resins, e.g. alkyd resins, epoxy resins, and melamine resins, which can be present in 100 % concentrated, dissolved or dispersed form or **polymer dispersions**.

Binders composed of small to medium-sized molecules, equivalent to (mean) molecular weights ranging from several hundred to 10,000 g mol<sup>-1</sup>, must be chemically transformed into large molecules or molecular networks during film formation. This is called hardening

or curing. Binders composed of large or long molecules (macromolecules) can form sufficiently solid films without chemical reaction; essentially, the solvent or dispersing agent in the formulation simply evaporates during film formation and the long thread-like molecules become matted, rather like felt. This type of film-forming process is called **physical drying**. The qualifier “physical” must be used in this case because “drying” can also include curing. Most films which are formed by curing additionally undergo physical drying or surface drying, especially in the early stages. Figure 1.1 shows a schematic diagram of the two basic film-forming mechanisms.

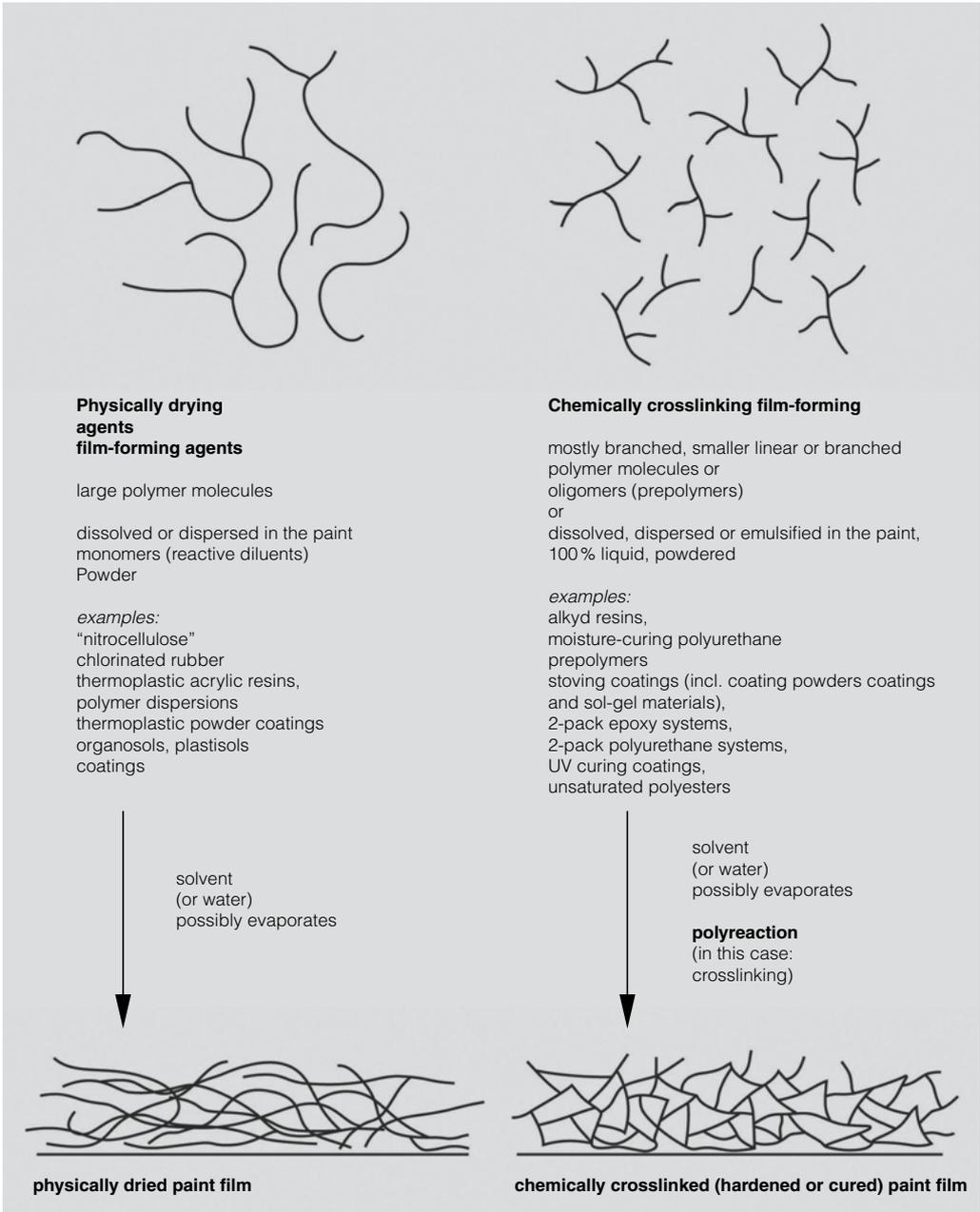


Figure 1.1: Film formation by physical drying (left) and curing (right)

## 1.2 General composition of coating materials

Once a specific coating material has been selected, it is a simple matter of referring to the instructions or technical leaflet to find out how it should be applied and dried. The leaflet or container will even contain general information about the chemical composition, possible health hazards and methods of disposal.

The composition of coating materials will be discussed in a very brief, generalised form below. Details and technical information are provided in this book as and when they are needed for an understanding of film formation. Table 1.1 presents an overview of the general composition of coating materials.

It should be pointed out that not all coating materials contain all classes of substance listed in Table 1.1. Thus, a clearcoat contains neither pigments nor extenders (in the classical sense), and a coating powder contains no solvents. Apart from binders, the ingredients mentioned in Table 1.1 will now be described in brief.

### Pigments

These are very finely divided powders which are practically insoluble in the application medium, i.e. the liquid ingredients of the coating material, and/or act as colorants and/or prevent corrosion and/or have other functions. Examples: titanium dioxide (white pigment), carbon black (black pigment), quinacridone pigment (coloured pigment), pearlescent pigment (effect pigment), zinc phosphate (corrosion-protection pigment).

### Fillers

Fillers, too, are powders which are virtually insoluble in the application medium. They impart volume or “build” to the coating material and provide or improve certain technological properties. They are typically used to modify flow properties, suppress cracking (provide reinforcement), improve ease of sanding, adhesive strength and weather resistance, matting, etc. The effect exerted by a filler depends critically on its particle size and particle shape (whether isometric, lamellar, or acicular). Examples: chalk, talcum, fibre fillers.

### Additives

Additives, traditionally called “adjuvants”, are substances which are added to the formulation in relatively small quantities and which, during manufacture and/or application of the coating material, engender or enhance certain properties or selectively improve the film properties. Additives vary in volatility, and will either remain in the coalescing film or escape from it more or less completely. Examples: Dispersing additives (nonvolatile), slip additives (nonvolatile), catalysts (mostly nonvolatile), defoamers (mostly nonvolatile), anti-skinning agents (volatile), film-forming agents (volatile).

### Solvents

This term refers to liquids that are truly capable of dissolving a binder to create a molecular dispersion. Solvents (in the broader sense) are organic liquids, but can also be water. Examples: xylene (aromatic hydrocarbon), butyl acetate (ester), methyl isobutyl ketone (ketone), butyl glycol (ether alcohol), butanol (alcohol).

Table 1.1: General composition of coating materials

Coating material	
nonvolatile content	volatile content
binders	solvents and dispersing agents
pigments	volatile additives
film-forming agents	
nonvolatile additives	(usually volatile cleavage products during stoving)

If the solvent is added to the coating material to adjust its viscosity prior to processing, it is called a **diluent** or **thinner**. **Reactive diluents** are diluents which are almost completely chemically incorporated into the coalescing film and are therefore classed as binders.

### **Dispersing agents**

Unlike solvents, these liquids (most often water) do not yield a molecular dispersion of a binder but rather contain it in the form of submicroscopic particles or droplets. The overall system is called a **dispersion** and – in contrast to a solution – usually has some cloudiness. A dispersing agent, too, may act as a diluent. Thus, it is quite common to lower the viscosity of an interior emulsion paint with a little bit of water for application by roller.

## **1.3 General formulation data**

The simple paint formulation presented in Table 1.2 will now be used to explain the most important general data relating to formulations.

The **nonvolatile matter** (also called **solids content**) is the

- mass fraction of coating material remaining after a specified drying time.

The content of nonvolatile matter is determined in accordance with ISO 3251 by accurately weighing out, e.g., 2 g of the coating material into a lid, drying it under defined (or agreed) conditions, e.g., one hour at 130 °C in a paint drying oven, and then reweighing it. If chemical reactions during drying cause minor products to be released, the nonvolatile values can vary substantially with the temperature and duration of drying.

The theoretical content of nonvolatile matter in the formulation shown in Table 1.2 is calculated as follows:

$$60 \% \cdot 0.75 + 27 \% = 72.0 \%$$

The additives are ignored if they are present in small quantities.

The content of nonvolatile matter is crucial for application because it indicates the mass of the film that will remain on an object after the coating has dried.

The **pigment-binder ratio** in the sample formulation is

$$27.0 : (60 \cdot 0.75) = 0.60 = 3 : 5$$

The pigment volume concentration, PVC, is the volume fraction of pigments and fillers in the dry film volume.

Table 1.2: Simple paint recipe (white house paint); from [3]

<b>Ingredient<sup>1)</sup></b>	<b>Mass fraction [%]</b>
alkyd resin, 75 %, in white spirit	60.0
titanium dioxide (white pigment)	27.0
cobalt octoate (10 % Co)	0.2
zirconium complex (6 % Zr)	0.5
calcium octoate (5 % Ca)	1.7
white spirit	10.6
	100.0

The PVC is calculated as follows:

Equation 1.1:

$$\text{PVC} = \frac{V_p + V_F}{V_p + V_F + V_B}$$

$V_p$  is the pigment volume,  $V_F$  is the filler volume,  $V_B$  is the binder volume

<sup>1)</sup> Figures quoted in percent are mass fractions (wt.%)

The binder volume here comprises the volume of all nonvolatile matter in the dry film without pigments and fillers, i.e. it also includes curing agents, reactive diluent and, perhaps, plasticiser.

The volumes have to be calculated from the mass fractions in the formulation and the corresponding densities, which are included in the leaflets supplied with the raw materials. In the example in Table 1.2, the density of the resin is  $1.04 \text{ g cm}^{-3}$ , and the pigment density is  $4.1 \text{ g cm}^{-3}$ .<sup>1)</sup>

The PVC is therefore:

$$\text{PVC} = \frac{\frac{27.0}{4.1} \cdot 100\%}{\frac{27.0}{4.1} + \frac{60 \cdot 0.75}{1.04}} = 13.2\%$$

The **critical pigment volume concentration, CPVC**, is the

- PVC at which the binder volume is just sufficient to fill the voids between the pigment and extender particles.

To calculate the CPVC, the size of the void volume of the pigment or pigment/filler in the formulation must be known. This is commonly measured by the **oil absorption value** (EN ISO 787-5), which is the quantity of linseed oil needed for converting 100 g of pigment or extender (or a mixture of both) into a coherent, non-lubricating paste. In practice, chemists determine these values direct from the binder solution or water used, instead of from linseed oil. Although oil absorption values have poor reproducibility, the oil absorption value remains important because of its direct use in calculating and developing the formulation.

The oil absorption value can be used to estimate the CPVC from the following, easily derived equation.

Equation 1.2:

$$\text{CPVC} = \frac{100\%}{1 + \frac{\rho_P \cdot \text{OA}}{100 \cdot \rho_L}}$$

- $\rho_P$  is the density of the pigment/extender
- $\text{OA}$  is the oil absorption value of the pigment/filler
- $\rho_L$  is the density of the linseed oil ( $0.935 \text{ g cm}^{-3}$ )

From this formula, the CPVC of the example formulation is

$$\text{CPVC} = \frac{100\%}{1 + \frac{4.1 \cdot 20}{100 \cdot 0.935}} = 53.3\%$$

Where several pigments or extenders are present, the mean density of the mixture is used for  $\rho_P$ ; the oil absorption value must be determined experimentally from the entire mixture, since the degree of packing (void filling) cannot be predicted from the individual data.

The **Q value** is the

- Quotient of PVC/CPVC ( $\cdot 100\%$ ).

$$Q = \frac{13.2}{53.3} \triangleq 0.249 = 24.9\%$$

In the example, the Q value computes to

<sup>1)</sup> In this book, the power notation is used for composite units, e.g.  $\text{J kg}^{-1} \text{K}^{-1}$  (Joules per kilogram per Kelvin) instead of  $\text{J}/(\text{kg K})$ .

Formulations having Q-values of less than 100 % are said to be **subcritical**. They contain more binder than is necessary for filling the voids. The dry film is therefore not porous, i.e. it resembles a typical paint. Coating materials having Q values over 100 % are said to be **supercritical**. The films are porous, i.e. absorbent, and typical examples are interior emulsion paints and zinc dust paints. Figure 1.2 illustrates the qualitative relationship between Q value, coating properties and the type of coating material.

## 1.4 Basic physical properties

### 1.4.1 Density

The density,  $\rho$ , is the ratio of the mass,  $m$ , to the volume,  $V$ :  $\rho = m/V$ .

The SI unit is  $\text{kg m}^{-3}$ , but in practice the more instructive unit  $\text{g cm}^{-3}$  is used. Note that  $1 \text{ g cm}^{-3} = 1000 \text{ kg m}^{-3}$ . An obsolete term for density is “specific weight”.

### 1.4.2 Viscosity and flow behaviour

The science of flow is called rheology. The most important rheological parameter is the **dynamic viscosity**,  $\eta$ , of a flowable substance (fluid). It is defined as the ratio of **shear stress**,  $\tau$ , to **shear rate** (velocity gradient)  $D$  or  $\dot{\gamma}$ <sup>2)</sup>:

Equation 1.3: 
$$\eta = \frac{\tau}{D} = \frac{\tau}{\dot{\gamma}}$$

The SI unit is Pa·s (pascal second) or one thousandth of it: mPa·s (millipascal second). It is related to the obsolete unit, cP, (centipoise), as follows: 1 cP = 1 mPa·s.

Rearranging the equation above to  $\tau = \eta D$  makes the definition more instructive: the shear stress, i.e. the shearing force per unit area of the sheared layer, increases with increase in

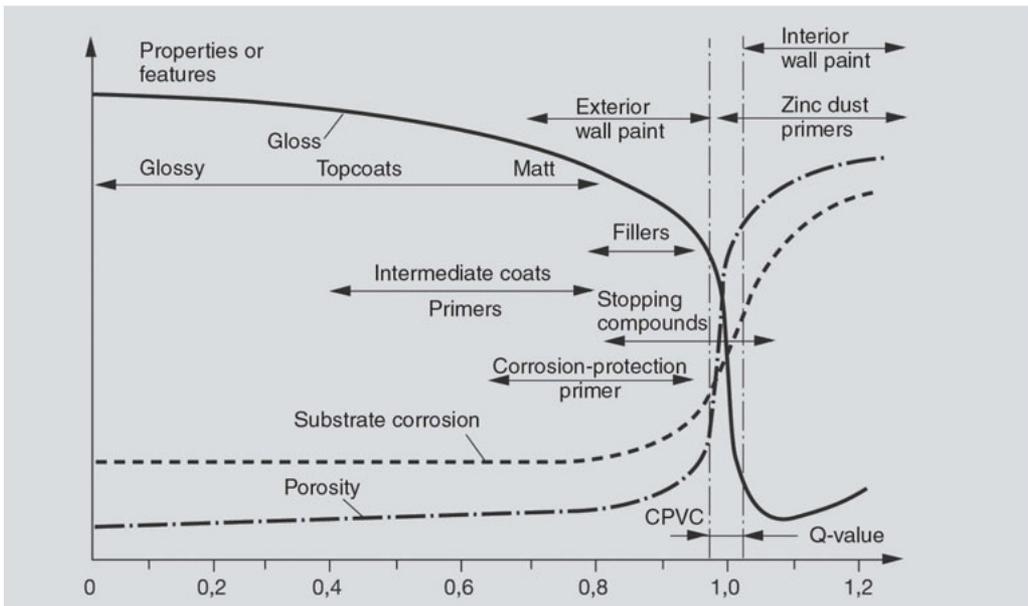


Figure 1.2: Various properties of coating materials, along with the corresponding Q value ranges from [3]

<sup>2)</sup> A dot above a symbol indicates derivation by time (divided by time, temporal change).

viscosity of the material and/or in the rate of shearing. Figure 1.3 shows a thought experiment that can be used to define the dynamic viscosity (for further information, see “The Rheology Handbook” by T. Mezger).

In certain contexts, the **kinematic viscosity**,  $\nu$ , is a useful parameter. It is the ratio of the dynamic viscosity to the density:  $\nu = \eta/\rho$ , and its SI units are  $\text{m}^2 \text{s}^{-1}$ .

If the viscosity is independent of the shear rate, i.e. stays constant when the shear rate changes, the flow behaviour is said to be **Newtonian**. Coating materials usually exhibit more or less **non-Newtonian** behaviour, i.e. the viscosity is dependent on the shear and perhaps on the duration of shearing. The following types of viscosity are distinguished (see also Figure 1.4):

**Structural viscosity (pseudoplasticity, shear thinning)**: the viscosity falls as the shear rate rises. The viscosity change is wholly reversible and responds almost instantaneously to the change in the shear rate.

**Dilatancy (shear thickening)** is the opposite of structural viscosity, i.e. the viscosity increases with increase in shear. Generally undesirable, dilatant behaviour is sometimes exhibited by very highly concentrated pigment or polymer dispersions.

**Thixotropy** exists when the viscosity at constant shear rate undergoes a fairly rapid asymptotic decrease and is restored when the shear stress is removed. Thixotropy originates from the reversible build up and degradation of loose **gel structures** in the fluid, and can be deliberately adjusted with appropriate **rheological additives**.

**Rheopexy** is the opposite of thixotropy, i.e. the viscosity increases under constant, weak shearing. Rheopexic materials are very rare.

A **yield point** is exhibited by a fluid which flows only after a minimum shear stress has been applied; it is nearly always observed in combination with structural viscosity or thixotropy. The presence of a yield point is also called **plasticity** and, if pronounced, leads to thickening. A yield point cannot be measured directly with simple viscometers, but rather only by extrapolation. Yield points are exhibited especially by products with high volume fractions of pigmentitious components, such as sealants and trowelling compounds, mastics, plastisols, emulsion paints and gels, whose non-sag properties can be seen with the eye.

The flow properties of coating materials are critical. For film formation, the two most important processes governed by rheology are levelling, which is generally desirable, and sagging, which is undesirable and takes the form of “runs” (or “tears”, “curtains”, etc; see Chapter 3).

### 1.4.3 Surface tension

The surface tension of a liquid,  $\sigma_l$ , or a solid (material),  $\sigma_s$ , is the work per unit area  $dW/dA^3$  needed to enlarge the surface (at constant mass) by  $dA$ , where “surface” is understood to be the interface to the adjacent gas phase or vacuum. The SI unit is  $\text{N m}^{-1}$  (or  $\text{mN m}^{-1}$ ).

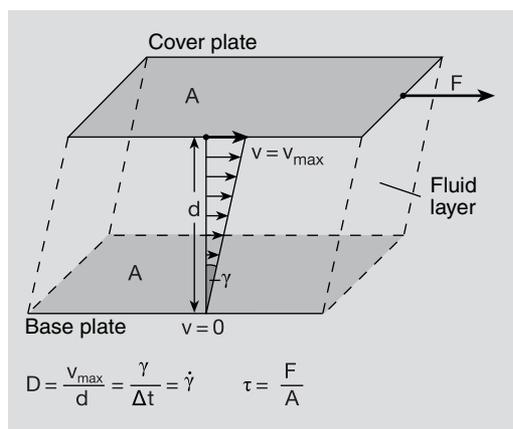


Figure 1.3: Thought experiment for defining dynamic viscosity

The word “tension” reflects the fact that the definition of  $\sigma$  above is based on another force-based equivalent:

The length  $L$  is called the edge line. Figure 1.5 shows schematically how the surface of a liquid lamella stretched in a wireframe can be enlarged. Downward displacement of the wire bracket by  $ds$  increases the surface area by  $dA = 2 L ds$  (front and back). At the same time, the lamella pulls the wire bracket up to the top with a force  $F = 2 \sigma L$ . Thus, the external work to be done is  $dW = F ds = (2 \sigma L) ds = \sigma (2 L ds) = \sigma dA$ , and this is present in the surface energy of the added surface  $dA$ .

For practical purposes, we can conceive of the surface tension generally as a force that acts along every actual or imaginary line in or at the boundary of a surface. For the purposes of film formation, substrate wetting and flow depend on the surface tension of the coating.

$$\sigma = \frac{dW}{dA} = \frac{F ds}{L ds} = \frac{F}{L}$$

Numerous other, often undesirable effects such as edge pulling, cratering and foaming, are also associated with surface tension (see Chapter 3).

## 1.5 Classification of film formation

Film formation – depending on the type of coating material – comprises various individual physical and chemical processes, which sometimes overlap and influence each other. The various types of film formation and drying undergone by coating materials can be classified as follows.

- **Physically drying coating materials**
  - solvent or dispersion-based (binders genuinely dissolved or dispersed)
  - film formation solely through evaporation of the solvent/water at different temperatures and, perhaps, air humidities
  - examples: cellulose nitrate, and chlorinated rubber paints, emulsion paints.
- **Chemically curing coating materials**
  - solvent-free or emulsion-free, yet flowable (“liquid, 100 % systems”)

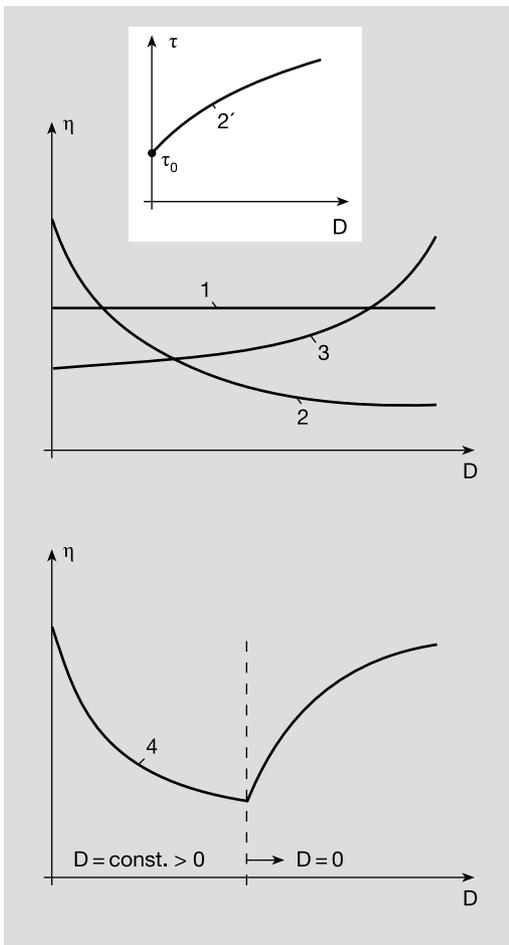


Figure 1.4: Basic rheological behaviour of coating materials: 1) Newtonian, 2) structurally viscous (shear thinning, pseudoplastic), 2') structurally viscous with yield point (in the  $\tau/D$  chart), 3) dilatant (shear thickening), 4) thixotropic

<sup>3)</sup> Where appropriate or necessary, physical quantities and or changes therein are expressed directly in the form of the differentials (d ... or  $\partial$  ...)

- film formation by spontaneous, chemical crosslinking reaction between **base paint** and **curing agent (two-component or 2-pack systems)** or through activation of crosslinking by means of heat, UV radiation or electron beams (1-pack systems)
- examples: 2-Pack materials based on urethane or epoxies for high-build coating in masonry and corrosion protection, heat-curing 1-pack polyurethane coating compounds, radiation-curing wood/furniture coatings based on acrylates.

- **Physically (surface) drying and chemically curing coating materials**

- binders genuinely dissolved or dispersed
- film formation initially by partial evaporation of the solvent/water, but mainly by chemical crosslinking, cold-curing 2-pack or heat-curing 1-pack
- examples: most industrial and automotive finishes.

- **Oxidatively curing or moisture-curing coating materials**

- solventless or solventborne 1-pack coating materials that - perhaps after surface physical drying - crosslink with atmospheric oxygen or air humidity at room temperature or slightly above
- examples: Alkyd resin house paints, moisture-curing polyurethane masonry paint.

- **Coating powders**

- thermoplastic powders: film formation by purely physical fusion on the preheated objects
- thermosetting (curing) powders: film formation by chemical crosslinking at elevated temperature after fusing and coalescence.

In summary, it should be noted that all types of drying entail an exchange of energy and, often, material with the surroundings. Thus, the external conditions during drying, i.e. the state of the environment around the object covered with the coating, determine the course of the film forming process. This particularly applies to the type and intensity of the energy input into the freshly applied layer (see Chapter 4).

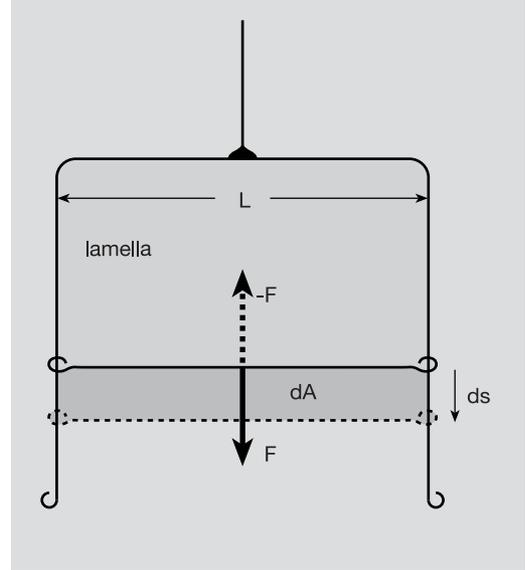


Figure 1.5: Surface tension of a liquid lamella in a wireframe (the area  $dA$  applies to the front and rear)

## 2 Application methods

Strictly speaking, application of a coating material is not part of film formation, but it is both a prerequisite and a direct precursor. To be sure, the type of application and the resulting structure of the wet film and layer of coating powder have no effect on the basic mechanisms of film formation; however, they do affect the outcome of the coating process, i.e. the perfection of the dried film.

What now follows is intended merely as an overview of the application methods, with some specific remarks. Much more detailed descriptions can be found in [3, 7, 11, 15], upon which most of this chapter is based.

### 2.1 Spreading (brush, roller), flow coating (roller coating, curtain coating, dipping)

#### 2.1.1 Brush and roller

Spreading of **paint materials** by brush still has its place in coating technology. The reasons are as follows:

- simple process
- high versatility as regards parts shape
- little or no masking of surfaces that are not to be coated
- good wetting of the substrate and incorporation of the coating into voids (cracks, holes, etc.)
- high **efficiency of application** (also known as **transfer efficiency**)<sup>4)</sup>
- wide range of materials processable without the need for precision adjustment

These are offset by weaknesses, such as

- low coverage rate
- uneven thickness
- uneven surface in the form of **brush marks**

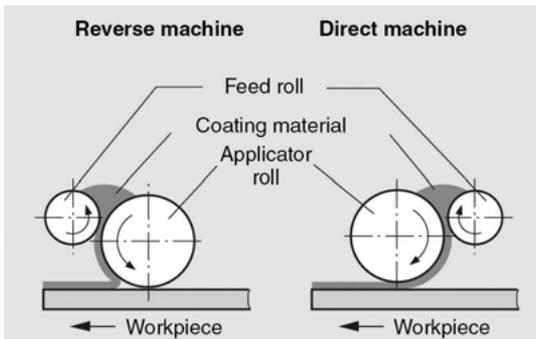


Figure 2.1: Roller coating; from [3]

Different types of **rollers**, such as long-haired or short-haired nylon wool or foam rollers yield much higher coverage rates and smoother surfaces. However, their use is largely limited to flat surfaces.

#### 2.1.2 Roller coating

In roller coating the material is applied by mechanical rolls at a correspondingly high coverage rate. The coating material is applied to flat, panel-like

<sup>4)</sup> By this is meant the mass of solids transferred to the workpiece as a ratio of the total mass of solids of coating material used (consumed), expressed as a percentage.