BASF Handbook

Basics of Coating Technology

3rd Revised Edition
Foreword to the 3rd Revised Edition

Glasurit’s “Paints and Coatings” handbook has been a standard work in the field of coating materials since it was first published in 1934. The latest German edition appeared in 2014 and serves as the basis for this third English edition, which is sponsored by BASF Coatings. Compared with its 2007 predecessor, this third edition contains more up-to-date market data and incorporates new raw materials, new application technologies, new legislative developments, mainly in Europe, as well as modern coating processes.

The main new developments covered in the raw materials and coatings sector are nanotechnology, polyurethane dispersions for water-borne coatings and smart coatings. As for pretreatment processes, application methods and recovery techniques, the latest advances here include workpiece rotation during electrocoating, the integrated paint process and new methods for handling overspray in the automotive industry. More than 200 new references have been added and some 500 others updated.

The proven arrangement of chapters has been left unchanged.

The handbook starts logically with a brief historical summary of painting, its economic and technical significance and the social framework underpinning the industry. Next comes a chapter on raw materials, product composition, the various production processes and the principles behind product formulation. Descriptions are then given of the properties of the liquid and solid coating materials employed in the various applications. This is followed by a chapter dealing with the theoretical aspects of coating compositions. Applications are then explained for the reader against the background of the current major industrial coating processes. This chapter clearly shows just how important the substrate is because of the impact it has on the coating outcome. A chapter follows dealing with the demands on environmental compliance, health, safety and quality as specified in current legislation, mainly in Europe and Germany. After that, the reader is taken on a journey through various sectors of the paint and coatings industry, accompanied by numerous examples and illustrations. This chapter will be of particular interest for newcomers to the industry and practically-minded readers alike. The book concludes with tables of selected standards, explanations of physical symbols, useful websites, definitions of terms and a comprehensive index round.

Literature references are provided for readers seeking more in-depth information. These are to be found at the end of each chapter and are repeated on occasion. Many of the comments and scenarios are based on experience gained by BASF Coatings and are not directly attributable.

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Director at the German DIN Institute for the trouble he took to ensure that the standards listed are up to date.

Finally, we would like to express our gratitude to the many companies which kindly provided us with pictures and charts for publication.

Prof Dr Artur Goldschmidt and Dr Achim Streitberger

Paderborn and Münster, November 2017
# Contents

1. Introduction
2. Coating Materials
3. Coatings
4. Coating Technology
5. Safety, Environmental Protection and Health
6. Principles of Quality Management
7. Coating Industries
8. Industrial Standards
9. Appendix
10. Index
## Contents

1 **Introduction** ......................................................................................... 15  
1.1 Definition, Tasks and Economic Importance ........................................ 15  
1.2 Retrospective ......................................................................................... 21  
1.3 References ............................................................................................. 25  

2 **Coating Materials** ............................................................................... 27  
2.1 Raw Materials ....................................................................................... 27  
2.1.1 Film Forming Agents ............................................................................ 30  
2.1.1.1 Natural Materials .................................................................................. 34  
2.1.1.2 Synthetic Resins .................................................................................... 49  
2.1.2 Solvents ................................................................................................. 127  
2.1.2.1 Theory of Solubility .............................................................................. 129  
2.1.2.2 Physical Properties ................................................................................ 131  
2.1.2.3 Chemical and Physiological Properties ................................................. 134  
2.1.2.4 Important Solvents for Paints ................................................................. 134  
2.1.3 Pigments and Extenders ........................................................................ 138  
2.1.3.1 Physical Principles behind Chroma and Hiding Power ......................... 142  
2.1.3.2 The most Important Pigments for Coating Materials ......................... 145  
2.1.3.3 Extenders ............................................................................................... 165  
2.1.4 Plasticisers and Additives ...................................................................... 167  
2.1.4.1 Plasticisers ............................................................................................. 168  
2.1.4.2 Additives ................................................................................................ 171  
2.1.5 Nanoproducts ......................................................................................... 191  
2.1.5.1 Description and Definition .................................................................... 191  
2.1.5.2 Synthesis of Nanoproducts ................................................................. 192  
2.1.5.3 Sample Applications .............................................................................. 194  
2.1.5.4 Outlook .................................................................................................. 198  
2.1.6 Summary ............................................................................................... 198  
2.2 From Raw Material to Coating Material ............................................... 199  
2.2.1 General Rules on Drawing up Formulations ......................................... 200  
2.2.1.1 Purpose and Quality .............................................................................. 200  
2.2.1.2 Production Resources, Application Systems and Object to be Painted .... 200  
2.2.1.3 Function in the Paint System ................................................................. 202  
2.2.1.4 Cost Effectiveness and Availability ...................................................... 203  
2.2.1.5 Occupational Health, Safety and Environmental Protection Regulations .. 203  
2.2.2 Material Flow in a Paint Factory ........................................................... 204  
2.2.3 Theory of Dispersion ............................................................................. 206  
2.2.3.1 Pigment-Specific Properties for Dispersion Processes ......................... 206  
2.2.3.2 Wetting and Separation of Agglomerates ............................................. 210  
2.2.3.3 Stabilisation of Pigment Dispersions ..................................................... 215  
2.2.3.4 Optimum Mill Base Formulation ......................................................... 223  
2.2.4 Production of Coating Materials ........................................................... 226  
2.2.4.1 Processing Sequences in a Paint Plant .................................................. 227  
2.2.4.2 Agitation and Agitators ........................................................................ 228
2.2.4.3 Dispersing and Dispersers ................................................................. 234
2.2.4.4 Separation Processes in the Manufacture of Paint .................... 250
2.2.5 Summary .......................................................................................... 258
2.3 Characterisation of Coating Materials ................................................ 258
2.3.1 Measurement Accuracy ................................................................. 260
2.3.2 Testing Raw Materials and Coating Materials ................................. 263
2.3.2.1 Safety and Environment-Related Performance Indicators ..... 264
2.3.2.2 Chemical Characterisation .......................................................... 268
2.3.2.3 Physical Indicators ........................................................................ 279
2.3.3 Pigment-Specific Tests ..................................................................... 305
2.3.3.1 Indicators of the Pigment as a Raw Material ............................... 305
2.3.3.2 Tests with the Pigmented Coating Material ................................ 314
2.3.4 Processability of Coating Materials ................................................ 319
2.3.5 Summary .......................................................................................... 322
2.4 Literature ........................................................................................... 322

3 Coatings ................................................................................................ 327
3.1 From Coating Material to Coating: Film Formation ............................ 327
3.1.1 Wetting and Levelling ...................................................................... 327
3.1.2 Solidification of the Film ................................................................. 329
3.1.2.1 Physical Drying ............................................................................. 330
3.1.2.2 Chemical Curing ........................................................................... 335
3.1.2.3 Flow Patterns in the Solidifying Film ............................................ 336
3.1.3 Film Shrinkage ................................................................................ 336
3.1.4 Special Features of High Solids Paints and Water-Borne Paints ...... 337
3.1.5 Monitoring the Film Forming Process with Measuring Instruments .. 340
3.1.5.1 Levelling and Sagging .................................................................... 340
3.1.5.2 Film Formation by Air Drying Paints ............................................ 342
3.1.5.3 Indirect Methods .......................................................................... 343
3.1.6 Summary .......................................................................................... 343
3.2 Properties and Testing of Coatings ..................................................... 344
3.2.1 Film Thickness ................................................................................. 344
3.2.1.1 Wet Films ....................................................................................... 345
3.2.1.2 Dry Films ...................................................................................... 346
3.2.2 Dry Film Density ............................................................................. 352
3.2.3 Measurement of Voids in Coating Films .......................................... 354
3.2.4 Visual Properties ................................................................................ 355
3.2.4.1 Gloss .............................................................................................. 355
3.2.4.2 Colour and Colourimetry ............................................................. 363
3.2.5 Mechanical Properties .................................................................... 375
3.2.5.1 Adhesion ......................................................................................... 376
3.2.5.2 Elasticity ......................................................................................... 387
3.2.5.3 Hardness ......................................................................................... 398
3.2.5.4 Abrasion Resistance and Mar Resistance .................................... 404
3.2.5.5 Other Tests .................................................................................... 407
3.2.6 Summary .......................................................................................... 408
3.3 Durability of Coatings ........................................................................ 408
## Contents

3.3.1 Fundamental Features of Ageing .......................................................... 408  
3.3.2 Ageing Tests ..........................................................................................416  
3.3.2.1 Methods for Testing Surface Durability................................................ 417  
3.3.2.2 Corrosion Protection Tests ....................................................................426  
3.3.2.3 Chemical Resistance ............................................................................. 433  
3.3.3 Summary ...............................................................................................435  
3.4 Literature ...............................................................................................435  

4 Coating Technology ............................................................................. 439  
4.1 Influence of the Substrate......................................................................441  
4.1.1 Wood and Wood Materials ....................................................................442  
4.1.1.1 Wood as a Material ................................................................................442  
4.1.1.2 Wood as a Workpiece ............................................................................444  
4.1.1.3 Pretreatment of Wood............................................................................446  
4.1.1.4 Surface Finishing of Wood Panels ........................................................447  
4.1.2 Metallic Materials .................................................................................448  
4.1.2.1 Properties of Metals ..............................................................................448  
4.1.2.2 From the Material to the Workpiece......................................................453  
4.1.2.3 Pretreatments .........................................................................................454  
4.1.3 Plastics ...................................................................................................465  
4.1.3.1 Types of Plastics and their Properties ...................................................465  
4.1.3.2 Pretreatments .........................................................................................468  
4.1.4 Mineral Substrates .................................................................................471  
4.1.4.1 Concrete, Mortar, Plaster ......................................................................471  
4.1.5 Other Substrates ...................................................................................473  
4.1.5.1 Rubber ...................................................................................................473  
4.1.5.2 Leather ...................................................................................................474  
4.1.6 Workpiece Design and Coatability ........................................................474  
4.1.7 Summary ...............................................................................................476  
4.2 Paint Processing ....................................................................................477  
4.2.1 Processing of Wet Paints .......................................................................478  
4.2.1.1 Dip Coating (Object Taken to Paint) .....................................................479  
4.2.1.2 Brushing, Manual and Mechanical Roller, Flow and Curtain Coating Methods (Paint Applied Directly to the Object) ............................................................................................................500  
4.2.1.3 Spray Process: Paint Applied Indirectly to the Object .......................... 506  
4.2.1.4 Paint Supply Systems ............................................................................539  
4.2.1.5 Booth Conditioning and Overspray Elimination ................................. 556  
4.2.1.6 Automated Systems and Robots for Paint Processing ..........................562  
4.2.1.7 Conveyors .............................................................................................566  
4.2.1.8 Paint Removal ........................................................................................567  
4.2.2 Processing of Powder Coatings .............................................................569  
4.2.2.1 Retrospective ..........................................................................................569  
4.2.2.2 Plant and Equipment Details .................................................................570  
4.2.2.3 Powder Coating Materials ....................................................................580  
4.2.2.4 Powder-Specific Test Methods ...............................................................582  
4.2.3 Summary ...............................................................................................584  

BASF Handbook Basics of Coating Technology
## Contents

4.3 Drying and Curing ........................................................................................................ 584
4.3.1 Film Formation by Heat Transfer ........................................................................ 585
4.3.1.1 Theory ........................................................................................................ 585
4.3.1.2 Oven Design ............................................................................................. 597
4.3.2 Curing by UV and Electron-Beam Radiation ..................................................... 603
4.3.3 Summary ............................................................................................................. 610
4.4 Literature .................................................................................................................. 611

5 Safety, Environmental Protection and Health ................................................................. 615
5.1 Legislative Framework ............................................................................................. 615
5.2 Safety .......................................................................................................................... 619
5.2.1 Manufacturing ..................................................................................................... 620
5.2.2 Storage .................................................................................................................. 622
5.2.3 Transportation .................................................................................................... 622
5.2.4 Application .......................................................................................................... 623
5.3 Environmental Protection ......................................................................................... 625
5.3.1 Exhaust Air ........................................................................................................... 625
5.3.2 Wastewater ......................................................................................................... 632
5.3.3 Recycling and Disposal ....................................................................................... 633
5.4 Health ........................................................................................................................ 635
5.5 Ecobalances ............................................................................................................... 638
5.6 Environment-Compatible Paints and Coatings ......................................................... 642
5.6.1 Low-Emissions Coatings ...................................................................................... 643
5.6.1.1 High Solids .................................................................................................... 643
5.6.1.2 Water-Borne Paints ....................................................................................... 644
5.6.1.3 Powder Coatings .......................................................................................... 647
5.6.1.4 Radiation Curable Paints and Coatings .......................................................... 648
5.6.1.5 Other Coating Systems .................................................................................. 651
5.6.2 Biobased Coating Systems .................................................................................. 652
5.6.3 Foil Coating .......................................................................................................... 653
5.7 Economics of Coating Processes .............................................................................. 654
5.8 Literature ................................................................................................................... 656

6 Principles of Quality Management ................................................................................. 659
6.1 Evolution of Quality Concepts over Time .................................................................. 659
6.2 Defects in Coating Processes and Applied Coatings ............................................... 661
6.2.1 Identifying Defects and their Causes .................................................................... 662
6.2.2 The Most Frequent Causes of Surface Defects .................................................... 666
6.2.3 Summary ............................................................................................................. 674
6.3 Material Control ...................................................................................................... 674
6.4 Defect Prevention by Process Control and Control Loops ......................................... 676
6.5 Quality Management ............................................................................................... 677
6.6 Literature ................................................................................................................... 683

7 Coating Industries .......................................................................................................... 685
7.1 Automotive OEM Coating ....................................................................................... 686
7.1.1 Pretreatment ......................................................................................................... 691
Contents

7.1.2 Electrocoating ................................................................. 694
7.1.3 Seam Sealant and Underbody Protection ......................... 698
7.1.4 Primer Surfacer ............................................................... 698
7.1.5 Topcoat Application ........................................................ 702
7.1.6 Repair in Automotive OEM Lines .................................. 707
7.1.7 Outlook ............................................................................. 709
7.2 Automotive Refinishing ...................................................... 711
7.3 Automotive Supply Industry ............................................... 718
7.4 Coil Coating ......................................................................... 725
7.5 Commercial Vehicles .......................................................... 730
7.6 Mechanical Engineering ..................................................... 733
7.7 White Goods ......................................................................... 734
7.8 Building Supplies ................................................................. 735
7.9 Rail Vehicles .......................................................................... 737
7.10 Wood Coating ...................................................................... 738
7.11 Other Fields of Application ................................................ 742
7.11.1 Protection of Structures ................................................. 742
7.11.2 Steel Furniture ............................................................... 743
7.11.3 Aviation Industry ............................................................. 744
7.11.4 Electrically Insulating Coatings ....................................... 746
7.11.5 Communications Equipment .......................................... 747
7.11.6 Road Marking paints ....................................................... 748
7.11.7 Shipbuilding ................................................................. 749
7.11.8 Wind Energy ................................................................. 750
7.11.9 Smart Coatings ............................................................... 752
7.11.10 Miscellaneous Coating Applications .............................. 753
7.12 Literature ............................................................................ 755

8 Standards .............................................................................. 759
8.1 General Information on Standardisation Work ....................... 759
8.2 Selection of DIN Standards for the Paints and Coatings Industry and their Circle of Users ........................................ 761
8.2.1 Standards by Numerical Order ......................................... 761
8.2.1.1 Standards on Terminology ................................................. 761
8.2.1.2 Standards on Coating Materials ....................................... 761
8.2.1.3 Standards on Coatings ..................................................... 762
8.2.1.4 Standards on Aluminium ............................................... 766
8.2.1.5 Standards on Coil Coatings ............................................. 766
8.2.1.6 Standards on Galvanised Steel ....................................... 766
8.2.1.7 Standards on Wood Outdoors ......................................... 767
8.2.1.8 Standards on Anticorrosion Protection of Steel Structures ........................................ 767
8.2.1.9 Standards on Nuclear Facilities ...................................... 768
8.2.1.10 Standards on Aerospace ............................................... 768
8.2.1.11 Standards on Exterior Masonry and Concrete ................ 768
8.2.1.12 Standards on Shipbuilding ............................................. 769
8.2.1.13 Dispersion Coatings for Indoors .................................... 769
8.2.1.14 Synthetic Resin Plasters ............................................... 769
### Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.2.1.15</td>
<td>Powder Coatings</td>
<td>769</td>
</tr>
<tr>
<td>8.2.1.16</td>
<td>Road Marking Paints</td>
<td>770</td>
</tr>
<tr>
<td>8.2.1.17</td>
<td>Radiator Coatings</td>
<td>770</td>
</tr>
<tr>
<td>8.2.1.18</td>
<td>Surface Preparation</td>
<td>770</td>
</tr>
<tr>
<td>8.2.1.19</td>
<td>External Thermal Insulation Composite Systems (ETICS)</td>
<td>771</td>
</tr>
<tr>
<td>8.2.1.20</td>
<td>Colourimetry</td>
<td>771</td>
</tr>
<tr>
<td>8.2.1.21</td>
<td>DIN Reports</td>
<td>771</td>
</tr>
<tr>
<td>8.2.2</td>
<td>Standards by Keyword</td>
<td>772</td>
</tr>
<tr>
<td>8.3</td>
<td>Literature</td>
<td>781</td>
</tr>
<tr>
<td>9</td>
<td>Appendix</td>
<td>783</td>
</tr>
<tr>
<td>9.1</td>
<td>List of Physical Constants</td>
<td>783</td>
</tr>
<tr>
<td>9.1.1</td>
<td>Latin Symbols</td>
<td>783</td>
</tr>
<tr>
<td>9.1.2</td>
<td>Greek Symbols</td>
<td>786</td>
</tr>
<tr>
<td>9.2</td>
<td>Internet Addresses of Interest to the Coatings World</td>
<td>787</td>
</tr>
<tr>
<td>9.2.1</td>
<td>Organisations/Associations/Authorities</td>
<td>787</td>
</tr>
<tr>
<td>9.2.2</td>
<td>Publications/Information</td>
<td>788</td>
</tr>
<tr>
<td>9.2.3</td>
<td>Institutes/Universities</td>
<td>789</td>
</tr>
<tr>
<td>9.2.4</td>
<td>Miscellaneous</td>
<td>790</td>
</tr>
<tr>
<td>9.3</td>
<td>Acronyms/Abbreviations</td>
<td>790</td>
</tr>
<tr>
<td></td>
<td>Authors</td>
<td>799</td>
</tr>
<tr>
<td></td>
<td>Index</td>
<td>801</td>
</tr>
</tbody>
</table>
1 Introduction

1.1 Definition, Tasks and Economic Importance

The task of coating technology is to provide surface protection, decorative finishes and numerous special functions for commodities and merchandise by means of organic coatings. Many everyday products are only made usable and thus saleable because of their surface treatment. For this, the right coating formulations, production plant, coating material and suitable coating processes for the product must be available. However, the level of quality attainable via the coating process is not solely a function of the coating material. The object to be coated, along with its design, specific material treatment and an appropriate application method, are further variables which play a significant role. In addressing the ongoing tasks of quality optimisation and rationalisation while minimising the impact on humans and the environment, it is vital that the dependencies mentioned above be not only recognized but also taken into account as the framework shaping the conditions in which work advances from development through to application. Coating technology, therefore, is an interdisciplinary subject.

Paints and coating materials are not end products, but merely starter or intermediate products which, for the above-mentioned reasons, require a skilled and conscientious user if they are to be converted into the actual end product, namely the coating itself. Only the cured coating, which in many cases is a system of several individual coats, can meet the wishes invested in and the requirements demanded of the coated products.

Two of the most important of the many functions which coatings have to meet are protection and decoration. Others worth noting are the informative tasks and the achievement of special physical effects. The conspicuousness of emergency service vehicles, the camouflaging of military equipment, and road or airport markings are just some of the
informative tasks required of coatings. Colour markings enable areas or spaces to be clearly signed or divided. Colour coding helps to indicate the contents of containers and the materials being conveyed in pipes. Optical effects induced by coloured or metallic pigments lend a coating a particular optical attraction. Deliberately generated surface textures such as scars or wrinkles expand the range of effects which can be achieved. The use of colour schemes based on the known physiological and psychological effects of colours also contributes in various ways to improved working conditions and enhanced safety wherever work is done in rooms and on machines. Functional pigments produce colours that vary with temperature, for example as a result of their thermochromic properties, and therefore afford an indirect way of measuring the temperatures of objects.

The most important task of coatings, in economic terms, is surface protection. Thus, coatings help to retain value and improve the usability properties of almost all products and so are of huge economic significance. Particular mention should be made of the protection of metal goods that acquire lasting anticorrosive protection only when they have been painted.

It is vital in this regard, e.g. in the automotive sector, for the resistance of the coating system to external, sometimes aggressive natural and anthropogenic atmospheric influences such as tree resins, bird droppings, acids, alkalis, salts and organic solvents, to be guaranteed.

The protective function of paint on cars must not be impaired even under extreme mechanical impact, such as stone chippings thrown up from the road by traffic or by brush action in carwashes.

Furthermore, coatings must withstand combined, i.e. physical and chemical, effects to which objects are subjected, for example, in different weather conditions. The interaction of sunshine, rain, heat and frost, combined with emissions from heating systems and internal combustion engines, ozone and salt fog makes great demands on a coating’s resistance and protective properties.

However, a surface protection coating can also be applied in order to meet quite different requirements. Floors and steps can be made non-slip, and their utility value enhanced, by means of rough or high-grip coatings. By contrast, surface friction can be reduced by using smooth coatings to produce a high degree of slip. Flammable materials can be rendered safe by means of flame retardant coatings. Antibacterial coatings help keep surfaces sterile in production and storage facilities in dairies and breweries and prevent the growth of barnacles and algae on ships’ hulls. In the electrical engineering sector, insulating coatings provide effective and lasting insulation for wire, windings and condenser materials. On the other hand, conductive coatings can be used to make insulating substrates electrically conductive or even to print electrical circuits. Furthermore, organic coatings can help to reduce noise pollution. Acoustic insulation coatings for machines and underbody protection coatings for passenger cars are examples of this.

This broad spectrum of requirements explains why no single coating material can satisfy every wish simultaneously and in the same way. The goal of providing coating materials for the lasting protection, decoration and improvement of objects made of wood, metal, plastic or mineral materials at reasonable prices can be met only by adopting different formulations based on a range of materials and material combinations. Each
of these combinations targets a limited field of substrates, a selected application method and a specific profile of film properties.

Coating technology is used in metal processing, in the manufacture of plant and machinery and in the electrical engineering industry. All kinds of road and rail vehicles, ships and aircraft are important objects which require painting or coating. Effective surface protection by means of paints and coatings is also indispensable in the civil engineering sector, for steel and concrete structures and in wood processing. Even plastics and leather require coating in many cases. Modern paper, plastic and sheet-metal packaging materials would be inconceivable without the protection and decoration afforded by coatings.

The global paint and coatings market reflects economic developments in the regions. It is most highly developed, for example, in the triad of North America, Europe, and South East Asia. Per capita consumption of paints and coatings in these regions is approx. 4.5 kg. Growth in coatings consumption is determined by economic development in the various regions and countries [1.3.1].

The broad field of applications for coatings and their widespread use are explained by the high value and great benefits which they offer. The fact that there are few objects which do not require coating is an indication of the enormous importance of coating technology. It would present an incomplete picture to evaluate this importance merely in terms of the 30.5 million tonnes of coating materials manufactured worldwide in 2010 with a value of some 80 billion euros (Figure 1.1.3).

Although quoting the quantities of coating materials is not a direct indication of the added value of industrial commodities, it does permit that area to be calculated which can be protected or decorated by means of coating materials, with due allowance for the film thickness to be applied. An annual production quantity of 30.5 million tonnes (see above) is enough to coat a surface area of some 340,000 km² in a wet film 100 µm (0.1 mm) thick. That is equivalent to about 3/4 of the surface area of Germany. The same quantity of paint applied to a 10 m wide strip in a film thickness of 100 µm, on the other hand, would stretch from the earth to the moon about 100 times or go around the world 650 times.

A more meaningful evaluation would consider the value of the effectively protected and improved products. On the assumption that painting or coating the goods produced generates an added value of 20 % in the form of extended service life and increased attractiveness, this translates to 140 billion euros for the German market in 2012, or 70 times the value of the paints and coatings sold.
The division of the market into branches and segments is not uniform around the world. A number of such divisions, however, seem to agree on certain segments, such as decorative paints, general industrial paints, automotive paints, and printing inks.

The largest market for paints and coatings, at 54%, is that of decorative paints. This is followed, at 38%, by the market for the industrial coating of a huge range of objects, from compact discs via plastic bumpers for cars to rail vehicles. Automotive coating lines and refinishing body shops are each clearly defined segments with a high technological value, though of less significance in terms of volume sales. Although not shown in Figure 1.1.4, printing inks represent approx. 4% of global demand for coating materials and are a separate segment in technological and marketing terms, though not from the point of view of their composition.

The size of the European market in 2011 was 9.4 million tonnes. It has undergone a slight shift towards industrial coatings and printing inks compared with the sectoral division in the rest of the world. Germany leads with a consumption of approx. 1.5 million tonnes, ahead of Italy, France, the UK and Spain, which are all in the range between 0.8 and 1.0 million tonnes. The North American market (NAFTA) had a volume of 6.6 million tonnes in 2010 and is served by about 800 companies.

Figure 1.1.5 gives an overview of the economic development of the paint and coatings industry in Germany since 2006 which is closely linked to the country’s overall economic development.

One of the characteristic features of coatings technology in addition to
coatings consumption is the ongoing high energy consumption for processing coatings which is estimated at approx. 200 billion kWh annually worldwide. This figure is the equivalent of the energy content of approx. 30 million tonnes of crude oil. If the raw materials required for paint production are also added to this figure in the form of crude oil equivalents, the result is a total crude oil requirement of approx. 120 million tonnes for the global manufacture and processing of coating materials, or some 3% of global annual crude oil extraction of approx. 4 billion tonnes in 2012.

The legal requirements imposed on environmentally compatible coating processes have led to the greater use of appropriate coating materials over the last 20 years. These include, in particular, solvent-free powder coatings, water-borne paints, in which organic solvents are replaced in whole or in part by water, high solid paints and radiation-curable paints, which are processed either in aqueous solution or completely without conventional solvents but with the aid of low-molecular reactive thinners. Statistics from the Association of the German Paint Industry (VdL) show that these coatings have achieved the greatest growth over the last 10 years.

As a result of stricter legislation and ongoing improvements in our knowledge of their toxicology, the raw materials are having to be replaced regularly, with all the attendant development costs, if the quality standard achieved is to be maintained.

As far as energy consumption is concerned, there is still a need to be more economical in the use of raw materials and energy. A proportion of the material is lost en route to the finished coating. Spray application, which is specified for many objects to be painted because of its optical attractiveness and range of colours, is prominent in this regard. As far as coating of wood and plastics is concerned, the more effective electrostatic spray methods have not yet found universal acceptance. In addition, paint lines lose substantial quantities of heat energy. In recent years a number of developments have increased the efficiency of coating processes to such an extent that growth in the paint and coatings market in the industrialized countries has only just been below the growth level of the gross domestic product (GDP).

As a result of the use of solvents as an application aid for coatings with an average organic solvent content of 50%, it has been estimated that additional hydrocarbon emissions of approx. 200,000 tonnes occurred in Germany alone in 2007 [1.3.2].

Whereas organic emissions from motor vehicles have been successfully reduced to less than 1/3 of their previous level in the last 30 years by the introduction of the catalytic converter, successes in coating technology have been much more modest so far by comparison. Despite the use of water-borne paints and powder coatings, including by small and medium-sized enterprises after the enactment of the EU VOC (volatile organic compounds) directive of 1999 and its implementation in Germany under 31 BImSchG (BundesImmissionsSchutzGesetz = Federal Immission Control Act), the German Ministry of the Environment estimates that 30% of all solvent emissions in 2020 will stem from the paints and coatings industry [1.3.3].

Manufacturers and processors of paints and coatings have substantial gains in terms of occupational health and safety. For some time, the chemical industry, for example, has led the accident statistics in Germany for the industry in having the least number of incidents. Health risks posed by paints and coatings are being kept as low as possible
Introductions

through REACH [1.3.4] and the Biocides Ordinance [1.3.5] in Europe and through the Clean Air Act (CAA) and the Toxic Substances Control Act (TSCA), legislation and civic engagement in North America, and these have brought about substantial changes in coatings technologies and formulations.

An analysis of this situation reveals that manufacturers and consumers of paints and coatings, though occupying different value added stages, are highly interconnected. Manufacturers develop and supply coatings materials to the consumers who, by applying the products, induce physical, physico-chemical and chemical processes that convert them into an adhering, mechanically solid and, at the same time, flexible coating.

The chemical path by means of which the raw material becomes a finished coating starts at the raw materials or paint manufacturer and is then deliberately interrupted before being taken up again during application by the paint consumer. Although the performance profile of a coating is initially shaped by the paint and thus by the paint manufacturer, it is the processor who actually generates the finished properties. The industrial scale coating of consumer goods is therefore a joint effort between paint and coatings manufacturers and processors.

Paint manufacturers who really know their job not only are responsible nowadays for developing, manufacturing and selling paint. Their task also includes creating the conditions for successful painting through the provision of a permanent technical presence and support. This relates primarily to materials and processes, but also extends to detailed environmental protection and occupational safety issues. Paint manufacturers offer a package, as it were, in which the material is just one component among many (see Figure 1.1.7). A consequence of this in past years has been that the responsibility for producing a coating outcome in the required quality has increasingly been transferred into the hands of the paint supplier (see Chapter 7.1.7).
Apart from the technical tasks of manufacturing and processing coating materials, particular attention needs to be paid to quality assurance methods. Quality assurance provides the link between production and R&D and sales within a company. Production must be capable of reproducibly providing the quality demanded by the customer, while sales must identify the total costs in order that appropriate prices may be obtained.

However, paint manufacturers face specific problems because they are expected to produce material of constant quality and, at the same time, paints of constant processability. This is the only way to create the best conditions for achieving a uniform result in the painted article. This means that there is more to the production of paint and coatings than merely manufacturing a product whose composition is identical with a defined standard. Rather, since physical variables can only rarely serve as criteria for the practical properties of coatings, paint testing of necessity must include simulating the application method used by the processor of these materials. This gives rise to a large number of different test methods because of the very wide range of specification conditions and the different requirements on the coating process resulting from them. Standardising these tests and reducing their overall number are also a priority task for all concerned.

Quality and costs of a coating are defined, as mentioned earlier, not only by the paint material and an appropriate application method but also and significantly by the substrate, i.e. by the material and the design of the object to be painted. It is therefore clear that it is extremely important to address surface treatment and the selection and design properties of the material during the product design stage and to incorporate these features into the overall planning.

Coating technology is therefore a complex marriage of chemical, physical, process-engineering, environmental, toxic and economic variables. This discipline is in a constant state of change as a result of technical progress and is further accelerated by legislative requirements. It is therefore incumbent on companies to link well known features with new knowledge. Industrial coating technology can only be fully understood if, in addition to detailed knowledge of paint processing, the properties of the coating material and of the object to be coated are known and also if all the quality-shaping variables within the range of economic and environmental requirements are addressed.

### 1.2 Retrospective

The aim of the following retrospective of materials and painting methods in the past is to highlight the entangled paths which coating technology has taken down to the present day by illustrating a few key events that will make its progress more transparent.

The early coating materials were natural resins. *Dioscorides* and *Plinius* report, among other things, on the use of countless exotic natural resins from the time of the Ancient Greeks and Romans. Later papers describe the importance of colophony, copals, shellac and dammar. Later still, in the 12th century, come reports of the combination of hardened natural resins such as amber with resinifying, i.e. chemically hardening, natural oils [1.3.6].

The application methods up to that point consisted solely of brushing or wiping techniques, without the generation of significant emissions, waste water or paint waste.
Rodgerus von Helmarshausen, also known as Theophilus, describes how to make coatings and provides a detailed recipe in chapter 21 of his book Schedula Diversarium Artium, which dates from around 1000 AD:

1* Put linseed oil into a small pot and add the gum which is called fornis ...
2* Then place fire carefully underneath until this gum liquefy.
3* Have also a third pot nigh, placed upon the coals, in which is hot linseed oil ...
4* Pour the warm oil into it and stir it with the iron ...
5* And take care in this, that in weight there are two parts of oil and the third part of gum...

Figure 1.2.1: First recipe of a coatings material by Theophilus

Around the end of the first millennium, the monk Rodgerus of Helmarshausen reports in his book Schedula Diversarium Artium the first details of the composition and manufacture of the then standard paint [1.3.7]. He is therefore, regarded as the creator of the first binding paint formulation and of the detailed instructions on how to make it.

Linseed oil and amber (called “rubber” in German back then), are boiled together in a ratio of 2:1, with the hardened resin acting as a nonvolatile film former, and the linseed oil as a chemically crosslinking reactive thinner. Solvents to regulate viscosity were not used at that time because they were not available in sufficient quantities.

In the 10th century it was the Arabs in the guise of the doctor Abu Mansur who taught the Europeans the art of distillation [1.3.8]. This art was then used in Europe for, among other things, extracting turpentine oil. When the van Eyck brothers took Rodgerus of Helmarshausen’s formulation, which was the first to be systematically described, and extended it by adding turpentine oil in the early 15th century, physical drying and thus emissions had been invented [1.3.9]. This outcome is noteworthy on one hand because it greatly expanded the use of painting and on the other because the associated environmental problems are still tying up a considerable part of paint-specific research capacity to this day.

The memorable “invention” of emissions was followed very much later by the “invention” of waste. By this is meant the introduction of the continuous production line by Henry Ford in the early 20th century and consequently the start of industrial-scale painting technology.

The production line has brought the world huge benefits in terms of speedy and economical production systems. However, the necessary faster coating processes could only be fully exploited by employing quick-drying paints and a new application method. Consequently, the oil paints which took several weeks to cure were superseded by quick-drying cellulose paints with solvent contents of up to 80%. At the same time the waste-free brush method which had been standard up to that point was replaced by the spray method. However, the introduction of the spray gun, which had been invented by de Vilbiss back in the 19th century, also ushered in a new problem because it had an extremely poor material application efficiency of less than 50%: the generation of paint waste and, at the same time, a dramatic increase in organic emissions because of the considerably higher solvent contents of the cellulose paints.
Retrospective

So, 1920 introduced a completely new situation into coating technology, but failed to provide an appropriate approach for the new problem. This approach had to be developed in the course of the following decades. The production line meant technical progress in the form of increased coating quality as a result of improved application and a more economical production system, though at the expense of the environment in the form of waste and emissions.

The introduction of the production line therefore shared the problems of emissions and waste which had been known since the time of the van Eyck brothers and also signalled the start of the metamorphosis of craftsmanship into a segment of industrial production technology.

It took government action in the form of environmental legislation for people finally to become aware of this situation and for themselves to take appropriate concerted action. The innovations which subsequently occurred were no longer the outcome of individual ideas but were increasingly achieved thanks to cooperation among all those involved in the finished coating.

The first goal was to rationalise the processes and optimise quality on the basis of conventional, i.e. solvent-borne, coating technology. Later, from the 1960s onwards, research started in a new direction from several different locations simultaneously, initially separated but later with a common goal in view: the development of low-solvent and low-waste painting methods [1.3.9].

The results of this work are new water-borne materials, radiation-curable systems and waste-free powder coatings in conjunction with new processing methods. Electrocoat painting, roller and curtain coating, e.g. for coil coating, and the application of solid powder coatings are the most noteworthy innovations of the last 50 years. Environmental protection on one hand and occupational safety issues on the other are beginning to become much more structured. With the passage of Germany’s Bundesimmissionsschutzgesetz (Federal Immission Control Act) in March 1974 and the oil crises, research into environmentally compatible coating technologies was expanded to include the aspect of resource conservation.

The various trade associations and technical bodies of the American and European paint and coatings industries were also involved in this. Efforts in this direction were
strengthened by the voluntary commitment (“responsible care”) of the paint and coatings industry in almost every region of the world.

Successful examples of such a concerted approach to dealing with a problem by a number of different groups and bodies include the development of the new paint process for the Mercedes A-Class in the late 1990s in which a paint manufacturer, a paint processor and a plant manufacturer cooperated, and also the “Expansion of the application fields for powder coating technology” research project funded by Germany’s Federal Ministry for Education and Research (i.e. BMBF) and coordinated by the German Research Association for Surface Treatment (i.e. DFO) together with a total of 20 companies from the fields of paint production, paint processing, plant engineering, the raw materials industry and countless research institutes. The same approach can be seen in North America, where the industry-supported LEPC (Low Emission Paint Consortium) under the umbrella of USCAR (United States Council for Automotive Research), invested a great deal of money in the 1990s to develop low-emissions paint technologies for automotive coating [1.3.10].

The globalization of the world economy, particularly the manufacturing industry, is currently confronting the paint and coatings industry with new challenges. Since quality requirements have been standardised worldwide as a result of consolidation, in the automotive industry for example, the major paint suppliers have positioned themselves globally and now guarantee the same quality standard for coatings everywhere. No end to this development is presently in sight. In addition, sales channels have expanded for many paint suppliers through the introduction of e-commerce, the electronic transaction of purchases over the internet. Of necessity, all aspects are steps in the direction of consolidation.

The quality requirements, particularly those imposed by the automotive industry in the form of ISO standards, VDA standards and the QS9000 series, mean that the entire process from the product idea, via development, scale-up, production and sale to the final application is falling more and more completely within the sphere of responsibility of paint and coatings companies. It now seems that the entire process chain, starting with the production of the paint materials to the finished (coated) article, will become a key competency of the major paint companies. It is therefore certain that the active players in this field will continue to grow closer together. Only in this way will it be possible to develop efficient processes for the respective sectors or applications.

The conditions for coating technologies that have zero environmental impact and make the most efficient use of resources are largely in place. Future success will depend on whether holistic concepts can be found [1.3.11]. Product life-cycle or ecoefficiency audits [1.3.12] aimed at achieving sustainable development will therefore provide the principles underpinning research and development programmes more and more frequently [1.3.13] (see Chapter 5.5).

In-depth knowledge is an essential factor for the successful introduction of environmentally compatible coating technologies in conjunction with the implementation of new ideas in processing technologies. This includes details on correlations and interdependencies between the individual scientific disciplines and thus of the various sectors involved in the paint process. This book has been written not least for this reason.
1.3 References

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2 Coating Materials

In accordance with the international standard ISO 4618-2 as well ISO 4618-3 and the supplementary German standard DIN 55 945, and in general agreement with the English speaking experts, the correct designation for materials for organic coatings that provide surface protection is coating materials. Paints, on the other hand, is the standard term for coating materials that possess particular properties. In the English speaking world, the term “coating” is often synonymous with paint, the layer on the coated product, and the painting process.

The standard defines paints as liquid, paste or powder coating materials which enable optically opaque coatings to be produced that have decorative, protective and, if necessary, specific technical properties. It should be noted that many terms in general use, such as varnish and vehicle, are different from the terms specified in international standards (see Chapter 8). Paints are therefore just one part of the large class of coating materials, but nevertheless have to meet a broad spectrum of extremely different requirements. They can be sub-divided in accordance with various principles: by the function of the coating (clearcoat, metallic paint, solid paint), by the particular layer in the coating system (primer, primer surfacer, topcoat), by the purpose of the paint (car paint, decorative paint, industrial paint), by the degree of environmental compatibility (water-borne paint, high solid paint, radiation-curable system, powder coating), by the chemistry of film forming agent (alkyd resin paint, acrylic resin paint, cellulose nitrate lacquer) and by the processing conditions (stoving enamel, oxidatively curing coating material), to name the major classification criteria.

The selection of the right coating materials the optimum performance profile therefore depends equally on the quality requirements, the specified application conditions, the curing process, the design features and the various constituent materials of the object to be painted. All coating materials, however varied their use may be, must have the same properties of wetting substrates, transforming into a closed film, flowing and then solidifying so that the desired mechanical and chemical protection of the object is achieved.

The performance profile of the paints therefore has to be tailored not only to application but also to subsequent film formation. A fresh paint finish applied by spray gun must exhibit sufficient flowability for the droplets to seal all pores. At the same time or subsequently, it must level out all the peaks and troughs in the film surface that are caused by application. Surface tension and viscosity are the most important paint parameters in this regard. Furthermore, special effects such as high-gloss finish, chroma and oriented reflection (metallic effect) may have to be achieved. Clearcoats for wooden panelling, for example, therefore have a completely different composition from anticorrosive paints and from coating materials for applying colour designs to leather.

2.1 Raw Materials

Resins in their capacity as film forming agents (often incorrectly termed binders), along with additives, solvents, pigments and extenders are the usual ingredients of liquid coating materials. Binders, according to ISO 4618, are the pigment-free and extender-free
Coating fractions of the dried or cured coating. They are, therefore, composed of the film forming agent and the nonvolatile fraction of the additives.

If there are no pigments and extenders, the material is a clearcoat, and if there are no solvents when higher molecular film forming agents are used, the coating material can be ground to produce a powder coating. If the film forming agents are lower molecular liquid products, it is also possible to eliminate some or all of the organic solvent. Where the resins or dispersions are miscible with water, the solvents can be replaced by water.

Irrespective of the intended application, a film forming agent which solidifies as a result of physical or chemical processes is the one indispensable component of a coating material. Traditional film forming agents are exclusively oligomeric to polymeric organic materials because of the range of requirements imposed on adhesion to the substrate, mechanical strength combined with elasticity, and resistance to ambient effects. They can be manufactured from natural substances which have been chemically modified or by industrial synthesis.

Despite the existence of a broad range of synthetic resins, the natural substances or modified natural substances have lost little of their importance. Cyclorubber or chlorinated rubber, cellulose esters and alkyd resins based on natural fatty acids are just a few examples of the technically important group of renewable paint raw materials. A foreseeable shortage of raw materials derived from crude oil has spurred activity aimed at finding a new basis for synthetic chemical raw materials and intermediates (see Chapter 5.6.2) [2.4.1].

Film forming agents can be divided into two basic groups, irrespective of their origin. The first group consists of the higher molecular, physically curing film forming agents such as cellulose nitrate, cellulose acetobutyratе, thermoplastic acrylates and also PVC copolymers. These resins set by releasing solvents, but do not undergo a chemical change during film formation.

The second group comprises chemically reactive film forming agents or combinations thereof and are used for high-grade decorative and industrial paints. A crosslinking reaction initiated by heat or catalysts after application enables lower molecular and thus high solid base resins to be used. As an example, consider stoving enamels based on acrylic-amino resin, alkyd-amino resin or phenolic resin combinations. Oxidatively curing alkyd resins (incorrectly termed “air drying”) start to crosslink at room temperature, though much more slowly.
Modern polyurethane and epoxy resin paints cure very quickly, even at room temperature. The latter can generally only be used in the form of 2-component materials because of their high chemical reactivity.

A coating material formulation usually contains solvents in addition to a film forming agent. Trouble-free processing and film formation are possible only if the right solvents are selected and combined. The most common organic solvents are aromatic hydrocarbons such as xylene and solvent naphtha, aliphatic hydrocarbons such as mineral spirit or vernice, esters such as ethyl acetate or butyl acetate, alcohols such as propanol or butanol, ethers such as butyl glycol, ether esters such as ethyl and butyl glycol acetate, and various ketones. It is important that the combination of solvents chosen from the huge range available matches the resin type.

It is critical, for the sake of the application process, to choose solvent combinations that have the correct evaporation properties. This is the only way to strike a balance between the levelling and the non-sag properties of fresh paint on vertical surfaces.

Traditionally, solvents have served merely as viscosity regulators, but they can also react chemically with the paint resins during film formation, i.e. they can do more than function as thinner. Such reactive thinners remain in the solidifying film and thus contribute to a reduction in organic emissions. Paints which can be cured by means of UV radiation or electron beams also deserve to be mentioned in this context, as do unsaturated polyesters cured by organic peroxides.

The pigments used in coating materials provide chroma and hiding power. Extenders influence technical properties, such as sandability and hardness, but also increase the nonvolatile content of the coating material. In many cases, by absorbing UV radiation, pigments and extenders prevent premature degradation both of the substrate to be protected by painting and of the polymeric protective coating itself. A further important task for certain special pigments and extenders is to optimise protection against corrosion.

The various types of pigment are divided into organic and inorganic absorption pigments, metallic and interference pigments, and anticorrosive pigments. The first two groups consist of extremely finely dispersed, generally crystalline solids. The most important among the inorganic pigments are titanium and iron oxides and the mixed-phase pigments. Organic pigments vary hugely in their composition. Modern, synthetically manufactured organic pigments also offer excellent lightfastness and long-term outdoor exposure properties. Their particular advantage lies in their brilliance and high tinting strength. At elevated temperatures, however, and with certain exceptions, they are inferior to the inorganic pigments in terms of heat stability.

Special optical effects are achieved by means of pearlescent, interference or metallic pigments. Coatings whose colour or brightness varies with the viewing angle are of particular interest in the automotive sector because of their attractiveness.

The final coating material components to be mentioned are the additives and plasticisers. With the exception of the plasticisers, these substances are added to the resin/solvent or pigment mixture in sometimes minute quantities. Despite this low concentration, they have a significant impact on the properties of coating materials and coatings.
Additives facilitate dispersion of the pigments during production. In the ready-to-use paint they suppress the tendency for the pigments to settle, enhance flowability when the paint is applied, improve levelling during film formation and improve technical properties by influencing the surface smoothness or roughness. They prevent the pigments from floating to the surface, accelerate curing, while also exerting an influence on the gloss, increasing resistance to harmful UV radiation and reducing premature degradation by bacteria or mildew which attack paint.

Whereas in the past raw materials were mostly chosen on the basis of their chemical and physico-chemical properties, recent insights have shifted the focus increasingly onto particle morphology, dimensions and the associated interaction with other surfaces. Particles or surface structures with dimensions on the nanometre scale exhibit interesting structure-related properties. The behaviour of such nanoparticles can differ quite substantially from that of individual molecules as well as that of particles of larger dimensions. This brings an additional variable into play for many technical areas, including the composition and formulation of coating materials.

The size, shape and surface structure of a wide range of established and new raw materials are therefore being adjusted for the purpose of trimming the size-dependent properties to the optimum extent for the intended application. For instance, it is possible to modify the dimensions of TiO$_2$ and SiO$_2$ particles such that they lose the ability to scatter light yet retain their UV stability and immobility in the coating. As a result, the use of micronized, i.e. nanoscale, TiO$_2$ to formulate clearcoats makes it possible to achieve stable UV absorption without adversely affecting permeability to visible light.

Numerous other applications of nanoparticles and nanostructured surfaces have opened up new problem-solving approaches in paint research (see Chapter 2.1.5).

### 2.1.1 Film Forming Agents

Whereas it is possible for a coating material to dispense with the raw materials such as solvents, additives or pigments mentioned in the first section, a film forming agent or a combination of such agents is absolutely essential if the specified tasks as a paint are to be met. The film forming agent must meet numerous criteria. These essentially concern adhesion to the substrate and the film’s mechanical strength (cohesion) in conjunction with retention of elasticity. Such a range of requirements makes it necessary to use macromolecular polymeric materials. Their molecular structure enables them to meet many requirements through mechanical entanglement of the molecular chains. It is just as feasible to achieve these properties with synthetically manufactured oligomeric or polymeric materials as with appropriate natural polymers, although the last of these must be chemically modified if they are to find practical application. However, optimum coating properties can only be obtained if the film forming agent can wet the substrate as a resin solution, as a dispersion or as a molten powder coating and can be transformed into a visually attractive, smooth film by means of subsequent levelling.

The mechanical strength can therefore be developed through the release of solvents (physical drying) or through molecular enlargement with simultaneous crosslinking of the molecules of the film forming agent (chemical hardening).
All film forming agents which solidify by physical drying, i.e. purely by releasing solvents, therefore remain sensitive to solvents and can be liquefied again by heat treatment. These film forming agents are thermoplastic. Consequently, coatings made with them are also thermoplastic.

Chemically reactive film forming agents, on the other hand, perform differently. These are chemically crosslinked with reactive groups of the resin molecules during film formation and are thereby transformed into an insoluble thermosetting film which cannot be liquefied.

Unlike purely physical drying, this supplementary chemical hardening also permits the use of low molecular film forming agents. This means that the amount of solvents which are needed for processing can be substantially reduced in the chemically reactive systems. Chemically reactive systems therefore help to lower solvent emissions, unlike thermoplastic materials.

The varied shapes and sizes of the film forming agent molecules (see Figure 2.1.2), and of those functional groups at the points of linkage within the polymer chains and of those at the end of the molecular chains, determine the film forming agents’ properties and thus the application for which they can be used.

Linearly structured molecules behave differently from branched ones in many respects. The large number of chain ends in dendrimers (tree-like polymers) affords much higher functionality despite the low molecular weight compared with the former, thereby providing the necessary conditions for high crosslinking density.

The size or size distribution of these resin molecules has a particular impact on the processing properties, though also, of course, on the quality of the end product. This applies as much to the processing state as to the structure of the molecular bond in the finished coating. In thermoplastic materials, i.e. where nonreactive film forming agents are used, the molecule size remains unchanged even after processing. Chemically reactive coating materials, on the other hand, undergo considerable changes in molecule size as a result of chemical crosslinking. When paint resins and their usability are being categorised, therefore, the molecular weight and molecular weight distribution serve as important indicators of the molecule size.

Polymer chemists have developed a number of methods for determining these indicators. Resin solution viscosity (viscometry), diffusability and the osmotic pressure...
(osmometry) which occurs when semi-permeable membranes are employed act as indicators of molecular weight. More up to date and informative are methods involving chromatographic separation of the individual film forming agent molecules which can vary considerably in size. With the appropriate equipment, different dwell times in the cavities of polystyrene gels can be used to determine average molecular weights and the molecular weight distribution concurrently (see Chapter 2.3.2). The molecular weight distribution is particularly important because the use properties cannot be specified by means of the average molecular weight alone.

Reactive end groups and the type of chemical link between the basic structural elements also help to shape properties. Information on the crosslinking capabilities of the resins and their polarity can be obtained by experimentally determining the number of free carboxyl, hydroxyl or isocyanate groups in the form of the acid, hydroxyl or isocyanate values. Similarly, the iodine absorption value provides information on the presence of carbon double bonds which in turn can be used to describe the oxidative curing of alkyd resins (see Chapter 2.3.2).

To understand the nature of the film forming agents’ basic structural elements, wet chemical degradation reactions must first be conducted. Only then can the functional groups created be identified. This can be done either by determining the aforementioned resin indicators or by identifying and quantifying functional groups or characteristic molecular moieties with the aid of analytical instruments. These are divided into spectroscopic, thermal and chromatographic techniques (see Chapter 2.3.2).

Film forming agents, which have proved their value over thousands of years for protecting and decorating objects, are extremely varied and belong to a huge range of classes of chemical substances. A number of
different approaches can be used to classify them systematically. One is to classify them by the chemical principle of the molecular structure; another consists in dividing them into film forming agents which either remain thermoplastic during film formation or are transformed into thermosets. A further meaningful classification method is to distinguish between natural materials, modified natural materials and materials which are obtained synthetically. As division into natural and synthetic products also reflects the history of paint, this chapter will also be structured in this way.

Accordingly, natural oils which have been important for thousands of years should be mentioned first. They were combined at an early stage with hard resins such as shellac to increase the initial hardness because solidification was a slow, purely chemical process. Other important representatives of such hard resins are colophon, copal, dammar and amber. They belong to the large group of natural isoprene derivatives. Latex milk which is produced from certain plants is also an isoprene derivative in the form of 1,4-cis-polyisoprene. It was used centuries ago as natural rubber to make water-repellent coatings. Later modifications to produce cyclorubber and chlorinated rubber gave access to those film forming agents which are still in use today for heavy-duty anticorrosive protection and the protection of damp rooms because of their hydrophobic properties.

Carbohydrates such as cellulose and starch which are produced in nature to excess by photosynthesis proved to be useful raw materials for paints in the form of organic or inorganic esters and ethers more than 100 years ago. Even in the 21st century, cellulose nitrate and cellulose acetobutyrate are still technically important base resins for the woodworking and furniture sectors on one hand and the automotive sector on the other.

Overall, with the invention or synthesis of artificial resins, natural materials have lost their pre-eminence because of their restricted availability and the limited adaptability of material and processing methods.

The economic breakthrough for synthetic resins came with the invention of phenolic resins and combinations of amino resins of enhanced yellowing resistance with alkyd resins and saturated polyesters. The first synthetic resins also included the unsaturated...
polyesters which, when combined with chemically reactive solvents, enabled paints
to be developed that offered a combination of high film thickness and low emissions
because of the chemical bond that formed between the film forming agent and the sol-
vent. A degree of long-term outdoor weatherability and chemical resistance which had
not been possible previously was made possible by the invention of polyurethane and
epoxy resins. Thanks to the resistance conferred by silicone resins to heat and long-
term outdoor exposure, coating materials can be designed that feature correspondingly
excellent properties.

Polymer resins such as polyacrylics, polyvinyl chloride, polyvinyl esters and ethers,
polystyrene and copolymers are now used in all kinds of paint systems, e.g. as aqueous
dispersions, radiation curable systems and powder coatings (see below).

Film forming agents are by far the largest component in a coatings formulation, in terms
of quantity. In 2010 they had a global market volume of around 8.9 million tonnes. In
first place came emulsion polymers, including acrylic resins, followed by alkyd resins
and then epoxies. Polyesters, the mostly water-borne polyurethane dispersions and the
crosslinkers for the various resin types have roughly the same market share.

The film forming agent, in being responsible for coating functionality, stability and
application properties, performs roughly 70 % of the tasks of the various paint compo-
nents found in all coating materials.

2.1.1.1 Natural Materials

By far the most important natural materials used as film forming agents are the natural
oils which are also known as fatty oils. Being tri-esters of glycerine with polyunsatura-
ted fatty acids, they became extremely important as film forming agents for surface pro-
tection a considerable time ago because of their ability to transform from a low viscosity
liquid into a solid by interaction with atmospheric oxygen. This capability distinguishes
them from fats based on saturated fatty acid esters. Fatty oils are pure natural materials
and are available in sufficient quantity as inexpensive raw materials for paints.

Even though natural oils have increasingly diminished in importance with the develop-
ment of synthetic film forming agents, their fatty acid components are still used by raw
materials suppliers for modern alkyd resins.

Numerous types of fatty oils are produced naturally by various plants and certain marine
animals. If they are to be used successfully in technical applications, they need to be
isolated from seeds and fruits by cold- or warm-pressing and to be freed of impurities.
These are mainly carbohydrates, proteins, and lecithin, which is of interest as a paint
additive. Due to its surfactant character, lecithin is used to improve the disper-
sibility of coloured pigments in stoving enamels. It has an inhibiting effect on
the oxidative crosslinking of fatty oils and so must be quantitatively removed
from them.

The huge diversity of oils which can be
used in paint production, without excep-
tion esters of glycerine, stems from the

Figure 2.1.6: Fatty oils as triglycerides of unsaturated fatty
acids

\[
\begin{align*}
H_2C&\text{O}\text{C}R \\
HC&\text{O}\text{C}R \\
HC&\text{C}R
\end{align*}
\]

R = alkyl chain of fatty acids
(see Figure 2.1.7)
wide availability of fatty acids, the acidic esterification component. Nature produces these in varying chain lengths and, at the same time, a fluctuating number of double bonds and different cis/trans forms.

The fatty acids shown in Figure 2.1.7, i.e. stearic and palmitic acid, cannot be cured by oxygen. Their analogue with a double bond in the cis position is oleic acid. Its ability to be crosslinked by oxidation is poor, and so it cannot be used by itself in practice as a paint raw material. The C_{18} fatty acids containing two or three double bonds are much more effective in terms of paint curing by means of atmospheric oxygen. In the former group, the most important role is taken by the 9,12- and 9,11-octadecanoic acids. Unlike the 9,12- variant, linoleic acid, 9,11-octadecanoic acid does not occur naturally. It is obtained by artificial transformation (isomerisation) of natural linoleic acid or by dehydration from castor oil or ricinoleic acid. Both double bonds occur proportionately in conjugated form and consequently confer increased reactivity on the film forming agents into which they are chemically incorporated.

Fatty acids containing three isolated double bonds are even more reactive than those with two double bonds. Linoleic acid, which has three isolated double bonds and is the main component of linseed oil, gives the oil an extremely pronounced oxidative curing capability which has been used since time immemorial. Elaosteearic acid, which is

![Figure 2.1.7: Important natural fatty acids as the constituents of fatty oils](image-url)
contained in tung oil and also has three double bonds, albeit in a conjugated configuration, is among the most reactive of all fatty acids. Unfortunately, the highly unsaturated oils are less resistant to yellowing and therefore unsuitable for white coatings.

Among the large group of oils which are of importance in paint and coating technology, special mention should be made of linseed oil, soy oil, tung oil, oiticica oil, groundnut oil, sunflower oil, cottonseed oil, castor oil and fish oil.

It is also worth noting that tall oil, an important raw material for synthetic paint resins, is not actually an oil. It is not, as would be anticipated from its name, a triester of glycerine, but rather is a mixture of various fatty acids formed during cellulose production by the alkaline saponification of oil-containing byproducts.

A proven indicator for the oxidative hardening of oils is the iodine value. This indicates the quantity of iodine which is added to the double bonds for every 100 g substance. An iodine value > 150 is a pointer to rapidly hardening oils, a figure of 150 to 100 to “semi-drying”, i.e. less reactive oils, and < 100 to non-drying oils. Although the last of these

<table>
<thead>
<tr>
<th>Oil Type</th>
<th>C_8</th>
<th>C_10</th>
<th>C_12</th>
<th>C_14</th>
<th>C_16</th>
<th>C_18</th>
<th>C_18'</th>
<th>C_18''</th>
<th>C_18'''</th>
<th>C_20'</th>
<th>C_20''</th>
<th>C_22'</th>
<th>C_20'''</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palm kernel oil</td>
<td>3–5</td>
<td>3–7</td>
<td>40–50</td>
<td>14–18</td>
<td>7–9</td>
<td>1–3</td>
<td>10–20</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Peanut oil</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>6–16</td>
<td>1–7</td>
<td>35–70</td>
<td>15–50</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Soya bean oil</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>7–11</td>
<td>2–6</td>
<td>15–30</td>
<td>40–55</td>
<td>4–10</td>
<td>–</td>
<td>–</td>
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<td>–</td>
</tr>
<tr>
<td>Sunflower oil</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>3–7</td>
<td>1–5</td>
<td>15–45</td>
<td>45–70</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Linseed oil</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>4–7</td>
<td>1</td>
<td>12–35</td>
<td>20–25</td>
<td>35–60</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Fish oil</td>
<td>–</td>
<td>6–8</td>
<td>15–20</td>
<td>2–4</td>
<td>10–18</td>
<td>1–3</td>
<td>0–2</td>
<td>2–8</td>
<td>15–30</td>
<td>1–8</td>
<td>5–20</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Tung oil</td>
<td>–</td>
<td>3–4</td>
<td>1–3</td>
<td>5–10</td>
<td>8–10</td>
<td>75–85*</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Oiticica oil</td>
<td>–</td>
<td>6–8</td>
<td>3–5</td>
<td>5–15</td>
<td>10–25</td>
<td>75–85**</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Castor oil</td>
<td>–</td>
<td>1–2</td>
<td>85–90***</td>
<td>2–7</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

* a-eleostearic acid (conjugated double bonds)
** a-licanic acid (conjugated double bonds)
*** ricinoleic acid

Figure 2.1.8: Selection of important natural oils and the composition of their fatty acids

Figure 2.1.9: First steps in the oxidative hardening of oils by forming hydroperoxides and peroxides
react with atmospheric oxygen, they solidify only incompletely such that mechanical hardness cannot be achieved even after an extended reaction period.

**Oxidative Drying of Oils**

The solidification caused by the action of atmospheric oxygen has been described by numerous authors [2.4.2, 2.4.3]. It is now known that there is no single mechanism by means of which all oils react in the same way [2.4.4]. Various reaction mechanisms have been identified that vary with the type of fatty acid and the number and configuration of the double bonds, as well as the temperature. Whereas it has been shown that the formation of cyclic peroxides is the first stage when conjugated double bonds are present, hydroperoxides are formed initially in the case of isolated double bonds. The atmospheric oxygen acts either directly on the double bonds or on the activated methylene group between the double bonds as a function of temperature. Whereas at low temperatures the action primarily occurs the activated methylene group, at higher temperatures the oxygen adds to a double bond and forms new conjugated double bonds at the same time.

![Figure 2.1.10: Mechanism of oxidative curing of unsaturated fatty acids](image)

---

**Figure 2.1.10: Mechanism of oxidative curing of unsaturated fatty acids**
When the peroxides and hydroperoxides decompose into radicals, the molecule-enlarging crosslinking process begins which then initiates radical polymerisation. At the same time, additional chain-transfer and recombination reactions start because of the high radical density. This extremely complex process is also subject to numerous secondary reactions.

The chemical crosslinking process can be accelerated substantially by the use of specific catalysts, known as siccatives. Metallic soaps, whose cations accelerate peroxide decomposition by reversible valence change, are suitable as siccatives.

The hydrogen and hydroxyl ions formed by hydroperoxide or peroxide decomposition combine to form water. They shift the equilibrium towards the radicals and are therefore the driving force behind the catalytic action.

The natural “drying” oils, with a molecular weight of approx. 880, are relatively low molecular substances. In chemical terms, therefore, it is a long journey until the crosslinking caused by oxidative hardening produces a hard and, at the same time, resistant coating.

The natural oils’ low molecular weight leads to a low viscosity and consequently a high tendency to run on vertical surfaces. To remedy these shortcomings, various methods of preliminary, targeted molecular enlargement of the oils have been used for years to increase the viscosity. One such method involves heating the oils in the absence of oxygen at temperatures of between 260 °C and 300 °C over a period of a few hours. This leads to thermally induced polymerisation reactions of the double bonds to form so-called stand oils of higher viscosity. The goal of molecular enlargement can be achieved in the same time-frame at temperatures of between 100 °C and 150 °C by heating in the presence of oxygen. By contrast with the stand oils mentioned above, the increase in the molecular weight in the case of the so-called blown oils is achieved by molecular enlargement via oxygen bridges.

![Figure 2.1.11: Acceleration of peroxide decomposition by siccatives](image1)

![Figure 2.1.12: Modification of oils by reaction with styrene](image2)
The reaction of oils with styrene or cyclopentadiene also leads to an increase in viscosity and thus to the faster formation of mechanically solid films.

One way of making natural oils more reactive is to increase the number of double bonds and simultaneously raise the content of conjugated double bonds. The number of double bonds can be increased by epoxidation of the double bonds in the fatty acids, followed by ring opening and dehydration.

Fatty oils, particularly linseed oil, can be also converted into candidate raw materials for coatings by reaction with maleic anhydride. Addition of the maleic anhydride to the fatty acids’ double bonds, followed by treatment with butanol to split open the ring and then neutralisation with amines yields anionic paint raw materials that are soluble in water. Such modification products have been highly successful for many years as film forming agents for anodic electrocoating (see Chapter 4.2.1).

Another way to improve the processing properties of oxidatively curing oils is to blend them with natural hardened resins. However, the resulting increased viscosity has to be lowered again by the addition of appropriate solvents. The hardened resins accelerate physical drying, while the oils ensure subsequent chemical crosslinking.

Figure 2.1.13: Increasing the number of conjugated double bonds of oils by epoxidation

Figure 2.1.14: Water-soluble resins obtained by reaction of oils with maleic anhydride