

# **Additives for Coatings**

Edited by  
Johan Bieleman

 **WILEY-VCH**

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# Preface

Coating additives comprise an extremely important class of coating raw materials that are used for the formulation of paints and coating materials, as well as for applications closely related to coating materials.

Quality, as well as various coating-application properties are determined to a large extent by the coating additives used. Selecting the correct additives from the wide range available is therefore very important.

In practice, it rather often happens that the coating technician literally only „finds“ the right additive for the application after experimentally testing a large range of products. With this type of method, an explanation of why one additive works, and another does not, is rarely found.

The primary goal of this book is to inform the coating technician who works with the formulation and application of coating materials such as paints, varnishes, inks, and related products, about the effects that can be obtained with additives. The main classes of additives and the advantages associated with their proper application in coating materials are emphasized.

The chemical composition and basic properties of the main groups of additives, such as thickening agents, surface-active agents, surface modifiers, catalysts, biocides, etc., are explained in detail. Not only the theoretical aspects are covered, the greater part of the information is directed at practical applications and properties, such as the influence on film properties such as appearance and protection.

The book is an ideal source of information for those working as coating technicians or chemical engineers in industry and trade; however, it is also suitable for those who work in professions that deal with coatings, for instance, in schools, colleges, universities, and public institutions.

Although, in a few cases, commercial names were used to support clear information, the aim of this book is not to list or describe additives according to their trade names.

This book also does not describe all related theories and publications on coating additives in detail, without presenting connections to practical conditions.

In editing this book, I had the support of various specialists in different subjects related to coatings, and I thank them all for the professional and pleasant cooperation. My sincere thanks are particularly extended to Dr. Stoye, Dorsten, Germany, for his stimulating ideas, and to Prof. Dr. Funke, Leonberg, Germany, for his very helpful advice and corrections. A special acknowledgment goes to the management of CONDEA Servo B.V., Delden, the Netherlands, for their support and for providing the technical means.

Goor, The Netherlands  
January 2000

*Johan H. Bieleman*

# Contents

<b>1</b>	<b>Introduction</b> .....	<b>1</b>
	<i>J. Bieleman</i>	
1.1	Additives in Coating Materials .....	1
1.2	Definitions .....	2
1.3	Classification According to Function .....	2
1.4	Quantities Used .....	3
1.5	Economic Significance of Coating Additives .....	4
	References .....	4
<b>2</b>	<b>Basics</b> .....	<b>5</b>
	<i>J. Bieleman</i>	
2.1	Introduction .....	5
2.2	Interactions .....	5
2.3	Chemical Composition .....	7
2.4	Effectiveness of Additives .....	7
2.5	Applications .....	8
	References .....	8
<b>3</b>	<b>Thickeners</b> .....	<b>9</b>
	<i>J. Bieleman and G. Kroon</i>	
3.0	Basics .....	9
3.0.1	Introduction .....	9
3.0.2	Rheology and Viscosity .....	9
3.0.3	Viscosity Measurement .....	14
3.1	Inorganic Thickeners .....	17
3.1.1	Introduction .....	17
3.1.2	Organoclays .....	17
3.1.3	Production of the Organoclays .....	20
3.1.4	Rheology and Organoclays .....	21
3.1.5	Influence of Organoclays on Various Coating Properties .....	25
3.1.5.1	Sedimentation .....	26
3.1.5.2	Sagging .....	27
3.1.5.3	Flow and Levelling .....	28

3.1.6	Incorporation Procedures	29
3.1.6.1	Powder Method	29
3.1.6.2	Paste Method	29
3.1.6.3	Easily Dispersable Organoclays	29
3.1.7	Trade Products	30
3.2	Organic Thickeners	31
3.2.0	Introduction	31
3.2.0.1	Organic Thickeners for Water-Borne Paints	31
3.2.0.2	Thickeners for Solvent-Based Paints	34
3.2.1	Cellulose Derivatives	35
3.2.1.1	The Chemistry of Cellulose Derivatives	36
3.2.1.2	The Addition of Cellulose Ethers to Paints	38
3.2.1.3	Paint Properties Influenced by Cellulose Ethers	39
3.2.1.4	Associative Cellulose Ethers	45
3.2.1.5	Commercial Products	47
3.2.1.6	New Developments	48
3.2.1.7	Toxicology and Disposal	49
3.2.2	PUR Thickeners	50
3.2.2.1	Introduction	50
3.2.2.2	Chemical Composition and Delivery Form	51
3.2.2.3	Thickening Mechanism	52
3.2.2.4	Application Properties of PUR Thickeners	53
3.2.2.5	Applications	55
3.2.2.6	Formulation of Coating Materials with PUR Thickeners	56
3.2.2.7	Coating Properties	57
3.2.2.8	Commercial Products	57
3.2.3	Organic Thickeners for Solvent-Borne Coatings	58
3.2.3.1	Introduction	58
3.2.3.2	Product Survey	58
3.2.3.3	Hydrogenated Castor-Oil-Based Thickeners	58
3.2.3.4	Polyamides	60
3.2.3.5	Overbased Sulphonates	61
3.2.3.6	Polyolefins	61
3.2.3.7	Commercial Products	62
	References	62
<b>4</b>	<b>Surface-Active Agents</b>	<b>65</b>
	<i>J. Bieleman, W. Heilen, S. Silber, M. Ortelt, and W. Scholz</i>	
4.1	Wetting and Dispersing Agents	67
4.1.1	Introduction	67
4.1.2	Definitions	67
4.1.3	The Dispersion Process	69
4.1.3.1	Pigment Wetting	70
4.1.3.2	Mechanical Disruption	75

4.1.3.3	Stabilization .....	75
4.1.3.4	Stabilization in Polar Media: Practical Evaluation .....	82
4.1.3.5	Stabilization in Nonpolar Media: Practical Evaluation .....	83
4.1.4	Chemical Composition of Wetting and Dispersing Agents .....	86
4.1.4.1	Polymeric Dispersing Agents .....	89
4.1.5	Problem-Solving .....	91
4.1.6	Procedures for Determining Dispersion Efficiency .....	94
4.1.6.1	Surface-Charge Measurement .....	94
4.1.6.2	Dispersant Demand .....	94
4.1.6.3	Monitoring the Dispersion Process .....	95
4.1.6.4	Degree of Dispersion .....	95
4.1.6.5	Degree of Flocculation .....	96
4.1.6.6	Flooding: Rub-Out Test .....	97
4.1.7	Biological and Toxicological Properties .....	98
4.1.7.1	Surfactants .....	98
4.1.7.2	Polymers .....	98
4.1.8	Commercial Products .....	99
4.2	Defoaming of Aqueous Paint Materials .....	100
4.2.1	Introduction .....	100
4.2.2	Foam Formation in Aqueous Paints .....	101
4.2.3	Causes of Foam Stabilization .....	102
4.2.3.1	Stability-Reducing Parameters .....	103
4.2.3.2	Parameters That Promote Foam Stability .....	104
4.2.4	Composition and Effect of Defoamers and Foam Inhibiting Agents .....	106
4.2.4.1	Defoamers .....	106
4.2.4.2	Foam Inhibiting Agents .....	107
4.2.5	Formulation of the Active Substances .....	108
4.2.6	Test Methods for the Evaluation of Defoamers .....	110
4.3	Adhesion Promoters .....	112
4.3.1	Definition .....	112
4.3.2	Models for Interpreting Adhesion Phenomena .....	112
4.3.3	Adhesive Strength in the Bond .....	114
4.3.4	Adhesion Promoters .....	115
4.3.4.1	General Remarks .....	115
4.3.4.2	Organofunctional Silanes .....	116
4.3.4.3	Organometallic Compounds .....	119
4.3.4.4	Chlorinated Polyolefins .....	122
4.3.4.5	Special Condensates .....	123
4.3.4.6	Phosphates .....	124
4.3.4.7	Polyethylenimine .....	124
4.3.4.8	Silicones and Silicone-Modified Polymers .....	125
4.3.4.9	Miscellaneous .....	126
4.3.4.10	Summary .....	126

4.4	Additives to Improve Substrate Wetting .....	128
4.4.1	Importance of Surface Tension for Substrate Wetting .....	128
4.4.2	Influencing the Surface Tension of Coatings .....	129
4.4.3	Measurement of Surface Tension .....	130
4.4.4	Chemistry of Silicone Additives .....	130
4.4.5	Usage of Silicone Additives .....	134
	References .....	136
<b>5</b>	<b>Additives for Surface Modification .....</b>	<b>139</b>
	<i>J. Bieleman, W. Scholz, W. Heilen, U. Ferner, and G. Lüers</i>	
5.1	Additives to Improve Surface Slip .....	140
5.1.1	Introduction .....	140
5.1.2	Important Terms .....	140
5.1.3	Practical Importance of Surface Slip .....	140
5.1.4	Factors Influencing Scratch Resistance .....	141
5.1.5	Slip Ability .....	141
5.1.6	Influencing the Surface Slip .....	142
5.1.7	Silicone Additives .....	142
5.1.8	Waxes .....	143
5.1.9	Measuring Surface Slip .....	144
5.2	Matting .....	146
5.2.1	Basic Physical Principles of Matting .....	146
5.2.1.1	Methods for the Characterization of Surfaces .....	147
5.2.1.2	Gloss and Sheen .....	147
5.2.1.3	Surface Roughness .....	147
5.2.1.4	Properties Not Influenced by the Matting Agent .....	148
5.2.1.5	Mechanism of Matting .....	149
5.2.2	Matting Agents .....	151
5.2.2.1	Introduction .....	151
5.2.2.2	Economical Importance .....	151
5.2.2.3	Requirements for Modern Matting Agents .....	153
5.2.2.4	Amorphous Silica .....	153
5.2.2.5	Natural Silica and Fillers .....	155
5.2.2.6	Organic Matting Agents .....	155
5.2.3	Application of Matting Agents .....	156
5.2.3.1	General Parameter That Influence Matting .....	156
5.2.3.2	Solventborne Systems .....	159
5.2.3.3	Waterborne Systems .....	159
5.2.3.4	High-Solids/Radiation-Curing Systems .....	160
5.2.3.5	Powder Coatings .....	160
5.2.4	Commercial Products .....	161
	References .....	161

<b>6</b>	<b>Flow-Levelling and Coalescing Agents</b> .....	163
	<i>J. Bieleman, J. Hajas, and K. Dören</i>	
6.1	Levelling Additives .....	164
6.1.1	Introduction .....	164
6.1.1.1	Definition and Measurement of Levelling .....	164
6.1.1.2	Physical Factors Influencing Levelling .....	166
6.1.1.3	Improvement of Levelling: Mode of Action of Levelling Additives .....	168
6.1.2	Commercially Available Levelling Additives .....	168
6.1.2.1	Polymers .....	168
6.1.2.2	Silicones .....	170
6.1.2.3	Fluorosurfactants .....	170
6.1.2.4	Solvents .....	170
6.1.2.5	Other Additives .....	171
6.1.3	Properties of Levelling Additives .....	172
6.1.4	Application of Levelling Additives .....	173
6.1.4.1	Polymers .....	173
6.1.4.2	Silicones .....	174
6.1.4.3	Fluorosurfactants .....	175
6.1.4.4	Solvents .....	176
6.1.4.5	Other Additives .....	177
6.1.5	Practical Experiences with Levelling .....	177
6.1.6	Toxicology and Waste Disposal .....	178
6.2	Coalescing Agents .....	180
6.2.1	Introduction .....	180
6.2.2	Polymer Dispersions: Structure/Film Formation .....	181
6.2.3	Coalescing Agents: Mode of Action .....	183
6.2.4	Coalescing Agents: Product Overview .....	187
6.2.5	Performance Aspects .....	191
6.2.6	Ecology/Toxicology .....	196
6.2.7	Manufacturers/Tradenames (Selection) .....	197
	References .....	198
<b>7</b>	<b>Catalytically Active Additives</b> .....	201
	<i>J. Bieleman and R. Lomölder</i>	
7.1	Driers .....	202
7.1.1	Introduction .....	202
7.1.2	Historical Overview of the Application of Driers .....	202
7.1.3	Composition .....	203
7.1.4	Manufacturing .....	206
7.1.4.1	Precipitation .....	206
7.1.4.2	Fusion .....	206
7.1.4.3	Direct Metal Reaction .....	207
7.1.5	Autooxidation Drying and the Function of Driers .....	207
7.1.6	Drier Metals .....	210

7.1.6.1	Active Driers	210
7.1.6.2	Auxiliary Driers	212
7.1.7	Combination Driers	214
7.1.8	Loss of Drying Ability	215
7.1.9	Lead-Free Drier Systems	216
7.1.9.1	Lead-Containing Drier Systems	217
7.1.9.2	Substitution of a Lead Drier	217
7.1.10	Waterborne Coatings	218
7.1.10.1	Characteristic Drying Phenomena of Air-Drying Waterborne Coatings	219
7.1.10.2	Coordination Effect on Driers	220
7.1.10.3	Precomplexed Driers	221
7.1.11	High-Solids Coatings	222
7.1.12	Analysis Procedures	224
7.1.13	Biological and Toxicological Properties	224
7.1.14	Trade Names	226
7.2	Catalysts	227
7.2.1	Introduction	227
7.2.2	Melamine Cross Linking Systems	229
7.2.2.1	Introduction	229
7.2.2.2	Catalysis of HMM-Based Systems – Cross Linking	231
7.2.2.3	Catalysis of Reactive Melamine Systems – Self-Condensation	234
7.2.2.4	Formulation Advice	234
7.2.3	Polyurethane Systems	236
7.2.3.1	Introduction	236
7.2.3.2	2K-PUR Systems	238
7.2.3.3	Blocked 1K-PUR Systems	242
7.2.3.4	PUR Powder Coatings	245
7.2.3.5	Moisture-Curing 1K-PUR Systems	246
7.2.4	Epoxy Systems	248
7.2.4.1	Introduction	248
7.2.4.2	Epoxy/Amine Systems	249
7.2.4.3	Epoxy/Carboxy Systems	251
7.2.4.4	Epoxy/Phenol/Formaldehyde Resin Systems	253
	References	254
<b>8</b>	<b>Additives for Special Functions</b>	<b>257</b>
	<i>J. Bieleman, T. Bolle, A. Braig, J. K. Glaser, R. Spang, M. Köhler, and A. Valet</i>	
8.1	Anti-Skinning Agents	258
8.1.1	Introduction	258
8.1.2	Definitions	258
8.1.3	Causes of Skinning	258
8.1.4	Consequences of Skinning	259

8.1.5	Avoiding Skinning .....	259
8.1.5.1	Antioxidants .....	260
8.1.5.2	Blocking Agents for Polymerization Catalysts .....	262
8.1.5.3	Solvents .....	266
8.1.5.4	Retention Agents .....	266
8.1.6	Practical Hints .....	267
8.1.7	Toxicological Properties of MEKO .....	268
8.1.8	Commercial Products .....	268
8.2	Light Stabilizers .....	269
8.2.1	Introduction .....	269
8.2.1.1	Environmental Influences on Coatings .....	269
8.2.1.2	Photooxidation of Polymers .....	270
8.2.1.3	Stabilization Possibilities .....	271
8.2.1.4	Economic Importance .....	272
8.2.2	Basic Principles .....	272
8.2.2.1	UV Absorbers .....	273
8.2.2.2	Hindered-Amine Light Stabilizers (HALS) .....	277
8.2.3	Properties of Light Stabilizers .....	279
8.2.3.1	Requirements for Light Stabilizers .....	279
8.2.3.2	Solubility and Compatibility of Light Stabilizers .....	280
8.2.3.3	Volatility of Light Stabilizers .....	280
8.2.3.4	Influence of the Own Colour of a Light Stabilizer .....	281
8.2.3.5	Interaction of UV Absorbers with Other Coating Components .....	281
8.2.3.6	Permanence of UV Absorbers .....	281
8.2.3.7	Side Reactions of HALS .....	283
8.2.4	Use of Light Stabilizers .....	283
8.2.4.1	Stabilization of Clear Coatings/Colour Coatings .....	283
8.2.4.2	Stabilization of One-Coat Solid Shades .....	285
8.2.4.3	Stabilization of Powder Coatings .....	286
8.2.4.4	Stabilization of UV-Curable Clear Coatings .....	287
8.2.4.5	Stabilization of Wood Coatings .....	288
8.2.5	Guidelines for the Use of Light Stabilizers .....	288
8.2.5.1	Evaluation Methods .....	288
8.2.5.2	Recommendations for the Use of Light Stabilizers .....	290
8.2.6	Trade Names .....	290
8.2.7	Toxicology and Waste Treatment .....	290
8.3	Corrosion Inhibitors .....	291
8.3.1	Introduction .....	291
8.3.1.1	Basics .....	291
8.3.1.2	Electrochemical Corrosion Processes .....	293
8.3.1.3	Corrosion Protection by Organic Coatings .....	295
8.3.2	Corrosion Inhibitors .....	296
8.3.2.1	Definition .....	296
8.3.2.2	Inhibition Mechanisms .....	296
8.3.2.3	Inhibitor Classes/Characteristics .....	299

8.3.3	Products and Product Characteristics	300
8.3.3.1	Flash-Rust Inhibitors	300
8.3.3.2	Inhibitors for Long-Term Corrosion Protection	301
8.3.4	Practical Hints, Formulation Guidelines	303
8.3.4.1	Flash-Rust Inhibitors	303
8.3.4.2	Inhibitors for Long-Term Protection	303
8.3.5	Toxicology and Disposal	305
8.3.6	Manufacturers and Trade Names	305
8.4	Biocides	306
8.4.1	Introduction	306
8.4.2	Definitions	307
8.4.3	In-Can or In-Tank Preservation	309
8.4.4	Plant Hygiene	310
8.4.5	In-Can Preservatives	312
8.4.5.1	Formaldehyde	313
8.4.5.2	Formaldehyde-Releasing Compounds	313
8.4.5.3	Glutaraldehyde	314
8.4.5.4	Phenol Derivatives	314
8.4.5.5	Acids	315
8.4.5.6	Carbonic Acid Amides	316
8.4.5.7	Quaternary Ammonium Compounds (QACs)	316
8.4.5.8	Isothiazolinone Derivatives	316
8.4.5.9	Alcohols	318
8.4.6	Film Preservation	318
8.4.7	Restoration of Surfaces	320
8.4.8	Film-Preserving Substances	321
8.4.8.1	Benzimidazoles	321
8.4.8.2	Carbamates and Dithiocarbamates	322
8.4.8.3	<i>N</i> -Haloalkylthio Compounds	322
8.4.8.4	2- <i>n</i> -Octyl-4-isothiazolin-3-one (OIT)	323
8.4.8.5	Zinc Pyrithione	323
8.4.8.6	Diuron	323
8.4.9	Conclusion	324
8.4.10	Commercial Products	324
8.5	Flame Retardants	325
8.5.1	General Information	325
8.5.1.1	Flammability Classification and Testing Methods	325
8.5.1.2	The Combustion Process	326
8.5.1.3	Mechanism of Flame Retardance	328
8.5.2	Common Flame Retardants – Structure, Mode of Action, Properties	330
8.5.2.1	Inorganic Flame Retardants	330
8.5.2.2	Halogen-Containing Flame Retardants	331
8.5.2.3	Phosphorus-Containing Flame Retardants	333
8.5.2.4	Char-Forming Flame Retardants	334

8.5.2.5	Intumescent Systems .....	334
8.5.3	Use and Consumption .....	336
8.5.4	Suppliers, Commercial Products .....	337
8.6	Photoinitiators as Additives in UV-Curable Lacquers .....	338
8.6.1	Introduction .....	338
8.6.1.1	Difference Between Photoinitiators and Other Coating Additives ..	338
8.6.1.2	Development of UV Curing .....	339
8.6.2	Main Components of UV-Curable Coatings .....	340
8.6.2.1	Photoinitiators .....	340
8.6.2.2	Reactive Resins and Diluents .....	341
8.6.3	Radical Photocuring .....	342
8.6.3.1	Mechanism .....	342
8.6.3.2	Investigating the Reaction Kinetics .....	343
8.6.4	UV-Curing Technique .....	343
8.6.5	Examples of Photoinitiator Use .....	344
8.6.5.1	Clear Coatings .....	345
8.6.5.2	Pigmented Coatings .....	347
8.6.6	Toxicology and Disposal .....	348
8.6.7	Trade Names .....	348
	References .....	348
<b>9</b>	<b>Industrial Hygiene and Environmental Management</b> .....	<b>353</b>
	<i>A. Postma</i>	
9.1	Introduction .....	353
9.2	Commonly Used Terms .....	353
9.3	Biological and Toxicological Properties .....	354
9.4	Safety Data .....	355
9.5	Industrial Hygiene .....	356
9.6	Waste Disposal and Packaging .....	356
	References .....	357
<b>10</b>	<b>Quality Assurance</b> .....	<b>359</b>
	<i>A. Postma</i>	
10.1	Introduction .....	359
10.2	Commonly Used Concepts .....	359
10.3	The Quality Standard ISO 9001 .....	361
10.4	Environment Protection and Industrial Hygiene .....	360
10.5	Quality Control of Additives .....	361
	References .....	362
<b>Subject Index</b>	.....	<b>363</b>

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# 1 Introduction

*Johan Bieleman*

## 1.1 Additives in Coating Materials

A coating material may be defined to be a product in liquid, paste, or powder form that, when applied to a substrate, forms a film which has protective, decorative, and/or other specific properties. The following main components are found in coating materials such as paints:

- binders
- pigments and extenders
- solvents
- additives

The binder determines most of the primary properties of the dried paint film, such as adhesion, various optical and mechanical properties, as well as the resistance against specific exposure conditions.

The other solid components of the paint layer, such as the pigments and extender, are fixed in the binder matrix.

The selection of the pigment determines not only the colour, but is also largely responsible for other properties such as the opacity and corrosion resistance of the paint.

Although the main contribution of the extenders is to reduce the raw-material costs of the paint formulation, they may also have some influence on various other paint properties.

The role of the solvent or diluent is, in the first place, to enable the processing of the solid or highly viscous components of the paint during manufacture, application, and film formation.

In addition to the indicated main ingredients, the additives in a paint composition have a major influence on the various paint properties. Additives may also modify the properties of the three main ingredients of a paint – binder, pigment/extender, and solvent – significantly.

## 1.2 Definitions

It is very difficult to give a clear and exact definition of a coating additive – they make up a very nonhomogeneous group. A wide range of additives is known, with various and widely differing functions in a coating formulation.

A possible definition is the following:

*Coating additives are any substances that are added in small quantities to a coating material to improve or to modify certain properties of the finished coating or of the coating material during its manufacture, storage, transport, or application*

## 1.3 Classification According to Function

The expression “to improve or to modify certain properties” refers not only to technical properties, it also includes economical aspects such as the reduction of manufacturing costs or the pigment yield optimization.

The amount of additives in a coating formulation is seldom more than 5% by weight. The average proportion of a single additive in a formulation is usually around 1.5% of the total quantity of the coating formulation.

There is a large variety of coating additives; they are classified according to their function below.

### **Thickening Agents**

These additives influence the rheological properties of a paint by increasing the viscosity.

### **Surface-Active Agents**

This group is subdivided into:

- wetting and dispersing agents
- anti-foaming agents
- adhesion promoters

### **Surface Modifiers**

This group is subdivided into:

- slip additives
- matting agents

### **Levelling Agents and Coalescing Agents**

The group of levelling agents includes flow agents.

### Catalytically Active Additives

This group includes:

- driers
- catalysts

### Special-Effect Additives

The remaining additives are included in this group, e. g.:

- anti-skinning agents
- light stabilizers
- corrosion inhibitors
- biocides
- flame retardants
- photoinitiators

## 1.4 Quantities Used

In terms of quantities used, the catalytically active additives make up the largest product group, as seen from the relative amounts of additives used (Table 1.4-1).<sup>[1-1]</sup> Next in used quantities are the surface-active additives, followed by the thickeners. The indicated percentages are of each specific group of additives, and are based on the volume of additives used globally; there may be considerable regional variations.

Driers, used as drying catalysts in oxidatively drying paints, make up the main part of the catalytically active additives. However, the use of driers is declining: firstly, more concentrated driers are being used (less solvent), and secondly, the market share of air-drying systems is declining in favour of physically drying paints.

**Table 1.4-1.** Relative amounts additives used according to group

Additive group	Usage in % of the total amount of applied additives
Catalytically active additives	28
Surface modifiers	12
Thickeners	16
Surface-active agents	19
Levelling- and coalescing agents	10
Special-effect additives	15

## 1.5 Economic Significance of Coating Additives

Although additives make up a small proportion of paint formulations, the total world consumption of additives is estimated to be more than 350 000 metric tons annually!<sup>[1-2]</sup>

The relative importance of additives is not simply expressed by total quantities or sales volumes, most important is the technical impact of the additives on the paint properties. The significance of an additive in a specific coating material is best expressed in terms of its contribution to the improvement in the quality of the paint. However, this economic contribution is not easily quantifiable into an “economic figure”.

If one were to base the economic importance of additives on the raw material costs for the production of paints, it would be found to be rather moderate (Table 1.4-2).<sup>[1-3]</sup>

**Table 1.4-2.** Average contributions of the various ingredients in paints

Paint raw material	Quantity in %	Value in %
Binder	29.5	31.7
Solvent	27.4	15.5
Water	10.6	–
Pigments	18.7	45.9
Extenders	12.3	3.5
Additives	1.5	3.4
Total	100	100

Obviously the average amount of additives in paints is rather small by weight. Additives contribute more to the total raw material costs because the various additives are more expensive than the average raw material costs of a paint.

Nevertheless, the data from Table 1.4-2 show that additives make up a very modest contribution to the total raw material costs of a coating material. The argument for the use of an additive is therefore mainly determined by the effect that the additive has on the quality of the coating material or the dried film.

## References

- [1-1] Bieleman, J. H., *Coatings Agenda Asia Pacific 1996/1997*, Campden Publ. London, p. 150
- [1-2] Stoye-Freitag, *Lackharze*, Carl Hanser Verlag, München 1996, p. 396
- [1-3] *The Demand for Coating Additives*, 3rd Ed.; IRL Ltd., London 1991, p. 118–120

## 2 Basics

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### 2.1 Introduction

Coating additives are auxiliary components that are used in the formulation of surface-coating materials such as paints and lacquers and are typically added in small quantities in order to realize certain desired properties during production, storage, application, or exposure of the coating (see Section 1.2). Other main components of coatings are binders, pigments/extenders and solvents. Clearly, there are several different application purposes for additives, and additives indeed make up quite a non-homogeneous group. Coating additives may differ significantly from each other regarding their chemical compositions and functions. The only common factors for the different additive groups are that they are by definition “added in small quantities” and that the purpose of their application is “to realize certain desired properties”.

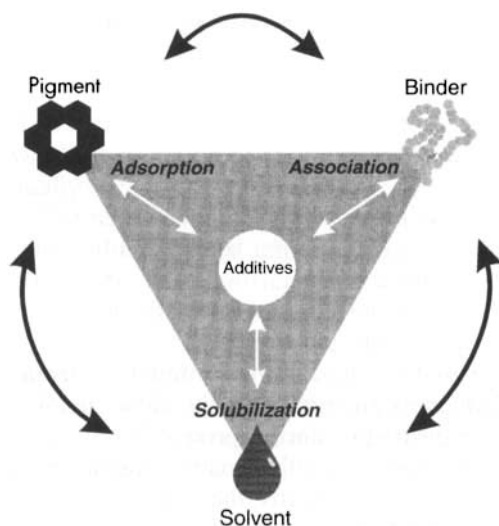
From this it is quite clear that there are no general characteristic physical and chemical properties for all additives and the various different groups of coating additives will therefore have to be considered separately. In this chapter some basic functional properties of coating additives will be explained in relation to typical applications.

### 2.2 Interactions

Coating additives are utilized to further modify the characteristic properties imparted by the main components of the coating material, namely the binder, pigment and solvent. Characteristic for additives is, furthermore, that these ingredients can be directed in such a way that, ideally, they develop their effect at certain predicted places within the coating formulation or layer. Indeed, one of the targets in developing additives is to devise the additives in such a way that the additive molecules are concentrated in the varnish right where they can fulfil their desired purpose (Fig. 2.2-1).

Typical characteristics of additives which are of great technical significance:

- surface activity
- vapour pressure
- solubility parameter
- chemical stability



**Figure 2.2-1.** Interaction between additives and the other coating-material ingredients

The importance of these characteristics will be demonstrated by the following examples.

### Surface Activity

Molecules can be tailor-made through chemical modifications so that they have a higher affinity for certain selected interfaces. This may be achieved, for instance, in the case of fatty alcohols, by introducing negatively charged groups such as carboxylates, sulphates, or phosphates. This chemical modification of the fatty alcohol results in improved adsorption on the surfaces of base pigments (covalent bonding forces).

### Vapour Pressure

In practice, methyl ethyl ketoxime is the main additive used as anti-skinning agent in oxidative drying alkyd paints. This oxime is a good ligand for certain metals, and it complexes drying catalysts such as cobalt driers, which are typically used in these paints. In contrast to the free drier, the cobalt oxime complex has no catalytic effect on the drying rate. When the paint is applied, the surface area is increased considerably. Because methyl ethyl ketoxime has a high vapour pressure, it evaporates soon after the coating has been applied, releasing the catalyst so that it can be active (see Section 8.1.5.2).

### Solubility

Defoaming and anti-foaming agents should be effective at the liquid/air interface. Defoaming and anti-foaming agents are usually poorly soluble in the liquid phase. As soon as the paint is applied, the defoaming agent separates and floats as a very

thin layer on top of the paint layer, resulting in a higher concentration of the de-foaming agent at the liquid/air interface.

### **Chemical Stability**

Limited chemical stability at higher temperatures of, for example, certain blocked acid catalysts causes the release of the acid at higher temperatures, thus effecting acid-catalysed curing of paints and coatings.

## **2.3 Chemical Composition**

The different additives vary significantly with regard to their chemical compositions. Some additives have clearly defined compositions, being made up of compounds such as oximes, silicones, cellulose-ether or metal soaps; other additives are very complex preparations made up of different components.

Some additives consist of natural products (for example lecithin) or modified or prepared natural products (such as cellulose derivatives). However, the majority of the additives are based on synthetic products.

## **2.4 Effectiveness of Additives**

The characteristic properties as well as the field of application of most additives can be clearly defined, for example, with defoaming agents. However, additives often do not have only a single function, but have several additional effects. Sometimes this multiple effectiveness is desired: wetting agents that cause better pigment wetting, resulting in better adhesion of the coating layer onto the substrate, also improve flow and levelling. Anti-skinning agents may have the additional desired side effect of functioning as flow agent.

But negative side effects may also occur: thickeners may affect the gloss of the coating layer and work as a kind of matting agent, pigment dispersing agents may operate as polymerization catalysts under storage conditions.

Many of these phenomena are the result of interactions between the various ingredients of the complicated coating formulation, to this is added the complicating factor of the complex composition of the additives themselves.

## 2.5 Applications

Usually additives are selected according to the following criteria:

- functionality
- availability
- compatibility
- price/performance relationship

The functionality is related to the composition as well as the usage levels and recommended application.

Additives are often used as “problem solvers”, i. e., they are selected to solve, for instance, an actual production or application problem and are therefore needed immediately. The availability of the additive is in such a case decisive.

Compatibility is a very important criterion as well. In practice different additives are used in the same formulation. Here some effects could be mutually neutralized. A good example is certain dispersing agents that can influence the effectiveness of the associative thickener negatively. The effectiveness and efficiency of an additive can be influenced by physical or chemical interactions with other ingredients of the coating formulation during storage of the paint product. A good understanding of the characteristic properties of all the ingredients in the particular coating formulation reduces the risk of being confronted with such unwanted interactions.

The sequence of addition of the raw materials can be very important, especially with regard to the additives. Some additives are typically added before the dispersing process, for example, dispersing agents, thickeners, bactericides, or the additives are added during the let-down stage of the coating-production process.

The dosage of some additives is critical; because of the complexity of a coating formulation, it is necessary to determine the optimal quantity empirically for each formulation individually.

As additives are substances which are only added in small quantities, the impact on the total raw material costs is relatively minor, the decisive factor is whether the desired improvement is obtained or not.

## References

- [2-1] Sharma, M. K., Parikh, A., *Surface Phenomena Waterborne Coatings*, Plenum Press, New York 1995, p. 203

## **3 Thickeners**

*Johan Bieleman*

### **3.0 Basics**

#### **3.0.1 Introduction**

Thickeners are used in coating materials and paints to impart the required rheological characteristics to the system. The rheological properties of a coating material influences its storage, processing, as well as application performance. Thickeners are usually added before the dispersing stage of the production process – the type and amount are adjusted to the dispersing equipment – to optimize the flow behaviour of the ground paste. If the pigments are dispersed in a medium which is too thin, turbulent flow behaviour results, which leads to a great loss in supplied energy, so that it is not used optimally during dispersing.

For storage, the viscosity of the paint should be high enough to prevent sedimentation of heavy pigment particles. The viscosity can be adjusted in a similar way to influence several application characteristics such as the flow, levelling, sag resistance, brushability, as well as film thickness and opacity. There are several possible ways in which the rheology can be adjusted. By adding a thickener the viscosity can be increased. In practice, organic as well as inorganic thickeners are used.

To understand how these coating-material thickeners function, some rheological basic knowledge is necessary, and therefore, first of all, a few rheological terms will be explained.

#### **3.0.2 Rheology and Viscosity**

The definition of rheology is “the science of the deformation and flow behaviour of matter under the influence of external forces”.<sup>[3-1, 3-2]</sup> Put differently, it is the study of viscosity under a wide range of conditions. The literal translation of the term “rheos”, of Greek origin, is “flowing”. The term viscosity refers to the resistance of a liquid against deformation, small resistance corresponds to low viscosity, and large resistance corresponds to high viscosity.

## Flow

The flow of liquids may be subdivided into two types: laminar and turbulent flow.

Laminar flow is the flow of infinite, thin, parallel layers of liquid films – from which a liquid may be considered to be made up of – which occurs in such a way that no mixing occurs.<sup>[3-3]</sup> It is easy to describe laminar flow mathematically, provided that no turbulent flow arises.

Turbulent flow is accompanied by eddy currents in sheared material and occurs at relatively high rates of shear, for both plastic and Newtonian systems. With turbulent flow a great part of the energy, supplied to the system to make flow possible, gets lost so that it can not be used for the actual aim, to get a flow, as with laminar flow.

During production, as well as during application, the flow in coating materials is mainly laminar.

## Shear Stress, Shear Rate, and Viscosity

To illustrate rheological dimensions, the two-plate-model is often used (Fig. 3.0-1). A liquid has an external force ( $F$ ) acting on its surface (with an area  $A$ , in  $\text{m}^2$ ). The external force pulls on the top layer of the liquid, with the pulling action defined as the shear stress ( $\tau$ ), equal to  $F/A$  ( $\text{N m}^{-2}$ ). The direction of the applied force is parallel to the boundary surfaces of the films. The shear stress is the force with which two related liquid films are moved in relation to one another.<sup>[3-1]</sup>

$$\text{shear stress } \tau = \frac{\text{force } F}{\text{surface } A} \text{ in [Pa]} = \frac{[\text{N}]}{[\text{m}^2]} \quad (1)$$

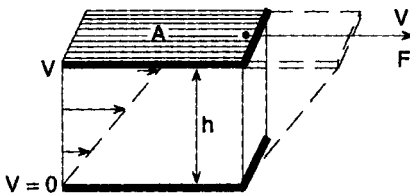


Figure 3.0-1. The two-plate model

When a force is applied to the upper layer of a liquid, this layer is pushed in the direction of the force. As the top layer moves under the applied shear stress, the layer directly beneath it is pushed along as well. This second layer, in its turn, will push the third layer along, the third will affect the fourth in the same one, and so on. The bottom layer, however, is held in place against the container. The resulting shear gradient, or shear rate,  $D$ , is defined by the following equation, where the thickness of the liquid is  $h$  and the velocity of the top layer is  $v$ .

$$\text{shear rate } D = \frac{\text{velocity } v}{\text{distance } h} \text{ in [s}^{-1}\text{]} \quad (2)$$

The shear rate is also known as the “shear strain rate”, and may also be indicated by  $\dot{\gamma}$  instead of  $D$ . Typical values for the shear rates of paints and coatings are given in Table 3.0-1.<sup>[3-1]</sup>

**Table 3.0-1.** Typical shear rates for different processes to do with paints and coatings

Process	Typical shear rate range, $D$ ( $s^{-1}$ )
Sedimentation of particles	$10^{-6}$ to $10^{-4}$
Levelling due to surface tension	$10^{-2}$ to $10^{-1}$
Sagging under gravity	$10^{-2}$ to $10^1$
Dipping bath	$10^0$ to $10^2$
Brushing	$10^2$ to $10^4$
Spraying	$10^3$ to $10^6$
Pigment dispersing	$10^3$ to $10^5$
Transfer of printing inks by rollers	$10^4$ to $10^6$

The quotient of  $\tau$  and  $D$  is the viscosity quotient,  $\eta$ , simply designated by viscosity.

$$\eta = \frac{\tau}{D} \left[ \frac{N \cdot s}{m^2} \right] = Pa \cdot s \quad (3)$$

Viscosity is therefore a measure of a liquid’s flow resistance against its deformation. Viscosity generally depends not only on the shear rate and the shear force, but also on the pressure  $p$ , the temperature  $T$ , the load duration  $t$  and the critical shear power  $\tau_0$ . The relationship between these factors is expressed by the following equation.

$$\eta = f(D, \tau, \tau_0, t, T, p) \quad (4)$$

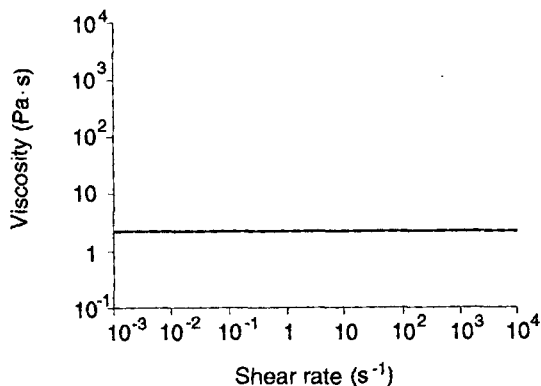
Other parameters are, for example, acidity, concentration, and magnetic- or electric field strength.

### Viscosity Curves

The rheological behaviour of a system under various conditions may be described by a viscosity curve, in which the viscosity is expressed as a function of the applied shear conditions. For a typical industrial coating material, the viscosity ranges from  $>1 Pa \cdot s$  to several tens of thousands of  $Pa \cdot s$ . Shear rates vary from  $<0.001 s^{-1}$  to  $100\,000 s^{-1}$ .

#### 1. Newtonian Flow Behaviour

Newtonian flow defines a process where the viscosity at the indicated pressure and temperature is constant regardless of the applied shear rate and time (Fig. 3.0-2). Therefore a single viscosity measurement will give its true value; the shear rate is



**Figure 3.0-2.** Newtonian flow behaviour

directly proportional to the shearing force. Mathematically the flow curve is described by Newton as follows:

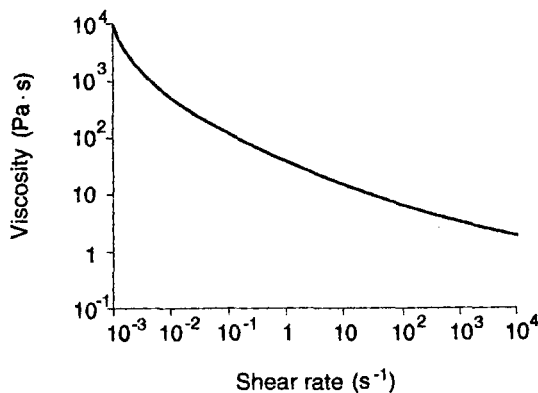
$$\tau = \eta \cdot D \quad (5)$$

Examples of Newtonian liquids are water and pure solvents. The viscosity is equivalent to the increase of the shear stress curve within the flow curve.

## 2. Pseudoplasticity and Plasticity

Pseudoplastic flow is illustrated in Fig. 3.0-3. In pseudoplastic systems the viscosity decreases under pre-determined pressure and temperature with increasing shear rate.

Various viscosity measurements across the shear rate range are necessary to establish a correct rheology profile. Almost all paints and varnishes show more or less pseudoplastic (*shear thinning*) flow behaviour! This rheological behaviour is explained by changes in the positions of the coating component particles under the influence of the applied shear force. For example, at increasing shear rate (or shear



**Figure 3.0-3.** Pseudoplastic flow behaviour

stress), the orientation of polymer molecules or dispersed particles may be induced to move parallel to each other. In a similar way, flocculated particles may be deflocculated, or loops between macromolecules may be disrupted.

Pseudoplasticity is a form of structural viscosity, however, it is a type of flow that has no yield value (it starts in the origin during the measurement procedure). This contrasts to plastic flow behaviour. The flow behaviour of a substance is plastic if it acts like an elastic body at a pre-determined pressure and temperature under a critical shear stress  $\tau_0$  and if the flow only starts after exceeding this flow limit. A yield value must be exceeded before plastic flow will take place. Examples are printing inks and “solid emulsion paints” as well as emulsion paints thickened with conventional cellulose thickeners.

For plastic flow there are two different types of flow curves.

*Bingham systems* show flow behaviour where there is no movement below a characteristic yield value. Above this yield value the system acts like a Newtonian liquid. The viscosity coefficient and the yield value jointly characterize a Bingham material. Examples are suspensions and pigment pastes.

The *Casson relation* is a special form of the relation between shear stress, shear rate, and yield value. The square roots of these values appear in the Casson relation, to simplify the representation of the flow curves.<sup>[3-4]</sup>

### 3. Thixotropy

The flow behaviour of a substance is thixotropic if, under a constant shear rate (or constant shear stress), at pre-determined pressure and temperature, its viscosity decreases with ongoing time, and, after the application of stress is ended, the viscosity increases again (Fig. 3.0-4). Therefore thixotropy is time-dependent and involves the breakdown of the rheological structure by stirring, followed by its recovery over time.

In a true thixotrope, the viscosity recovers completely, to regain its original value. The way in which the internal structure re-forms determines how long it takes to re-

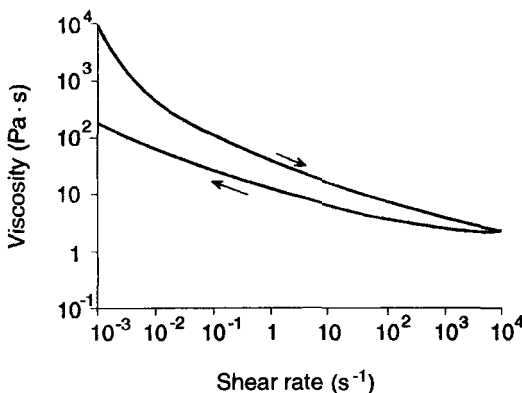


Figure 3.0-4. Thixotropic flow behaviour

cover the original viscosity. The area between the two curves in Fig. 3.0-4 represents the hysteresis loop, which is a measure of thixotropy. Rapid viscosity recovery can result in little or no hysteresis loop being formed. Viscosity recovery can range from seconds to months depending on the material. A certain degree of thixotropy is of great importance for emulsion paints; the correct balance needs to be achieved for the structure of the stored material, its flow, levelling, and sag resistance.

#### 4. Dilatancy

The flow behaviour of a substance is dilatant if the viscosity is time-independent under shear conditions at pre-determined pressure and temperature at a constant shear rate (or constant shear strength), and if the viscosity increases with rising shear rate (or shear strength) (Fig. 3.0-5). Dilatant behaviour (shear thickening) is the opposite of pseudoplasticity and occurs typically in very concentrated suspensions such as aqueous grinding pastes.

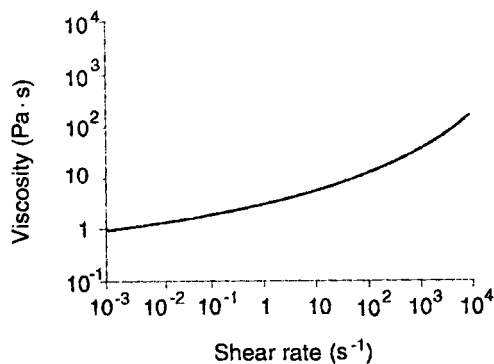


Figure 3.0-5. Dilatant flow behaviour

### 3.0.3 Viscosity Measurement

Several approaches to the study of the flow behaviour of coating materials have been developed. A simple and quick measurement system is the flow cup. The cup is filled with a known, constant volume of paint. Assessment requires monitoring the time taken for the paint (or other liquid material) to drain from the reservoir through a defined orifice, located at the base of the cup. Flow cups measure only the time taken for a liquid to flow through a fixed orifice, under gravity. They do not give a proper measure of the rheological properties. Standardized cups have been made available, such as the DIN cups in Germany, the Ford cup in the United States, and the globally used ISO-flow cup.

Flow cups can be used for near-Newtonian fluids. To determine the flow curves of non-Newtonian liquid paints, rotation viscosity meters are preferable, e.g., vis-

**Table 3.0-2.** Rheological expressions

Expression	Meaning
Deformation	Change in form or volume (qualitative)
Dynamic viscosity	<p>a) The viscosity coefficient decisive for shear flow (material constant for Newtonian liquids).</p> <p>b) For non-Newtonian liquids and plastic materials it is the shear viscosity at a defined shear stress or shear rate. The correct term is “dynamic shear viscosity”, which contains “dynamic” to distinguish it from kinematic (shear) viscosity, and “shear” to distinguish it from strain or volume viscosity. The parameter for dynamic viscosity is called fluidity.</p>
Elasticity	Property of a material which recovers its original size and shape immediately after removal of the force causing deformation. The energy from external forces is saved as reversible deformation energy.
Yield value	This is the minimum shear stress $\tau$ needed to induce flow. It is expressed in $\text{N} \cdot \text{m}^{-2}$ or Pa. Above the yield value, materials exhibit plastic flow behaviour.
Flow curve	Graphic representation of the relation between shear stress $\tau$ and shear rate $D$ for a liquid submitted to laminar flow or for a plastic substance above the yield value.
Kinematic viscosity	Quotient of dynamic viscosity and density.
Laminar flow	Flow pattern in which no significant turbulence occurs (opposite: turbulent flow).
Structural viscosity	Flow behaviour of substances whose viscosity decreases with increasing shear stress or shear rate. The structural viscosity of a substance does not give any information about the time-dependence of its flow behaviour.
Structured paints	These paints have a gel-like consistency which breaks down under the kind of shear exerted during brushing or roller application which re-forms when the shearing force is removed. When there is a time lag between the removal of the shearing force and the start of the gel re-formation, the paint is said to be thixotropic.
Turbulence	A deviation from laminar flow, turbulence occurs at relatively high rates of shear and indicates the existence of eddy currents in sheared material.
Viscoelasticity	Attribute of substances that are both elastic and viscous. Viscoelastic substances save a part of the deformation energy.
Viscosity	<p>a) Qualitative: the flow behaviour of a substance under the influence of stress to become irreversibly deformed (a “viscous” substance has high viscosity). The flow energy is transferred into heat.</p> <p>b) It may also refer to the viscosity coefficient, for example, the dynamic viscosity <math>\eta</math></p> <p>c) It may also refer to a viscosity function.</p>
Viscosity curve	Graphic representation of the shear viscosity function versus the shear rate or the shear stress.

cometers with a concentrically turning cylinder in a cylindrical cup filled with the coating material to be measured.

Other widely used instruments for paint and coating materials are the cone and plate rheometers; this technique provides a detailed picture of the flow properties of liquids. Various rheometers have been designed in which either the plate remains stationary while the cone rotates above it, thus shearing the sample, or the cone remains stationary while the plate rotates. A major advantage of the cone-and-plate rheometers is that they allow the shear rate to be kept constant throughout the sample during the measurement. Only small amounts of sample are required.

Table 3.0-2 lists some more expressions dealing with rheology (DIN 1342).

## 3.1 Inorganic Thickeners

*Johan Bieleman*

### 3.1.1 Introduction

Organoclays, organically modified laminar silicates, are the most widely used inorganic thickeners and have found many applications in the paint- and coatings industry. Well-known laminar or phyllosilicates are hectorite and bentonite. Other important silica thickeners are the synthetic amorphous silicates.

In this chapter, typical properties and applications of organoclays (also known as “organophilic clays”) will be dealt with in detail.<sup>[3-5]</sup>

### 3.1.2 Organoclays

Nature has many mineral substances which have the ability to swell in water and can be turned into masses that are easily formed into shapes. Clays are a good example of such minerals. They give a heavy structure to loamy earth, and has been used for millenniums by mankind as raw material for the production of ceramic objects. In the mid-thirties of this century it was discovered that within this wide-branched family, there is a group of minerals, the so-called smectites, that are capable of forming gel-like structures when exposed to sufficient shear forces within a suitable pH-range.

The smectites have been analysed very intensively by X-ray diffraction spectroscopy, and they were found to generally have the morphological structure shown in Fig. 3.1-1. They are composed of silicates made up of layers of trimorphic (3-layered) sheets. The middle layer consisting of  $Al_2O_3$  octahedra is surrounded on both sides with  $SiO_2$  tetrahedra. These elementary modules are in turn stacked

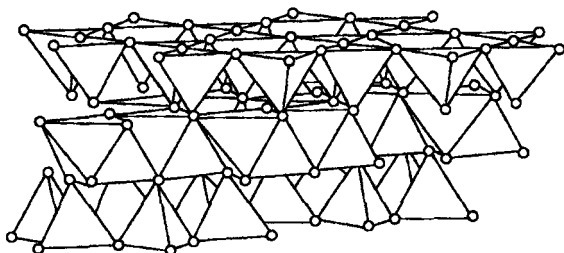


Figure 3.1-1. Smectite structure

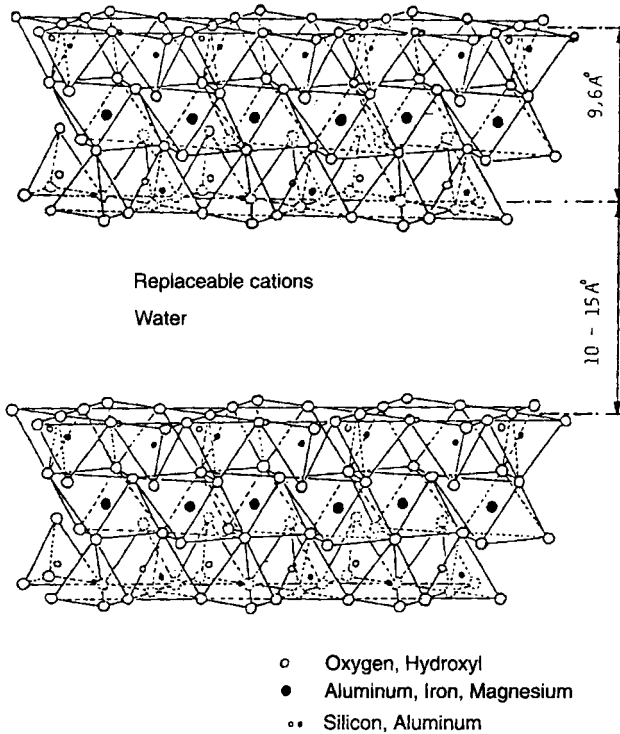


Figure 3.1-2. Smectite layers

as plates one above the other, like cards in a stack of playing cards (Fig. 3.1-2). The distance between two neighbouring layers is approximately 10–15 Å. The thickness of such an elementary layer has been measured to be 9.6 Å.

The smectite octahedral layers are not all constructed similarly, in contrast to other laminar silicates. The central, positively charged metal ion has partly been replaced in an isomorphous way by another ion of lower valency. This confers a negative charge on the entire crystal lattice, compensated for by absorbed cations on the basal surfaces (Fig. 3.1-3).

Two smectites, montmorillonite and hectorite, have found extremely important practical applications.

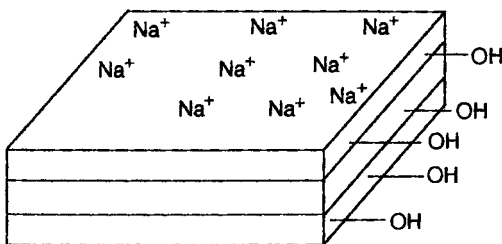
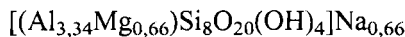


Figure 3.1-3. Elementary layers of a smectite

Montmorillonite is an aluminium laminar silicate with the following theoretical composition:



In the central aluminium oxide octahedral layers, every sixth  $Al^{3+}$  ion is isomorphously replaced by a  $Mg^{2+}$  ion. The negative lattice charge is compensated by  $Na^+$  ions on the basal surfaces. The montmorillonites in nature contain, apart from  $Na^+$  ions, often  $Ca^{2+}$  ions or mixtures of both as well. It is practically impossible to find pure montmorillonite, as it is almost always mixed with other minerals. Laminar silicates with a very high content of montmorillonite are the well-known bentonites. Deposits of it are found on many places on earth.

Hectorite is a magnesium laminar silicate with the following theoretical composition:<sup>[3-6, 3-7]</sup>



In the magnesium oxide octahedral layer, every ninth  $Mg^{2+}$  ion is isomorphously replaced by a  $Li^+$  ion. The charge compensation essentially occurs by  $Na^+$  ions on the two faces of the platelet. Worldwide there is only one single workable deposit of hectorite, close to the city Hector in California, U.S.A. The dimensions of the montmorillonite (bentonite) primary platelets were found by electron microscopy to be:

0.8  $\mu m$  length  
0.8  $\mu m$  width  
0.001  $\mu m$  thickness

The hectorite primary platelet dimensions are:

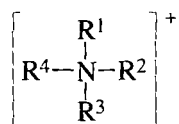
0.8  $\mu m$  length  
0.08  $\mu m$  width  
0.001  $\mu m$  thickness

Hectorites are, because of their low iron content, generally whiter than bentonites, but bentonites can be treated more easily.

A significant factor in the development of applications for smectites has been the fact that the cations absorbed on the plate surfaces can be readily replaced by other cations.<sup>[3-8, 3-9]</sup> It is also possible to replace the metal cations with organic cations, a method that can be used to transform a hydrophilic smectite into a hydrophobic one. These substances form gel-like structures under specific conditions in organic-solvent-based systems.

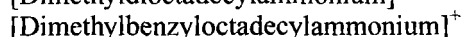
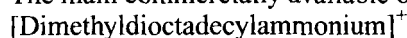
The ion-exchange capacity of smectites is 80–150 milliequivalent per 100 g laminar silicate. There is 80  $\text{\AA}^2$  basal surface area available per replaceable cation. Although this subject has been studied very intensively and has led to the publication of about a hundred articles so far, only a very small number of organic com-

pounds have found technical application in practice. Only the quaternary ammonium compounds gained special importance:



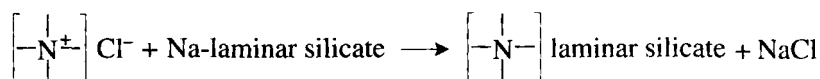
At least one of the four ligands has to be a long-chained alkyl group with a minimum length of 12 C atoms.

The main commercially available organoclays contain the following cations:



By replacing  $\text{R}^1 - \text{R}^4$  with special groups or by further modification of the ion-exchange reaction, different characteristics of the organoclays – such as compatibility with aromatic or highly polar solvents, the dispersability in organic systems – can be influenced and controlled considerably.

The ion-exchange reaction takes place as follows:



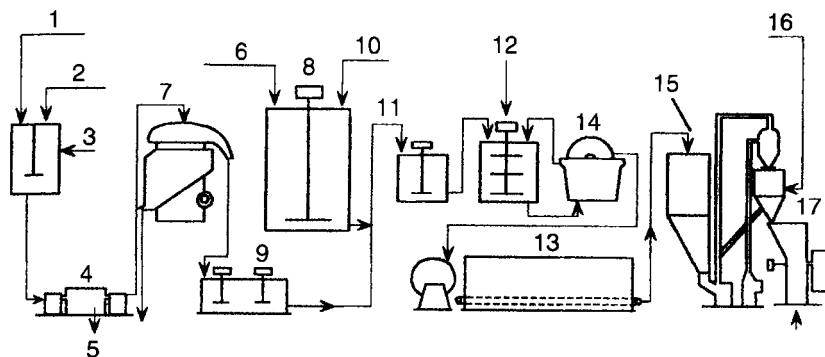
For bentonite and hectorite it takes 24 hours for the reaction to proceed quantitatively.

X-ray structure analysis of organoclays have shown the slice distance to be 17–25 Å. The alkyl groups are placed parallel to the surface where partly, because of steric reasons, overlapping occurs.

### 3.1.3 Production of the Organoclays

The natural laminar silicates are unsuitable because of their impurity and organophobic nature. Only after highly sophisticated purification steps and reaction with specific organic compounds is the silicate suitable for use in organic systems.

To explain the working mechanism of organoclays, the general production process first needs to be described briefly (Fig. 3.1-4). The process starts with the raw material smectite, which has to be released from all mineral impurities as far as possible. For this it is dispersed in warm water and the suspension is centrifuged intensively.<sup>[3-9]</sup> After this, the purified suspension is fed into the reaction tank. After determination of the solids, the quantity of quaternary ammonium chloride necessary for ion exchange can be calculated. This amount is added slowly to the suspension with constant stirring, which continues until the end of the ion exchange. The resultant organoclay suspension is subsequently filtered off. A careful wash process



**Figure 3.1-4.** Production scheme for organoclays

1 Water	6 Quaternary ammonium compound	10 Water	14 Filter
2 Smectite	7 Centrifuge	11 Reaction tank	15 Grinder
3 Vapor	8 Dispersion tank	12 Rough filter	16 Air separator
4 Centrifuge	9 Mixer	13 Drier	17 Packing
5 Residues			

takes place simultaneously with this step, to quantitatively remove the NaCl formed during the reaction. The filtrate paste is then dried. Finally, grinding takes place, and the organoclay is ready to be offered commercially, usually in powder form.

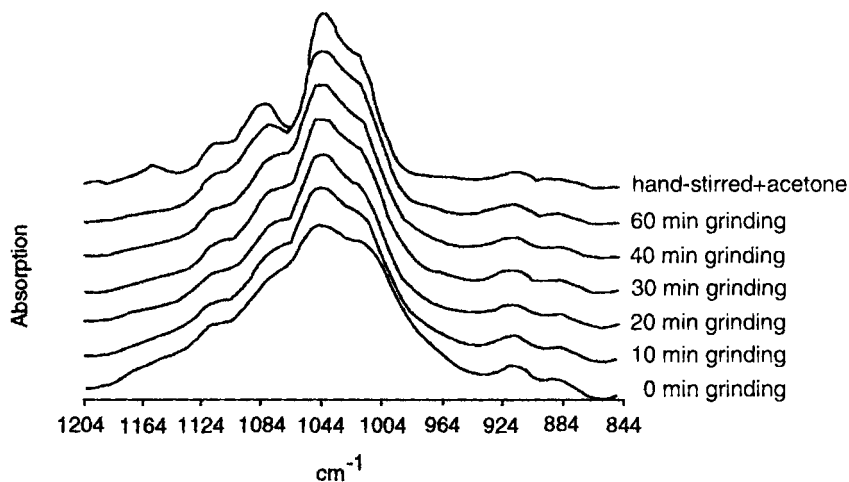
### 3.1.4 Rheology and Organoclays

The commercially offered organoclay powder is composed of stacks of agglomerated platelets. Only 1 g of such an organoclay contains  $10^{16}$ – $10^{18}$  silicate platelets. This large number of platelets indicates that one only needs to add a small amount of organoclay to an organic solvent system in order to form a rheological structure. However, such a structure only forms if the organoclay is separated into its elementary platelets, and these platelets link to each other into a reversible, house-of-cards-like structure.

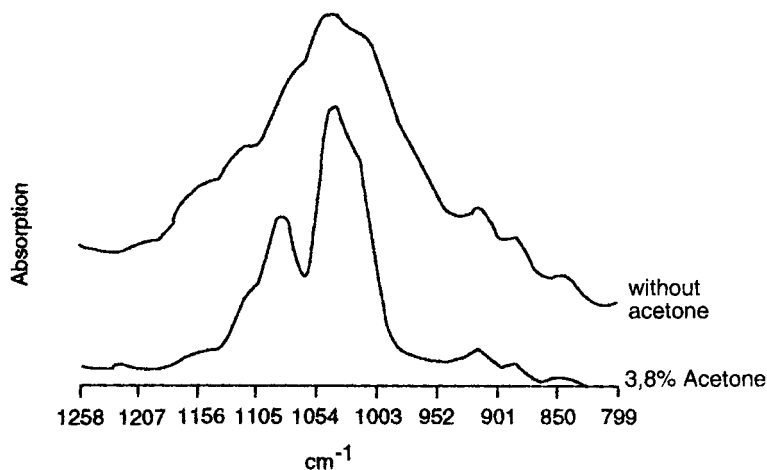
X-ray diffraction spectroscopy and infrared spectroscopy are suitable for examining the dispersing process of an organoclay. A 10% suspension of an organoclay in mineral oil is used to model this process. The silicate IR bands of the Si–O–Si valency vibrations are observed at  $1040\text{ cm}^{-1}$  (Fig. 3.1-5).

If the model suspension system is stirred only manually (weak dispersion forces), a relatively broad band appears (Fig. 3.1-5). More intensive dispersing results in narrower bands. When 3.8% acetone is added to the hand-stirred system an even greater narrowing occurs.

The biggest narrowing occurs if the system is dispersed intensively after adding acetone (Fig. 3.1-6). This change in the width of the silicate band is due to the inter-



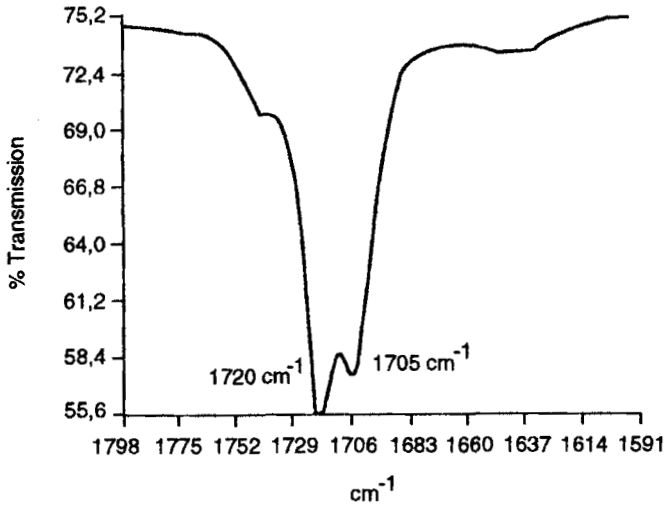
**Figure 3.1-5.** IR spectrum of the Si–O–Si valency vibration sectors of hand-stirred and ground 10% organoclay suspension in a mineral oil system



**Figure 3.1-6.** IR spectrum of the Si–O–Si valency vibration area of a dispersed 10% organoclay/mineral oil system with and without the addition of acetone

connection of the stacked platelets which results in strongly communicated molecule movements between neighbouring platelets to give a wide vibrating conveyor. That is why increasing distance between neighbouring platelets leads to the isolation of Si–O–Si valency vibrations and therefore to a decrease in band width.

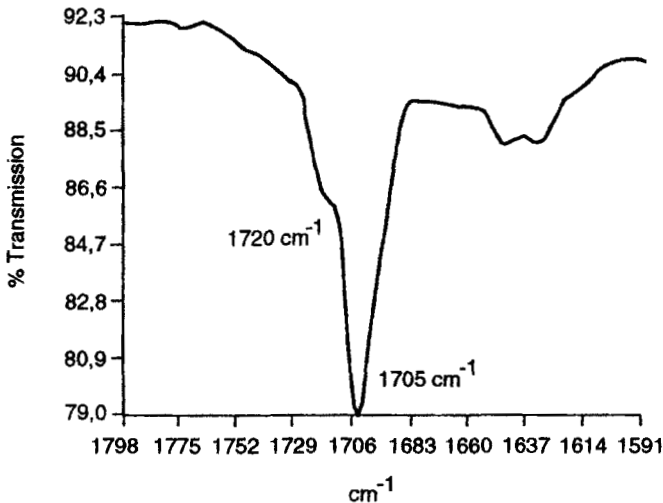
With complete dispersal, the band would have to break down to monochromatic Si–O–Si valency vibrations. A narrower band at  $1040\text{ cm}^{-1}$  indicates larger slice distances and better dispersion.



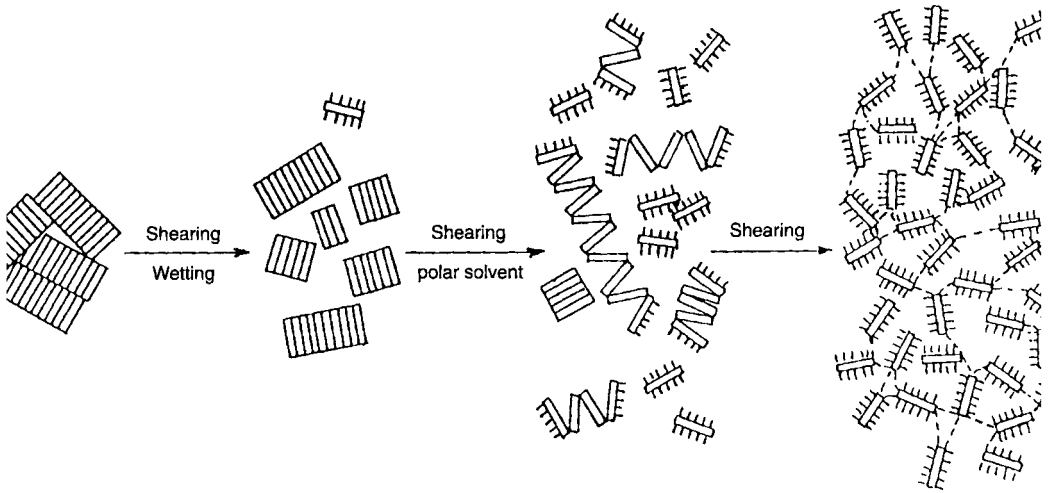
**Figure 3.1-7.** IR spectrum of the C=O valency vibration area after the addition of 3.8% acetone to a hand-stirred 10% organoclay/mineral oil suspension

The effect of acetone on the model substance can be followed by IR spectroscopy. The spectrum shown in Fig. 3.1-7 shows the addition of 3.8% acetone to the hand-stirred organoclay/mineral oil system. The band at 1720 cm<sup>-1</sup> corresponds to “free” acetone, i. e., acetone diluted in mineral oil, whereas the band at 1705 cm<sup>-1</sup> corresponds to the acetone connected to the organoclay.

Intensive dispersing leads to the spectrum shown in Fig. 3.1-8. Apparently all the acetone is connected to the organoclay.

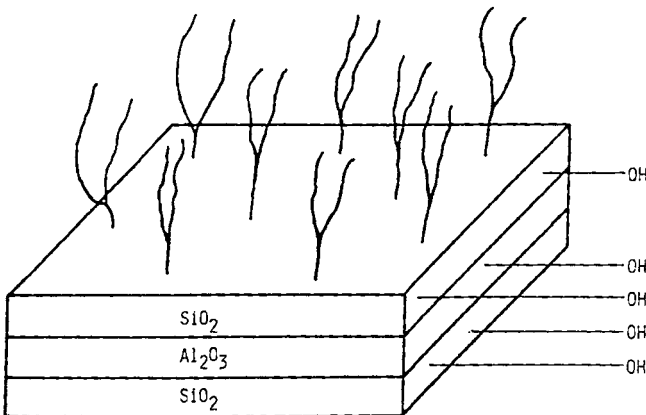


**Figure 3.1-8.** IR spectrum of an intensively dispersed 10% organoclay/mineral oil system with 3% acetone



**Figure 3.1-9.** The gelation process of a conventional organophilic laminar silicate

The dispersion of an organoclay may be described as follows (Fig. 3.1-9). When a strong shear force is applied, the agglomerated platelet stacks come apart first. The addition of a polar solvent leads to an increase in distance between the slices within the stacks, the Van der Waals forces of attraction is reduced and the stacks break up into the elementary slices when further shear force is used. Solvation of the organic cations on the planar surfaces takes place at the same time. Fig. 3.1-10 shows the condition of a totally activated organoclay platelet. Methyl alcohol, ethyl alcohol, propylene carbonate, and acetone are used for this purpose in practice. Finally, edge-to-edge hydrogen bonding between the hydroxyl groups on the organoclay platelet edges produces a three-dimensional lattice structure (Fig. 3.1-11). This structure is reversible. It breaks down readily in the presence of low-shear forces and can be regenerated in the rest state. This process explains the mechanism of thickening of organoclays.



**Figure 3.1-10.** Activated organolaminar silicate slice

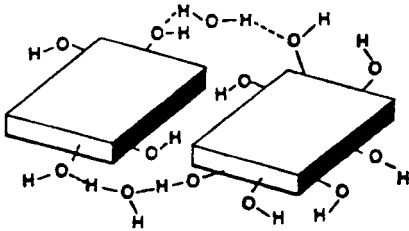


Figure 3.1-11. Hydrogen bondings

By dispersing an organoclay in a paint, the viscosity increases by the formation of this structure. The crucial operative mechanism of an organoclay is not the viscosity increasing effect, but the reversibility of the three-dimensional network. Because of this thixotropic as well as pseudoplastic flow behaviour (see Section 3.0.2) becomes possible, depending on how fast the starting condition is recovered.

### 3.1.5 Influence of Organoclays on Various Coating Properties

Rheological processes are important during production, storage, and application of coating materials; see Fig. 3.1-12 for the relation between shear rate and various coating properties and procedures (also refer to Section 3.0.2).

During the production of coating materials (for example by dispersing pigments with fast-running stirrers, sand mills, etc.) the shear rates vary between approxi-

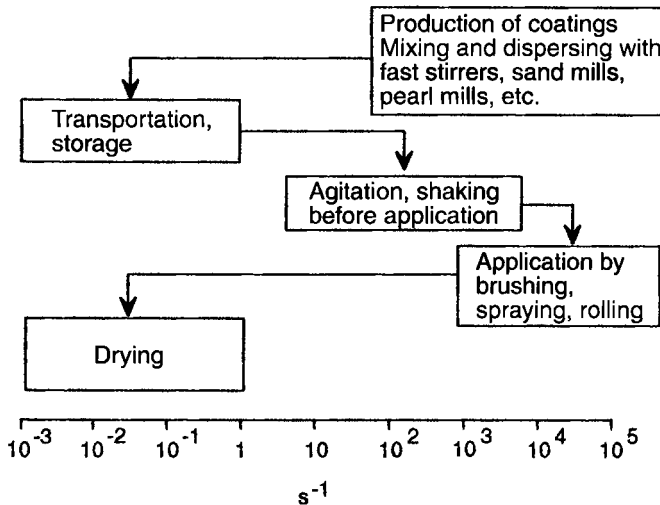


Figure 3.1-12. Shear rates during production and application of coatings

mately  $10^2$ – $10^5$   $s^{-1}$ . During storage and transportation of the end product the relevant shear rate is quite low, below  $1$   $s^{-1}$ . Mixing and homogenizing just before the application of the paint are effected at  $10$ – $10^2$   $s^{-1}$ . The application by spraying, rolling, or brushing requires shear rates of  $10^3$ – $10^5$   $s^{-1}$ . During the drying stage that follows this value is below  $1$   $s^{-1}$ .

With high shear rates the rheological behaviour of solvent-borne coatings is largely determined by the main components, notably the binder, solvent, pigments, and extenders as well as their interactions. The effect of the organoclay only operates at low shear rates, i. e., below approximately  $100$   $s^{-1}$  to mainly influence properties such as:

- sedimentation of pigments and extenders
- sagging
- flow and levelling

### 3.1.5.1 Sedimentation

The following forces act on a spherical particle of density  $\rho$  in a liquid of density  $\rho_1$  during its dispersal:

$$\text{gravitational force } F_g = 4/3 (r^3 \pi \rho g) \quad (1)$$

$$\text{aerodynamic force } F_a = 4/3 (r^3 \pi \sigma_1 g) \quad (2)$$

$$\text{flow resistance (Stoke's law): } F_v = 6 \pi \eta v r \quad (3)$$

For the stationary condition:

$$F_v = F_g - F_a \quad (4)$$

and the sedimentation velocity is expressed as:

$$v = 222 r^2 (\rho - \rho_1) / \eta \text{ [cm s}^{-1}\text{]} \quad (5)$$

where:

$\eta$  Viscosity

$\rho$  Density of the sphere

$\rho_1$  Density of the liquid

$v$  Velocity of the sphere

$r$  Spherical radius

$g$  Gravitational constant, acceleration due to gravity

Boundary layers and interactions between the particles which at the most reduce the sedimentation velocity strongly, are not considered. The sedimentation velocity is inversely proportional to the viscosity. To reduce the sedimentation of pigments, the viscosity at low shear rate must be made as high as possible.

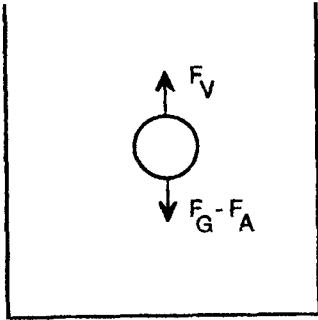


Figure 3.1-13. Sedimentation

3.1.5.2 Sagging

If a vertical substrate has been painted with a coating of thickness  $X$ , then, at position  $x$  ( $0 < x < X$ ) the shear stress  $\tau_x = \rho x g$ , and the shear rate  $D_x = dv_x/dx$ , if the film flows under the influence of gravity with velocity  $x$ . Therefore:

$$\eta = \frac{\tau_x}{D_x} = \frac{\rho x g}{\frac{dv_x}{dx}} \tag{6}$$

or

$$dv_x = \frac{\rho x g}{\eta} dx \tag{7}$$

$$v_x = \int_0^x \frac{\rho x g}{\eta} dx = \frac{\rho g}{2 \eta} X^2 \tag{8}$$

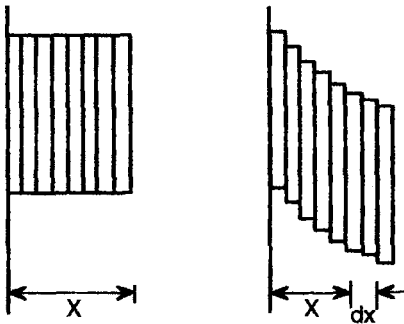


Figure 3.1-14. Sagging

The sagged volume  $V_a$  is calculated as:

$$\frac{dV_a}{dt} = \int_0^X x dv_x = \int_0^X \frac{\rho g}{\eta} x^2 dx = \frac{\rho g}{3 \eta} X^3 \quad (9)$$

$$V_a = \frac{\rho g}{3 \eta} X^3 t \quad (10)$$

Therefore the velocity of sagging is proportional to the square of the film thickness and is inversely proportional to the viscosity. To reduce sagging, the viscosity of the coating layer at low shear velocities must be increased.

### 3.1.5.3 Flow and Levelling

Assuming that there are parallel highs and lows on the wave that represents the surface that results from the application of a paint, where the average film thickness is  $X$ , the wave amplitude is  $A_0$ , and the wavelength is  $\lambda$ . Under the influence of the surface tension  $\gamma$  the film surface flattens. Therefore, for amplitude  $A_t$  at time  $t$ :

$$\log \frac{A_a}{A_t} = 226 \frac{\gamma X^3}{\lambda^4} \int_0^X \frac{dt}{\eta} \quad (11)$$

Therefore, the lower the viscosity of the paint at low shear rate, the better the flow and levelling! That implies that the sedimentation of pigments in a coating system, the sagging tendency when applied onto vertical surfaces, and the flow and levelling properties of the coating surface are opposite characteristics with regards to rheology.

When formulating coatings and controlling their rheological properties with organoclay it is therefore always necessary to find the best compromise between the effects on the various coating properties.

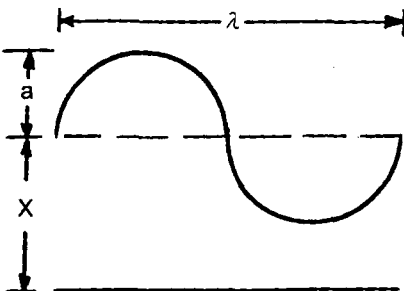


Figure 3.1-15. Flow and levelling

### 3.1.6 Incorporation Procedures

Various methods may be considered for the incorporation of organoclays into a coating materials. However, the two basic methods are the powder method and the paste method.

#### 3.1.6.1 Powder Method

For this, the dry organoclay powder is dispersed in the system together with the pigment. Variations in the order of addition are possible, depending on the available quantity and quality of solvents/binders in the formulation as well as the wetting properties of the binders and the dispersing equipment used. A polar solvent has to be added during the dispersing phase.

#### 3.1.6.2 Paste Method

With this method a master batch paste of the organoclay is produced first of all, e. g., as follows:

- solvent: 90.0 parts by weight
- organoclay: 7.5 parts by weight
- dispersed over 5 min with a high-speed dissolver
  
- polar solvent: 2.5 parts by weight
- dispersed for another 5 min

The quantity of organoclay within the paste may vary but it should not exceed 10% as more concentrated pastes are difficult to work with and a good predispersion of the organoclay can then usually not be ensured.

The master-batch paste is added to the milling paste or during the let-down procedure of the coating manufacture. It is possible to vary the time of adding, depending on the wetting properties of the binders and dispersing equipment used. However, it is important that the master-batch paste is subjected to an intensive shear load when it is worked into the coating system, if its full effectiveness is to be realized.

#### 3.1.6.3 Easily Dispersable Organoclays

The use of easily dispersable grades of organoclays allows incorporation of dry powders straight into the final system. In contrast to the conventional organoclays, these “easily dispersable” grades may be post-added under turbulent mixing conditions. Addition of a polar solvent is not necessary for these grades.

### **3.1.7 Trade Products**

Bentone (Elementis/Rheox Inc.)

Tixogel (Süd-Chemie GmbH)

## 3.2 Organic Thickeners

*Gijsbert Kroon*

### 3.2.0 Introduction

Organic thickeners are used in paint systems to achieve particular rheological properties such as the shear-rate-dependent behaviour, to control the viscosity at low and high shear rates, sag resistance, and application viscosity. It is also possible to give the paint system a yield point or a time-dependent rheology by choosing the right thickener. Organic thickeners are used in both solvent-based and water-borne paint systems.

#### 3.2.0.1 Organic Thickeners for Water-Borne Paints

For water-borne paints, different types of thickeners are distinguished on the basis of the manner in which they thicken the paint. There are products that only thicken the aqueous phase and there are associative thickeners that give the paint its viscosity by interacting with other paint ingredients.

##### Water-Phase Thickeners

Among the group of products that only thicken the aqueous phase, cellulose ethers are the ones most commonly used. It is, however, possible to distinguish the following groups of products:

- cellulose derivatives
- starch derivatives
- acrylic thickeners

Various starch-based products are used in very highly pigmented cheap paints to replace both the binder and the thickener. These are paints with a pigment-volume concentration of more than 85%. The use of these types of paint systems has decreased significantly over the past few decades.

Acrylic thickeners are also used to a limited extent in wall paints, particularly for interior use. The advantage of these products is the fact that they are available in liquid form as an emulsion. The drawback is that their thickening action is a function of the pH of the paint system. When the pH of the paint varies, it will also cause the viscosity of the paint to vary.

For decorative emulsion paints, the most commonly used thickeners are the cellulose derivatives. The most widely used of these are hydroxyethyl cellulose, ethylhydroxy-

ethyl cellulose, methylhydroxyethyl cellulose, methylhydroxypropyl cellulose, and carboxymethyl cellulose. These products are discussed in detail in Section 3.2.1.

The advantage of products that only thicken the paint through the aqueous phase is the fact that they operate independently of the system and that the rheological behaviour of the paint is predictable. The products thicken the aqueous phase in two stages. The water is bonded through the formation of hydrogen bonds; a process that produces only a slight increase in viscosity. Raising the concentration results in overlapping of the polymer chains and an enormous increase in viscosity to produce the final viscosity of the paint. A paint system behaves like a viscoelastic material and thus exhibits the properties of a liquid, but it also partially acts as an elastic material. The drawback of such a thickening mechanism is the fact that the elastic component is so high that the degree of flow of the paint is insufficient for the thickeners to be used in high-gloss paints that are to be applied by brush. In addition, high-molecular-weight thickeners can also contribute to the flocculation of pigment and binder particles if the pigment or binder is insufficiently stable. This will then lead to a reduction in film gloss in the case of high-gloss paints and increased sensitivity to water of the final coating. These problems have been the reason for the development of associative thickeners.

### Associative Thickeners

Associative thickeners are organic thickeners that, although they are somewhat soluble in water, thicken the paint through their interaction with other paint components. It is assumed that these interactions are based on hydrophobic forces. Such an operating mechanism is schematically represented in Fig. 3.2-1.

Within the group of associative thickeners, three product groups can be distinguished:

- hydrophobically modified polyoxyethylenes
- associative acrylic thickeners
- associative cellulose ethers

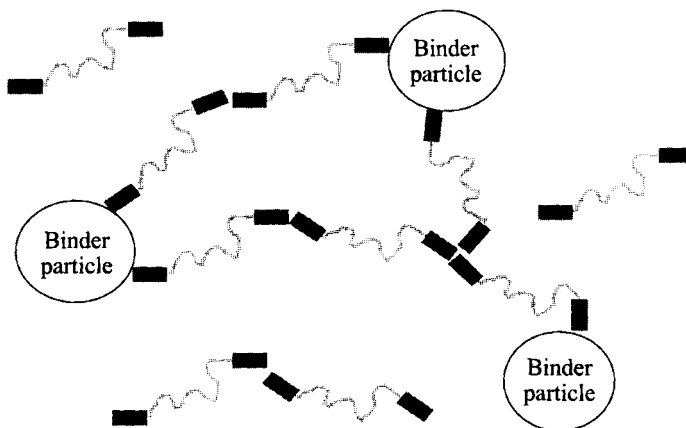


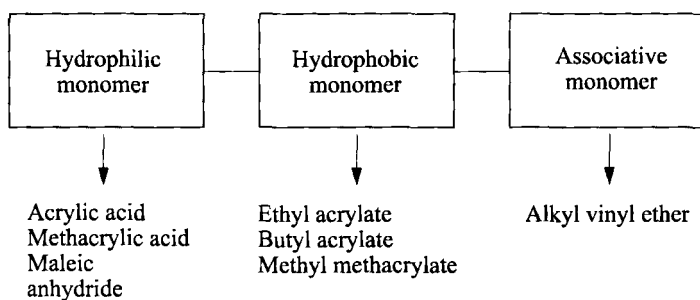
Figure 3.2-1. The operating mechanism of associative thickeners

### *Hydrophobically Modified Polyethylene Oxide*

These products are more commonly known as polyurethane thickeners or as hydrophobically modified ethoxylated urethanes (HEUR). They are, however, based on polyoxyethylene, onto which hydrophobic groups are chemically bonded in a number of ways. In polyurethane thickeners this is achieved through reaction with polyisocyanates, but it is also possible through reaction with, for instance, alkyl halides or epoxides. Although the linkage of the hydrophobic groups onto the polyethylene oxide base polymer can vary, this has hardly any influence on the behaviour of these products in the final paint. These products will be further covered in detail in Section 3.2.2.

### *Associative Acrylic Thickeners*

Associative acrylic thickeners are known as hydrophobically modified alkali-swelable emulsions (HASE). They are made up chemically of three blocks, as represented in Fig. 3.2-2.



**Figure 3.2-2.** Structural building blocks of associative acrylic thickeners

To ensure solubility in water or alkali, a hydrophilic monomer such as acrylic acid is included in the synthesis. To obtain the correct balance between water-sensitivity and water-tolerance, a hydrophobic monomer such as ethyl acrylate is used as comonomer. This monomer does not, however, contribute to the associative behaviour of these products. To influence the associative behaviour, a third, stronger hydrophobic group is required. For this reason a third monomer is included, for instance, an alkyl vinyl ether with an alkyl group containing at least eight carbon atoms. The solubility in water can be further limited through cross-linking of the polymer. The final product is a watery emulsion with a milky-white colour. These acrylic thickeners only dissolve within a pH range of 8 to 10. Outside this pH range their viscosity decreases, and thus also their thickening action. This is one of the drawbacks of these materials. Another drawback is their anionic nature in an alkaline environment. This entails an increased water-sensitivity, which means that these products are not really suitable for paints intended for outdoor use, although this can be corrected by adjusting the paint formula.

### *Associative Cellulose Ethers*

In addition to the traditional cellulose ethers, associative cellulose ethers are also used in the paint industry. Their primary function is to increase the spatter resistance and covering ability of the paint. These products are made of hydroxyethyl cellulose and ethylhydroxyethyl cellulose, with the base polymer modified with hydrophobic groups. The hydrophobic groups are able to interact with other paint components. A detailed description of these products is given in Section 3.2.1.

### **3.2.0.2 Thickeners for Solvent-Based Paints**

In solvent-based paints, the viscosity is largely determined by the binder itself and thickeners are used to produce thixotropy and to counteract the sedimentation of the pigments. Certain thickeners also produce an increase in viscosity and a more pseudoplastic rheology.

These thickeners will be described in detail in Section 3.2.3. As an introduction, the various product groups and their mode of action will be described briefly.

Castor-oil-based products require a certain degree of dispersion and an increase in temperature to be activated and to induce the right properties in the paint. They operate on the basis of a gelling mechanism. Metal soaps such as aluminium stearate are easier to handle because they only require some shear and can be readily added to the paint during dispersion. These metal soaps also cause the solvent to gel and thus produce the viscosity. There are, however, also products that thicken the paint in other ways than through gelling. This may be through the controlled flocculation of pigments or through the formation of hydrogen bonds with the polar groups of the binder. The latter group of products often includes polymerized petroleum derivatives.

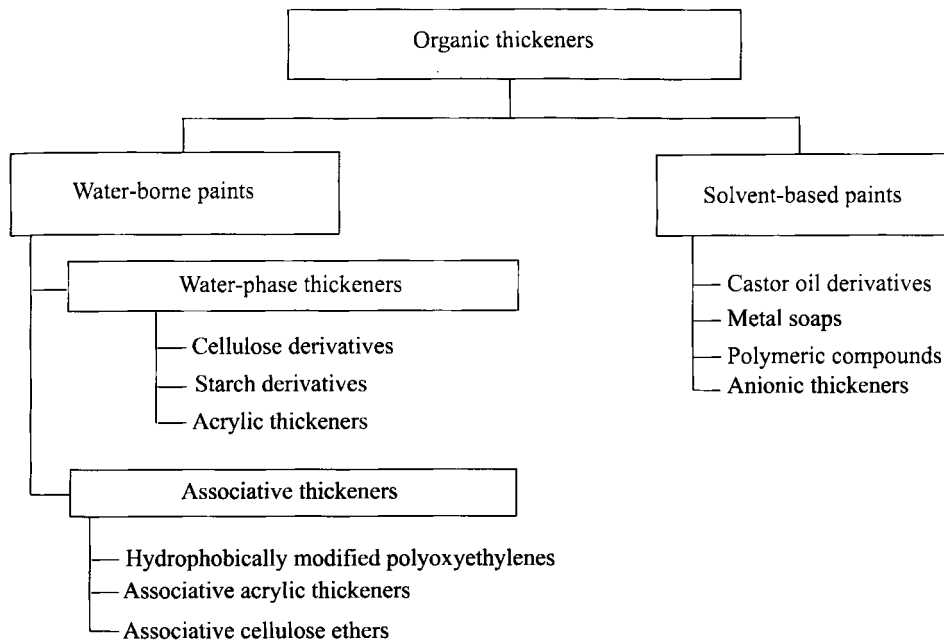
The organic thickeners can be summarized schematically as shown in Fig. 3.2-3.

The main functions of thickeners in paint systems can be summarized by three key terms:

1. Stability
2. Solvent retention
3. Rheology

In Sections 3.2.1 to 3.2.3 these specific aspects will be considered in detail for the various products.

For literature references, refer to Sections 3.2.1 to 3.2.3 in which the various products are described individually.



**Figure 3.2-3.** Thickeners

### 3.2.1 Cellulose Derivatives

*Gijsbert Kroon*

Cellulose ethers have been used as thickeners for latex paints for many decades.<sup>[3-10]</sup> Worldwide, some 35 000 tons, a considerable volume, of non-ionic cellulose ethers are used each year as thickeners in latex paints. In this section both the traditional cellulose ethers and the associative cellulose ethers used in latex paints will be considered. The following aspects will be covered:

- 3.2.1.1 The Chemistry of Cellulose Derivatives
- 3.2.1.2 The Addition of Cellulose Ethers to Paints
- 3.2.1.3 Paint Properties Influenced by Cellulose Ethers
- 3.2.1.4 Associative Cellulose Ethers
- 3.2.1.5 Commercial Products
- 3.2.1.6 New Developments
- 3.2.1.7 Toxicology and Disposal

### 3.2.1.1 The Chemistry of Cellulose Derivatives

The basic material from which cellulose derivatives are made, is cellulose.<sup>[3-11-3-15]</sup> Cellulose is a polysaccharide and is made up of so-called anhydroglucose units that are linked together by  $\beta$ -1,4'-glycosidic linkages (Fig. 3.2-4).

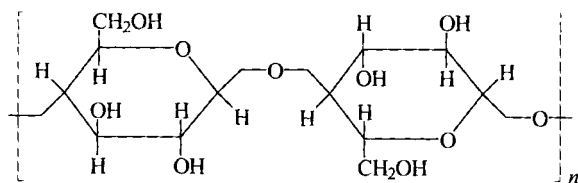


Figure 3.2-4. Structure of cellulose

Both the origin of the cellulose and the method(s) used to purify it influence the quality and physical properties of the cellulose ether produced from it. The most important sources of cellulose are cotton linters and wood (pulp). Cotton linters contain approximately 90% cellulose, while the purity of wood pulp is only 50%. Cotton linters have a much higher average degree of polymerization than wood pulp and they are therefore the most important source for the production of the higher-molecular-weight cellulose ethers.

Each anhydroglucose unit contains three functional hydroxyl groups suitable for chemical modification.

Modification of cellulose is usually achieved through esterification or etherification and is a relatively complex process. Although the reactivity of the hydroxyl groups is comparable to that of the lower aliphatic alcohols, it is nevertheless quite difficult to make the reactions proceed. This is due to the crystalline nature of cellulose. The polymer chains are highly ordered (Fig. 3.2-5) because of the formation of hydrogen

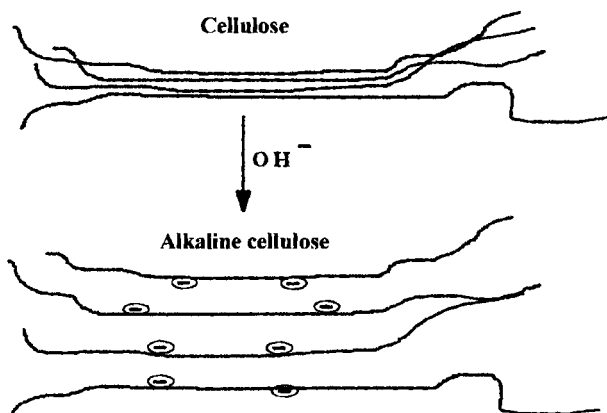


Figure 3.2-5. Modifying cellulose

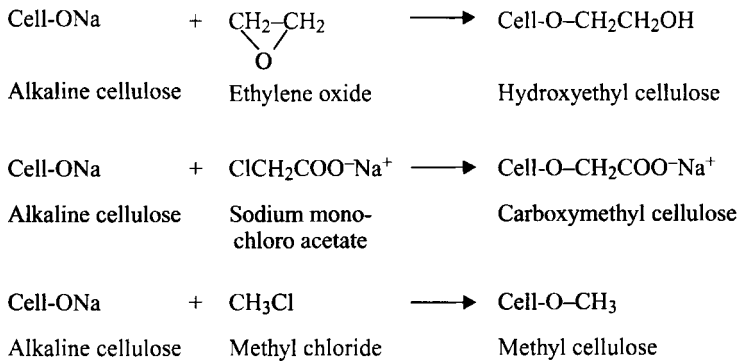
bonds between adjacent chains. By treating cellulose with sodium hydroxide a negative, repulsive charge is produced on the chain. This breaks down the crystallinity of the polymer, thus making the hydroxyl groups accessible to reagents.

With sodium hydroxide the hydroxyl groups are converted into the even more reactive alkoxide ions. This reactive cellulose is called alkaline cellulose, the production of which is one of the secrets of making good products.

Esterification can proceed by the Williamson synthesis, involving reaction with an alkyl halide, or by epoxidation.

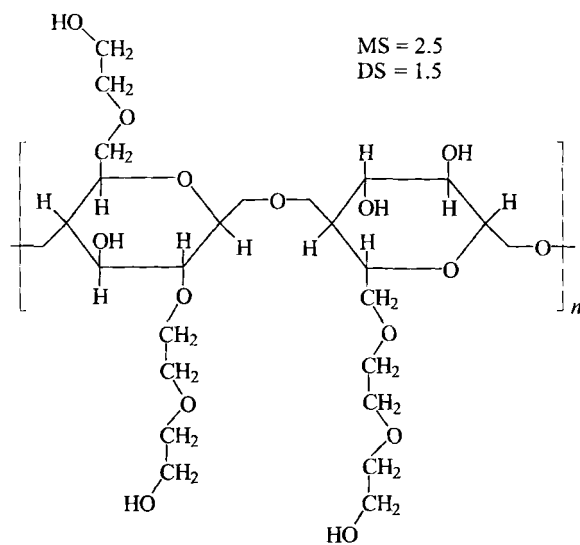
The more important reactions for paint applications are summarized in Fig. 3.2-6.

The reaction of alkaline cellulose with ethylene oxide produces hydroxyethyl cellulose, while with monochloroacetic acid, carboxymethyl cellulose is formed. Methyl cellulose is obtained through the reaction of cellulose with methyl chloride in the presence of sodium hydroxide. It is usually not methyl cellulose that is used as a thickener, but rather the mixed ethers methylhydroxyethyl cellulose and methylhydroxypropyl cellulose. To characterize these products it is not sufficient to know which substituent the material contains, it is also necessary to know how much substituent is bonded onto the polymer.<sup>[3-15-3-17]</sup> For this purpose, two definitions were introduced. The degree of substitution (DS) is defined as the average number of hydroxyl groups substituted per anhydroglucose unit. The molar degree of substitution (MS) is defined as the average number of moles of substituent per anhydroglucose unit.



**Figure 3.2-6.** Examples of cellulose-derivative synthesis

For methyl cellulose and carboxymethyl cellulose the DS by itself is sufficient for characterizing the material. For hydroxyethyl cellulose this is, however, not the case. The reason for this is that after reacting with ethylene oxide, the substituent again contains a hydroxyl group capable of further reaction, so that it is possible to have more than one substituent per hydroxyl group after reaction. This is evident from the structural formula for hydroxyethyl cellulose (HEC), shown in Fig. 3.2-7. In terms of the definitions given above, the molar degree of substitution is 2.5 and the degree of substitution is 1.5.



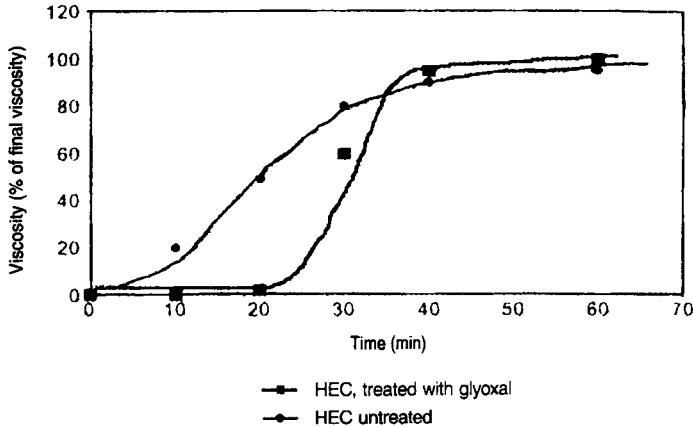
**Figure 3.2-7.** Structure of hydroxyethyl cellulose

### 3.2.1.2 The Addition of Cellulose Ethers to Paints

The thickener can be added at various stages of the production process.<sup>[3-18, 3-19]</sup> The most commonly used method is to add the product in the pre-mix stage for the grinding of the pigment and the fillers. Cellulose ethers are usually sold in powder form. Most of the water-soluble polymers have a tendency to agglomerate while going into solution if they have been added to the aqueous phase without sufficient care. The outer layer of the polymer particle swells up into a gel, which makes it difficult for the interior parts to dissolve. The time required for the product to dissolve depends on the degree of agglomeration. It is important that the particles should first be well dispersed throughout the aqueous phase before going into solution. For this reason most of the cellulose ethers used in paints are treated with glyoxal. This causes a temporary netting of the polymer, which ensures that the material has sufficient time to disperse itself throughout the aqueous phase before dissolving. The hydration time can be adjusted by varying the quantity of glyoxal added to the product. The process of netting using glyoxal avoids the formation of lump, while the hydration time also depends on the temperature and the pH of the system. The effect that treatment with glyoxal has on the solution behaviour of cellulose ethers is shown in Fig. 3.2-8.

The cellulose ether can be added in the form of a powder, a polymer solution, or as a suspension. The polymer solution can be added without problems during any stage of the production process. In the case of a bulk solution it is important to add a preservative.

The cellulose ether can also be added in the form of a suspension in organic solvents such as glycols and coalescing agents. The advantage of using a suspension is that the cellulose ether can be used in a higher concentration than would be the



**Figure 3.2-8.** Influence of glyoxal on the solution behaviour of cellulose ethers

case for a polymer solution. This means that there is more free water available for the paint formula. It is even possible, and a commonly used method, to suspend glyoxal-treated cellulose ethers in water before it is added to the paint. Addition in the form of a powder is mainly used in the grinding stage. After the thickener has been added, the pH of the pre-mix is often raised in order to shorten the time required for it to go into solution. Adding the cellulose ether in the form of a powder at the end of the paint production process is not recommended. The quantity of thickener to be added depends on the desired viscosity of the final product, the paint.

In cheaper types of ceiling paint, carboxymethyl cellulose is used as a thickener and binder and the amount added can be up to 3 wt %. In wall paints with a pigment volume concentration of 30–80%, the amount of cellulose ether used is approximately 0.3–0.6 wt %. To illustrate this, two recipes are given: the first is for a matt interior wall paint (Table 3.2-1) containing a styrene acrylate binder, and the second is for a solvent-free matt interior wall paint including a vinyl acetate/ethylene copolymer (Table 3.2-2).

In silicate paints the amount used is much lower, approximately 0.1–0.3 wt %. In these paint systems only the more hydrophilic cellulose ethers can be used, such as hydroxyethyl cellulose, hydrophobically modified hydroxyethyl cellulose, and carboxymethyl cellulose. Because of their high electrolyte content, ethylhydroxyethyl cellulose and the methyl cellulose derivatives are not sufficiently soluble in such systems.

### 3.2.1.3 Paint Properties Influenced by Cellulose Ethers

Cellulose ethers provides the paint with three basic properties: viscosity, stability, and water retention.<sup>[3-16, 3-18–3-22]</sup> The thickener is important during all stages of the processing and use of the paint, including production, storage, and application.

**Table 3.2-1.** Formula for an interior wall paint (PVC 80%) based on a styrene acrylate binder with 0.4 wt % medium-viscosity cellulose ether

	Parts by weight
Water	140
Sodium hexametaphosphate [wetting agent]	2
Polyacrylic acid, ammonium salt [dispersant]	3
Defoamer	2
Cellulose ether (MV*)	4
Preservative	2
Titanium dioxide	92
Calcium carbonate ( 2 $\mu\text{m}$ )	168
Calcium carbonate (5 $\mu\text{m}$ )	252
Talc	42
Styrene acrylate latex (50% solids)	100
Methoxypropanol	9
Coalescing agent	15
Water	169
Total	1000

\* Medium viscosity type: 2% Brookfield viscosity:  $\sim 6000$  mPas

**Table 3.2-2.** Formula for a solvent-free interior wall paint (PVC 80%) based on a vinyl acetate

	Parts by weight
Water	170
Sodium hexametaphosphate [wetting agent]	2
Polyacrylic acid, ammonium salt [dispersant]	3
Defoamer	2
Cellulose ether (MV*)	4
Preservative	2
Titanium dioxide	92
Calcium carbonate ( 2 $\mu\text{m}$ )	168
Calcium carbonate (5 $\mu\text{m}$ )	252
Talc	42
VAc-E latex (50% solids)	115
Water	148
Total	1000

\* Medium viscosity type: 2% Brookfield viscosity:  $\sim 6000$  mPas

During the production process, the thickener provides the pre-mix with sufficient viscosity during grinding to ensure the proper mixing and dispersion of pigments. If the viscosity was too low during the grinding stage, the mixing energy would be lost to turbulent flow and not used for grinding the pigments.

While storing the paint, the thickener provides the necessary stability to keep the pigment and filler particles in suspension and to prevent sedimentation. By minimizing the clotting tendency of the dispersed particles, thickeners improve the mechanical stability and the freeze/thaw stability of the paint.

During application of the paint, the thickener ensures a proper loading of the applicator, whether roller or brush, and ensures acceptable transport of the paint from the tin to the substrate. In addition, the thickener also helps to produce the right application viscosity, which significantly benefits the covering ability of the paint, while it also influences its rheology. On porous substrates the water-retention capacity of the cellulose ether is important to ensure that the water is not immediately sucked into the substrate.

Although the main functions of the cellulose ethers are those mentioned above, numerous other properties of the paint are also influenced by the choice of the type of cellulose ether.

### Influence of Choice of Substituent

Although there is not a “best” cellulose ether in terms of paint properties, experience and experimental investigations do serve as a guide in determining the influence of the choice of the substituent on the properties of the paint. The various paint properties that can be influenced by the choice of thickener can be compared for various products. For this purpose we shall compare hydroxyethyl cellulose (HEC), methylhydroxyethyl cellulose (MHEC), ethylhydroxyethyl cellulose (EHEC) and carboxymethyl cellulose (CMC) with each other for a number of paint properties. Their relative performance is shown in Table 3.2-3.

To ensure proper *dispersion of the pigment* and the fillers it is important that the thickener should not negatively influence the degree of dispersion. The best results

**Table 3.2-3.** Influence of the choice of cellulose ether substituent on various paint properties

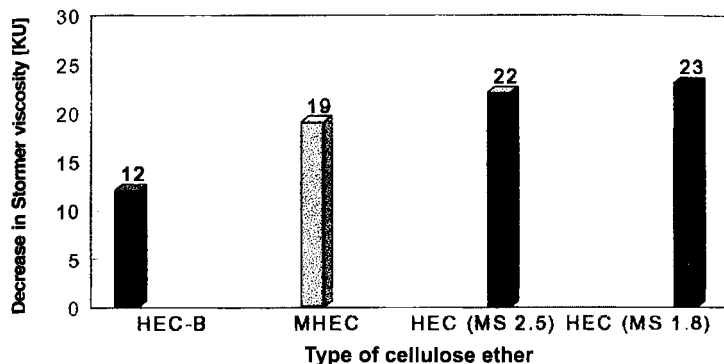
	Poorest results			Best results			
Pigment dispersion	HEC	>	CMC	>	EHEC	>	MHEC
Foaming	HEC	=	CMC	<	EHEC	<	MHEC
Thickening efficiency	MHEC	>	HEC	>	EHEC	>	CMC
Storage stability	HEC	>	EHEC	=	MHEC	>	CMC
Biostability	HEC	>	EHEC	>	MHEC	>	CMC
Spreadability	HEC	>	EHEC	>	CMC	>	MHEC
Brush viscosity	MHEC	>	CMC	>	HEC	=	EHEC
Spatter resistance	MHEC	>	HEC	=	CMC	=	EHEC
Rheology	MHEC	=	CMC	>	HEC	=	EHEC
Sag resistance	HEC	=	EHEC	>	CMC	=	MHEC
Water retention	HEC	>	CMC	>	EHEC	>	MHEC
Colour development	HEC	>	CMC	>	EHEC	>	MHEC
Scrub resistance	HEC	=	MHEC	=	EHEC	>	CMC

are obtained with hydroxyethyl cellulose. This can be readily established by means of polymer-solution titration of titanium dioxide pastes. This becomes evident for paint systems in which relatively little polymer dispersant is used. *Foaming* must also, as far as possible, be kept to a minimum, not only during the grinding stage but also during the remainder of the production process. This means that the thickener must lower the surface tension of the continuous phase by as little as possible, which is why the more hydrophilic cellulose ethers (CMC and HEC) work best in this respect. The *thickening action* of the cellulose ether is more a function of its molecular weight than of the choice of substituent. There is, nevertheless, an indirect effect. Methyl cellulose derivatives do interact to some degree with the pigments, resulting in a slightly lower degree of dispersion of the paint. This has a slight effect on the viscosity of the paint and this may give the appearance that the MHEC is somewhat more efficient in its thickening action. In addition, it has been established that the *pseudoplasticity* of methyl cellulose solutions is slightly lower than that of hydroxyethyl cellulose and ethylhydroxyethyl cellulose. This results in a somewhat higher viscosity in the middle (Brookfield viscosity, Stormer viscosity) shear range and at higher shear rates, and has a positive effect on the thickening action of the product and on its application viscosity. This is why paints containing methyl cellulose derivatives as thickeners frequently have a slightly higher ICI viscosity.

The higher *application viscosity* benefits the *covering ability* (thicker paint coat) and the *spatter resistance* during roller application. The lower viscosity at low shear rates benefits the *rheology*, but has a negative effect on the *sag resistance* during application on vertical substrates.

As a rule, the best *storage stability* of the paint is achieved with hydroxyethyl cellulose because of its very slight interaction with the pigment, fillers, and binder of the paint. The storage stability is also improved by the fact that water is a very good solvent for HEC in the temperature range from 0 to 100 °C despite the presence of electrolytes and glycols.

*Resistance to enzymes* is important in the case of contamination with microorganisms. These can get into the paint from a variety of sources. Specific enzymes can chemically break the cellulose ether chain at the oxygen atom of the 1,4-glucosidic bond. This results in the end product having a shorter chain length, which in turn means a loss of viscosity. When the anhydroglucose unit contains a substituent, the enzyme is sterically prevented from attacking the oxygen so that the chain remains intact. If one can ensure that each anhydroglucose unit contains a substituent, the material will be 100% biostable. This is, however, not the case. Most cellulose ethers contain 10 to 20% unsubstituted monomer units and will lose the major part of their built-up viscosity after enzyme contamination. Nowadays, however, more uniformly substituted hydroxyethyl celluloses<sup>[3-16, 3-23]</sup> are available that contain less than 3 wt% of unsubstituted anhydroglucose units. This is the reason why these products have the highest degree of resistance against enzymes, as shown in Fig. 3.2-9. From the curve it can be seen that after a polymer solution with a viscosity of 100 KU has been contaminated with an enzyme, the decrease in viscosity is lowest for the "biostable" hydroxyethyl cellulose (HEC-B), so that in practice the paint can still be used without it needing to be reprocessed. The availability of cellulose



**Figure 3.2-9.** Loss of viscosity of polymer solutions after contamination with 10 ppm cellulose, as a function of the type of cellulose substituent

ethers with improved resistance against degradation by enzymes does not, however, mean that it is no longer necessary to add preservatives. It does, however, give a certain degree of security.

For the application of paint on porous substrates it is very important that the thickener should have a good *water-retention capacity*. In practice it is found that water retention is best for the more hydrophilic HEC cellulose ether.

Paint systems with colour pigments will normally not present any problem for hydroxyethyl cellulose as far as flocculation of the colour pigments is concerned. The *colour development* for HEC is therefore hardly, if at all, influenced by the amount of shear applied. In rub-out tests this is clearly reflected in the very slight difference between the part of the paint film subjected to shear compared to the part not subjected to shear. This is an important advantage of hydroxyethyl cellulose. Methyl cellulose derivatives, as well as ethylhydroxyethyl cellulose, frequently undergo an interaction with colour pigments, giving rise to a limited flocculation of the pigment. The flocculation is enhanced when shear is applied.

The anionic nature of carboxymethyl cellulose makes this product less resistant against the influence of the weather and it also has a clearly lower *scrub resistance* than the non-ionic cellulose ethers.

In summary, it can be concluded that there is no single cellulose ether that gives the best results in all respects. It is nevertheless possible to see from Table 3.2-3 that HEC most often yields a positive result, a fact reflected by the popularity of this product in Europe and the US and its universal use. There can, however, still be major differences from one region to the next. In Germany, for instance, methyl cellulose is extensively used, something that can be historically explained by the presence of methyl cellulose producers in that country.

### **Influence of Molecular Weight**

Apart from the choice of substituent, the molecular weight of the cellulose ether also influences the properties of a paint. The influence of the molecular weight is

summarized in Table 3.2-4. To keep it simple, paints with two different viscosities are compared, namely a product with a 2% Brookfield viscosity (20 rpm) of 6000 mPa and a product with a viscosity of 100 000 mPa. For hydroxyethyl cellulose with a MS of 2.5 this means a comparison between a molecular weight of 650 000 (6000-type) and a molecular weight of 1 100 000 (100 000-type). It goes without saying that the higher the molecular weight of the cellulose ether, the better is its thickening action. A higher molecular weight does, however, produce an increase in the tendency to spatter when applied by roller, though the rheology of the paint is slightly improved. In general this is not what one would expect, but it is easily verified experimentally, that after application the structure is covered much faster in the case of a low-molecular-weight product than for a high-molecular-weight material. This comparison must of course be made with paints with the same viscosity. Though long molecules are more elastic (more spatter), short molecules return much more rapidly to the energetically favourable tangled condition after stretching.

**Table 3.2-4.** Influence of the molecular weight of the cellulose ether on paint properties

	Type with best viscosity
Thickening coefficient	100 000
Spatter resistance	6 000
Rheology	100 000
Sag resistance	6 000 and 100 000
Covering ability	6 000
Open-time	6 000
Spreadability	100 000
Scrub resistance	100 000
Prevention of pigment flocculation	6 000

One can also expect such low-molecular-weight products to have a better sag resistance. In practice this is the case, but since the thickness of the layer to be applied will usually not exceed 400  $\mu\text{m}$ , the difference is not noticeable.

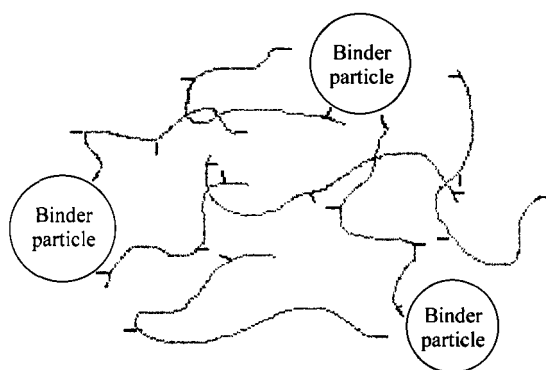
The open-time of a paint is better for lower molecular weights and appears to be a function of the concentration of polymer molecules. At higher molecular weights, the colour development of pigments can be negatively influenced because of the partial flocculation of the colour pigments. This is enhanced by the choice of a poor stabilizer for these pigments and the titanium dioxide.

The sensitivity to water of a paint is increased if a lower molecular weight is chosen. Shorter polymer chains will go into solution sooner than longer chains, and the scrub resistance also increases as the molecular weight is increased. It is therefore clear that once again there is no single molecular weight that yields the best results for all properties and requirements for a paint. To improve the quality of a paint, lower-molecular-weight material is generally used because it gives improved spatter resistance, hiding power, and open time.

### 3.2.1.4 Associative Cellulose Ethers

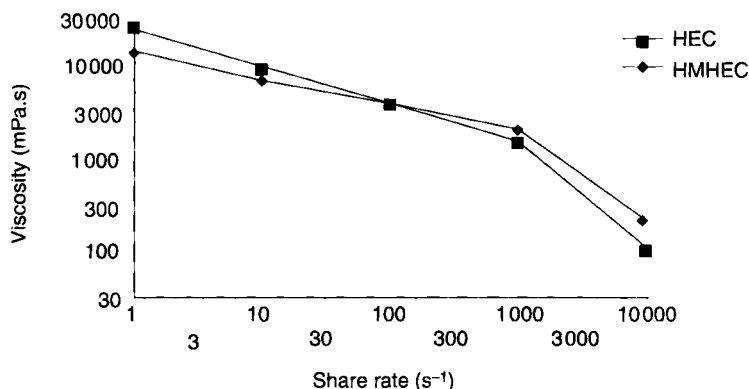
The traditional cellulose ethers provide latex paints with a broad range of useful properties. As for most products, however, there is still room for improvement in a number of respects. The paint industry has set stricter requirements for the rheology of paints<sup>[3-18, 3-19, 3-24, 3-25]</sup> in order to develop higher quality paints. The coating ability had to be improved in order to create a “one-coating” product. This is now possible by adjusting the titanium dioxide concentration and by optimizing filler combinations and particle-size distributions. To save costs, increasing the application viscosity is also a useful way to achieve this goal. The ICI viscosity would then have to be around 200 mPa. This has proved possible only for cellulose ethers with a very low molecular weight (300 000), in which case the thickening action is limited. This means that at the high concentrations required this solution becomes too expensive, while at the same time too many hydrophilic components are added to the paint, thus increasing its sensitivity to water. In the eighties there was also a demand for more spatter-free paints and for improvement of its rheological properties. The demand for a less pseudoplastic rheology arose.

This led to the introduction of associative thickeners such as associative acrylic thickeners and polyurethane thickeners. As a response, a cellulose-based associative thickener was developed. The mode of action of such a product is shown in Fig. 3.2-10.



**Figure 3.2-10.** The mode of action of associative thickeners

The base polymer is either hydroxyethyl cellulose or ethylhydroxyethyl cellulose. The molecular weight of the base polymer is significantly lower than that of water-phase thickeners, e. g. approximately 300 000 dalton. The polymer is also modified with hydrophobic alkyl or alkylaryl groups. The concentration of these hydrophobic groups is less than 2 wt% so that the hydrophobicity of the product itself is not significantly changed. The hydrophobic groups are able to interact with the binder particles and thus contribute to the viscosity. This thickening mechanism results in a less Newtonian flow, as shown in Fig. 3.2-11. The viscosity is lowered at low shearing rates, while at high shearing rates a higher viscosity is achieved. This produces the desired rheology improvements: spatter resistance and coating ability.



**Figure 3.2-11.** Thickening mechanism of a traditional cellulose ether (HEC) and an associative cellulose ether (HMHEC)

The associative cellulose ethers thicken a paint by means of two mechanisms<sup>[3-26, 3-27]</sup>: aqueous-phase thickening and associative thickening. This means that these products are to a certain degree dependent on the composition of the paint. The dependence is not as strong as for associative thickeners such as the polyurethanes but it is nevertheless important to know how the associative-thickening component depends on the composition of the paint.<sup>[3-28-3-30]</sup> There are three main components with which interaction is possible:

- the binder
- pigments and fillers
- surface-active ingredients

The thickening action of associative cellulose ethers is mainly dependent on the binder. The presence of a sufficient amount of dispersant helps to limit the interaction with titanium dioxide and fillers. Thus, interaction with surfactants only starts playing a role in situations where an overstabilized binder is used. In this section, only the influence of the binder composition on the thickening action of associative cellulose ethers will be considered. Research by companies and research institutes has shown that the interaction is based on hydrophobic forces and that the thickening action can be enhanced by:

- decreasing the particle size of the binder
- lowering the amount of surfactants, i. e., less stabilizer/emulsifier
- choosing emulsifiers with shorter ethylene oxide chains
- lowering the quantity of acrylic- and methacrylic acid comonomers
- increasing the hydrophobicity of the polymer particles of the latex

In summary, the interaction between the associative cellulose ether and the binder increases as the hydrophobicity of the binder is increased and as the free surface area of the binder particles is enlarged.

Therefore acrylic dispersions and for styrene acrylate dispersions result in the highest degree of thickening. Adequate interaction is achieved with vinyl acrylates and vinyl acetate copolymers. Only slight interaction is observed for vinyl acetate homopolymers.

The advantage of these associative cellulose ethers is that the products can serve as a single thickener in a broad range of paint systems from semigloss to matt ceiling paints. They retain the properties of the traditional thickeners and in addition provide improved rheology, coating ability, and spatter resistance.

### 3.2.1.5 Commercial Products

Table 3.2-5 lists the most important companies, the types of products supplied to the paint industry, and the product names. The traditional types of cellulose ether are abbreviated as follows:

- carboxymethyl cellulose (CMC)
- hydroxyethyl cellulose (HEC)
- methylhydroxyethyl cellulose (MHEC)
- methylhydroxypropyl cellulose (MHPC)
- hydroxypropyl cellulose (HPC)
- ethylhydroxyethyl cellulose (EHEC)

Associative cellulose ethers have been assigned the following abbreviations:

- hydrophobically modified hydroxyethyl cellulose (HMHEC)
- hydrophobically modified ethylhydroxyethyl cellulose (HMEHEC)

**Table 3.2-5.** Commercial cellulose ethers for the paint industry

Company	Product name	Product type
Hercules	Natrosol	HEC
	Culminal	MHEC, MHPC
	Klucel	HPC
	Blanose	CMC
	Natrosol Plus	HMHEC
AKZO Nobel	Bermocol	EHEC, HMEHEC
	AKU-CMC	CMC
Hoechst	Tylose MH	MHEC
	Tylose H	HEC
	Tylose C	CMC
Wolff [Bayer]	Walocel M	MHEC, MHPC
	Walocel C	CMC
	Walocel XM	CMC/MHEC
Dow Chemical	Methocel	MHPC
Union Carbide	Cellosize	HEC
Courtaulds	Celacol	MHPC

The various suppliers publish extensive documentation on their products. The data provided<sup>[3-21, 3-31-3-36]</sup> differ from one supplier to the next, but would contain information on the various types, names, chemical composition, and viscosity ranges of the products, as well as paint formulation guidelines. The materials available from various suppliers are described in reference<sup>[3-37]</sup>.

### 3.2.1.6 New Developments

In the field of cellulose derivatives for the paint industry there have been two recent developments that warrant brief mention. They are the development of liquid cellulose ethers and the development of cellulose ethers for market sectors such as high-gloss paints, primers, and topcoats for metal and wood, as well as varnish stains.

#### Liquid Cellulose Ethers

Hydroxyethyl cellulose and associative cellulose ether is available in liquid form. The product is an aqueous suspension of these cellulose ethers and has an active ingredient content of 25%. The advantage of a product in this form is the ease with which a liquid can be added and pumped. This can speed up the production process and also makes it easy to correct the viscosity at the end of the production process. The products are environmentally friendly because the system is water-based and contains no solvents or alkyl/aryl ethoxylates.

#### Cellulose Ethers for New Market Sectors

Cellulose ethers are mainly used in paints with a pigment volume concentration in the range of 30 to 85%. Cellulose ethers have never really found application as industrially used high-gloss paints and water-based paints. This is because of the strict requirements of such systems in terms of rheology, application viscosity, water-sensitivity, film gloss, and sprayability. Cellulose ethers had to be combined with polyurethane thickeners before they could be used in these systems. New developments<sup>[3-26, 3-28]</sup> in the field of low-molecular-weight associative cellulose ethers now make it possible for them to function well as thickeners in high-gloss paints (brush application) and in sprayable paints for wood, metal, and plastics.

Publications on this topic have appeared regularly since 1992. The molecular weight of these low-molecular-weight associative cellulose ethers is in the order of 50 000 dalton. Through associative behaviour, networks are formed with the binder and a more viscous rheology obtained, which results in paints with good spreading after application by brush, roller, or spray gun. These materials can be used for various spray-techniques such as air, airless, and HVLP.

The composition of these materials is such that flocculation of binder and pigments is limited, thus producing an optimum dispersion of the paint ingredients, which benefits film gloss and the water-resistance of the paint.

The reference section contains a listing of some of the more important literature available on these products.

### 3.2.1.7 Toxicology and Disposal

Cellulose ethers do not present a long-term ecological problem. They readily degrade biologically at a slow rate. Small quantities of waste can be discharged down normal effluent systems, while larger quantities must be removed to a central waste disposal site. The maximum biological oxygen consumption is 20 mg O<sub>2</sub>/g.

Cellulose ethers for the paint industry are not acceptable as food additives because their purity is below specified standards.

There are no known hazards that can result from exposure to cellulose ethers. Nevertheless, Safety Data Sheets do give instructions for first aid after contact with these products.

In the case of eye contact, rinsing with water is recommended. After skin contact, the skin should be washed with soap and water. If swallowed, large quantities of water should be drunk and the mouth should be rinsed with water. If the powder is inhaled, it is recommended to put the patient in the open air and to consult a doctor.

Fire and explosion hazards arise only when the powder is finely dispersed in air in the presence of a source of ignition. Proper ventilation is therefore a condition for storage. In the case of fire, water, foam, carbon dioxide, sand, and powder extinguishers can be used. Dispersed cellulose ether powder on a wet floor will make the floor slippery and should be avoided.

Recommended personal protection equipment for working with these powdery products includes gloves (skin protection), protective goggles (eye protection), and mouth and nose filters. The materials are generally odourless and tasteless and have a neutral pH in solution (pH 5.5–8.5). A minimum explosion limit of 156 g/m<sup>3</sup> has been set and the spontaneous ignition temperature is approximately 370 °C. Apart from this, the material is stable, and the LD<sub>50</sub> value for rats is more than 5 g of product per kg. As far as eye irritation tests are concerned, it has been reported that rabbits showed a slight lens irritation after exposure to a cellulose ether.

### 3.2.2 PUR Thickeners

*Johan Bieleman*

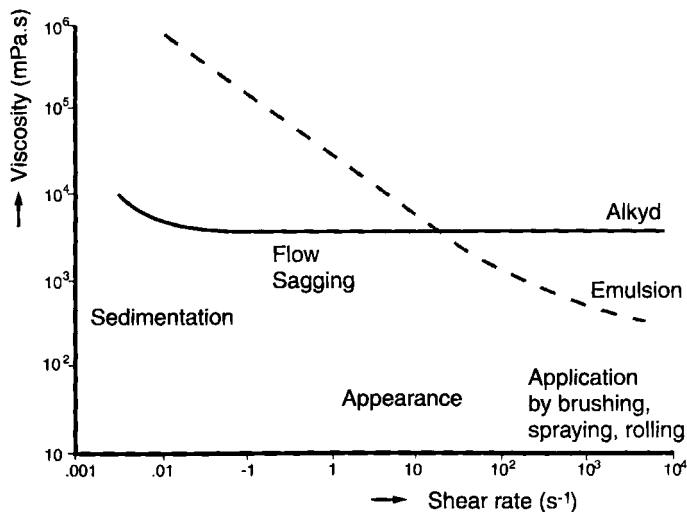
#### 3.2.2.1 Introduction

The development of polyurethane or PUR (abbreviation PU used in US literature) thickeners is one of the most important advances in the area of rheological additives. These thickeners can improve the rheology of aqueous varnishes considerably.

The first PUR thickeners were already presented in the 1970s. Because of their thickening mechanism, which led to the alternative name of “associative thickeners”, they have since become one of the most important thickeners for aqueous paints and coatings. Compared to the traditional cellulose and acrylate thickeners, these thickeners result in better flow and levelling properties upon application. They were originally recommended especially for gloss emulsion paints because of their better levelling properties. In the meantime, their good performance in other aqueous systems has extended their application range. They are, for example, of advantage in industrial coating systems because of their relatively hydrophobic nature; in high-pigmented emulsions less roller spattering occurs during application.

The rheology of conventionally formulated emulsion paints is adjusted with cellulose thickeners. The flow and levelling characteristics of these emulsion paints are quite different to those of conventional solvated alkyd paints (Fig. 3.2-12).

The viscosity curve of an emulsion paint shows that the viscosity is nonlinearly dependent on the applied shear stress. Increasing shear stress is associated with reduced viscosity (shear thinning, see Section 3.0.2). The alkyd paint undergoes a much



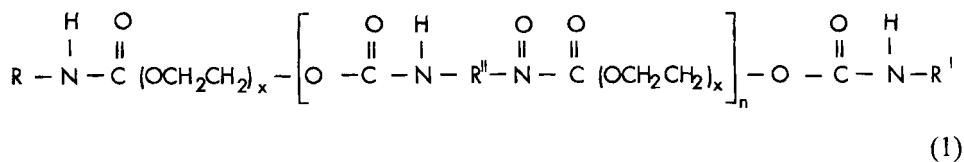
**Figure 3.2-12.** Characteristic viscosity curve of an emulsion paint compared to that of a solvated alkyd paint

smaller reduction in viscosity, i. e., the paint has much less structural viscosity and almost Newtonian flow behaviour. Various application-relevant property differences between emulsion paints and alkyd paints are explained by these differences in rheological behaviour; for instance, paint stability, flow and levelling, as well as the sagging resistance. Because of the higher structural viscosity in the lower shear region, the flow properties of such emulsion paints are worse, but the sagging resistance is better (see also Section 3.1.4). The brush-drag resistance during application is less because of the low viscosity in the high shear region (see Section 3.0.2).

### 3.2.2.2 Chemical Composition and Delivery Form

PUR thickeners usually consist of non-ionic hydrophobic polymers that are available either in liquid form, for example as a 50% solution in water or organic solvents, or in powder form. These synthetic thickeners are based on water-soluble polyurethane with a relative low molecular weight (typically between 10 000 and 50 000).

The PUR polymers are formed by reaction of diisocyanates with diols and hydrophobic blocking components. A typical example is shown in the following chemical structure, where R and R' represent hydrophobic, aliphatic, or aromatic groups.



The following three components can be distinguished in the molecule:

- hydrophobic terminal segments
- several hydrophilic segments, and
- urethane groups

Hydrophobic segments are, for example, oleyl, stearyl, dodecylphenyl, and nonylphenyl. The composition of the hydrophobic segment is very important for the viscosity-increasing characteristics, especially the adsorption behaviour (see Chapter 4).<sup>[3-38]</sup>

Several molecular structures are possible, but PUR thickeners with linear and comb-like polymer structures are the ones used especially in practice.

The decisive factor for the viscosity increasing effect is that each molecule should have at least two hydrophobic terminal segments. The hydrophilic segments are polyethers or polyesters, for example, maleic acid and ethylene glycol polyesters, and polyethers such as polyethylene glycol or polyethylene glycol derivatives. Examples of diisocyanates are IPDI, TDI and H<sub>12</sub>MDI.

The product properties of PUR thickeners are not only determined by these base components but also by the ratio of the hydrophobic and hydrophilic segments.

Of the two forms in which PUR thickeners are made available, the powder form has the advantage that the emulsion paints may be formulated completely solvent-free.

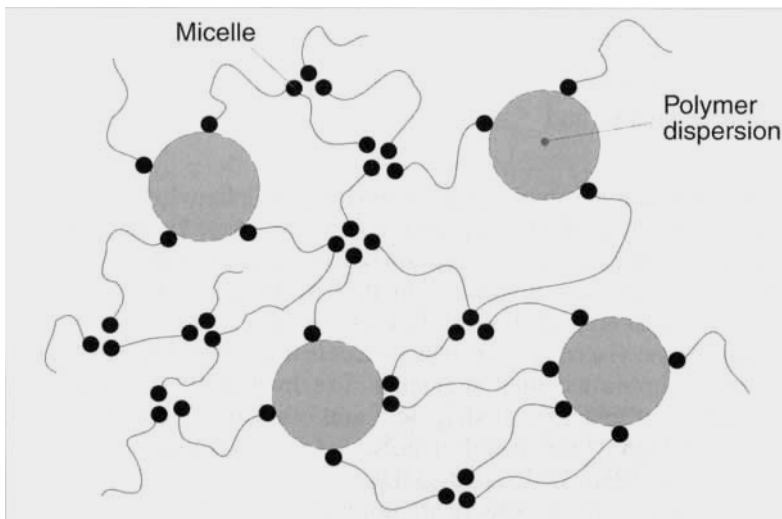
The powder is added as a 3% aqueous gel. The liquid forms are supplied at different concentrations, as solutions in water or water/glycols; these liquid PUR thickeners can be further prediluted before they are added to the coating formulation.

### 3.2.2.3 Thickening Mechanism

The presence of hydrophobic and hydrophilic groups within the same molecule indicates a certain surface activity. On solution in water, formation of micelles does in fact occur above a specific concentration. In contrast to monomeric surfactants, the same PUR molecule may be present in more than one micelle.<sup>[3-18, 3-20, 3-39]</sup> In this way, structures are formed that reduce the mobility of water molecules and increase the viscosity (Fig. 3.2-13).

The hydrophobic segments within the molecule can adsorb onto the surface of the binder particles, the emulsion polymer, and eventually – depending on the properties of the surface – on the surface of solid particles such as pigments and paint extenders, too. The adsorption or association of the hydrophobic groups on the emulsion particles is very important for the thickening effect of PUR thickeners. Because they associate with emulsion particles, PUR thickeners are also referred to as associative thickeners.

As each PUR molecule has at least two hydrophobic segments, it is possible for two emulsion polymer particles to be connected to one another through the PUR molecule and thereby forming a three-dimensional structure or network. In the same way, the polymeric emulsion particle will be connected to the micelles,



**Figure 3.2-13.** Thickening mechanism of associative thickeners

formed by the PUR thickener, to make the structure more dense (Fig. 3.2-13). The network results in immobilization of the liquid phase of the coating system, thereby causing a viscosity increase. The extent of the association with the polymer particle depends on the characteristics of the hydrophobic group as well as on the surface properties of the polymer emulsion particles, the binder. Finer emulsions (larger total surface area) will therefore be thickened more with PUR thickeners than coarse emulsions will. It has been shown that the number of bonds per molecule is proportional to the thickening effect under shear conditions.<sup>[3-40]</sup> The structure that results from the PUR thickener and the emulsion particles is essentially resistant to mechanical influences, leading to virtually Newtonian flow behaviour.

The viscosity increase achieved with a PUR thickener is the sum of the following thickening effects:

1. Solution of the PUR polymer increases the viscosity of the water
2. Micelle formation and/or formation of connections between PUR micelles
3. Associations with emulsion polymer particles

It was found empirically that, when applied in emulsion paints and coatings, the contribution to viscosity increase gets less in the following order<sup>[3-39]</sup>:

Order of magnitude:  $3 \gg 2 \gg 1$ .

The strongest influence on increasing the viscosity is the interaction of PUR with the emulsion particle.

#### 3.2.2.4 Application Properties of PUR Thickeners

##### General Properties

PUR thickeners belong to the most important recent developments regarding additives for waterborne coating materials.

The properties of PUR thickeners (compared to cellulose thickeners) are the following:

##### *Strengths:*

Flow and levelling  
Alkyd-like rheology  
Opacity  
Hydrophobic properties  
Reduced roller spattering  
Biological stability

##### *Weaknesses:*

Sag resistance  
Compatibility with glycol-containing tinting pastes

### Thickening in the Mid- and Higher-Shear Regions

PUR associative thickeners may be further classified according to the thickening effect in the mid-shear and high-shear regions, with regard to their application in paints and coatings:

#### *“Mid-shear” PUR Thickener*

The viscosity of these associative thickeners increase strongly within the medium shear region ( $10$  to  $1000\text{ s}^{-1}$ ) and the thickened systems exhibit nearly Newtonian flow behaviour and great shear stability.

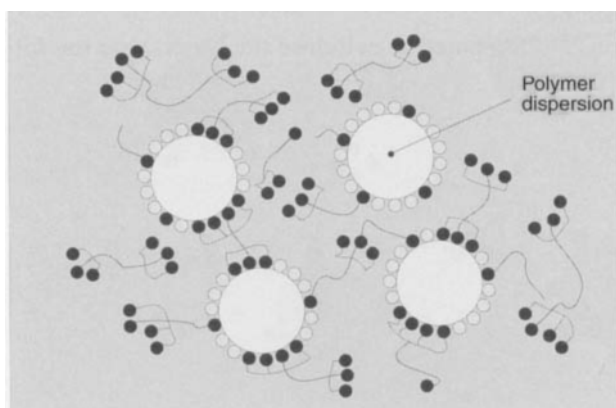
Under higher shear conditions the network structure is only deformed slowly and the flow behaviour is pseudoplastic. This effect is explained by desorption of PUR thickener from the polymer particle surface.<sup>[3-38]</sup> The extent to which these deformations result in lower viscosity under shear conditions depends on the strength of the association between the PUR thickener molecules and the polymer particles.

Deflocculation of pigment particles also contribute to decreasing the viscosity under shear conditions.

#### *“High-shear” PUR Thickener*

These thickeners, similarly known as associative thickeners, are more shear-resistant than the mid-shear PUR thickeners, and are therefore useful for the formulation of shear-stable emulsion paints.

High-shear PUR thickeners perform best in the shear range of about  $1000\text{ s}^{-1}$  onwards. They contain multifunctional hydrophobic segments which are strongly adsorbed onto emulsion polymer particles (Fig. 3.2-14).



**Figure 3.2-14.** Thickening mechanism of high-shear PUR thickeners

The thickening effect in the mid- and low-shear ranges is quite low, compared to, for instance, the mid-shear thickeners described above; high-shear thickeners can be used in conjunction with mid-shear or low-shear thickeners.

### 3.2.2.5 Applications

Polyurethane thickeners enable the formulation of water-borne paints and coating formulations with rheological properties virtually identical to those of solvent-borne alkyd paints. As described above, the structure formed from the PUR thickener and the emulsion particles is to a large extent stable against mechanical influences, resulting in an almost Newtonian flow behaviour (Fig. 3.2-15). Properties such as brush-drag during application, flow and levelling, as well as film properties such as film thickness can be better optimized with PUR thickeners than with the more conventional thickeners such as cellulose thickeners.

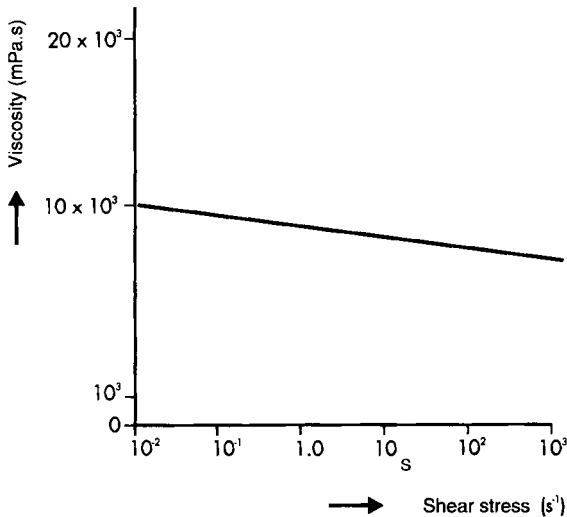


Figure 3.2-15. Flow curve of an emulsion paint with PUR thickener

PUR thickeners prevent spattering during roller application. This is due to the relatively low molecular mass of the PUR thickener molecules and consequently the low degree of elastic flow behaviour. Precisely because of their lower spatter tendency, PUR thickeners are used in medium- and highly pigmented emulsion paints to optimize the sag resistance of these highly charged systems, often in combination with a low-shear thickener such as a cellulose- or acrylate thickener. For such systems the better flow properties reached with PUR thickeners do not play such an important role.

The optimum viscosity is achieved only after the association interactions between the emulsion particles and the micelles have reached equilibrium. A certain matur-

ing time is required, which may vary from two hours to two days, depending on the properties of the thickener and emulsion. To optimize the viscosity of a particular system, the high-shear viscosity is adjusted first; this viscosity is to some degree, below a characteristic maximum, directly proportional to the thickener concentration. The mid- and low-shear viscosities are subsequently adjusted. Organic, but water-soluble solvents such as ethylene- or propylene glycol reduce the mid- and low-shear viscosity of emulsion paints thickened with PUR thickeners. These solvents reduce the number of micelles, thus reducing the density of the network structure, leading to a lower viscosity. The associations in which micelles participate are assumed to be weak associations, easily broken under influence of shear.<sup>[3-39]</sup>

A similar low-shear viscosity-reducing effect as that mentioned for the water-soluble organic solvents takes place when surfactants are added; above the concentration that is characteristic for that specific surfactant, the surfactant competes with the associative thickener molecule regarding the formation of micelles. The surfactant also compete with the PUR thickener with regard to association onto the emulsion polymer particles.

### 3.2.2.6 Formulation of Coating Materials with PUR Thickeners

Many components that are normally used for the production of paints and coatings influence the effect of PUR thickeners. From the described thickening mechanism it is obvious that the components that influence the association between the PUR thickener and the emulsion particles, as well as those affecting micelle formation, would influence the thickening achieved by the PUR thickener.

Some common interactions are with the following ingredients:

- Surface-active agents, which are used to stabilize the emulsion polymer particles. These surfactants compete directly with the PUR thickeners regarding association processes. It is also possible for the PUR thickeners to be directly adsorbed onto the polymer particles via the surfactant molecules.
- Water-soluble, organic solvents such as ethylene glycol, propylene glycol, glycol ether, etc., impair micelle-formation because the difference in interfacial tension between micelle and continuous (water) phase is reduced, to reduce the number of micelles and hence their contribution to structure-formation as well.
- Dispersing agents such as low-molecular-mass polyelectrolytes such as polyacrylate salts are usually used in water-borne paints and coating materials for pigment dispersal and stabilization. According to the DLVO theory, polyelectrolytes increase the number of molecules present in one micelle. Therefore the number of micelles decreases, as well as the number of bridges between micelles and micelle/emulsion particles, leading to a reduced density and strength of the structure.
- Water-insoluble coating additives, such as coalescing agents and antifoaming agents generally have a viscosity-increasing effect. Since these products are dissolved in the micelles, the volume of each micelle increases, decreasing the distance between micelles and a polymer particles. The result is that low-molecular

mass fractions of the PUR thickener can also take part in the bridging and structure formation, leading to a strengthening of the structure and hence a viscosity increase.<sup>[3-38]</sup> Apart from this contribution, coalescing agents and co-solvents may soften the surface of the polymer particles and therefore increase the possibilities of adhesion or adsorption of the hydrophobic groups of the PUR molecule.

### 3.2.2.7 Coating Properties

PUR thickeners consist of relatively hydrophobic polymers. Compared to more hydrophilic thickeners, such as polyacrylates and cellulose ether, PUR thickeners reduce the water-absorbency of the coating. There are of course great differences between the various available PUR thickeners, and the composition and quantity of the hydrophobic components play a decisive role (Table 3.2-6).

**Table 3.2-6.** Influence on the water absorbency

Thickener	Water absorption of the paint film after 24 h/weight %
PUR thickener I	22
PUR thickener II	32.5

PUR thickener I: water-insoluble, soluble in ethylene glycol  
 PUR thickener II: water-soluble

With regard to the influence on scrub resistance of coatings, the PUR thickeners are superior to the more hydrophilic cellulose and polyacrylate thickeners (Table 3.2-7).

**Table 3.2-7.** Influence on the scrub resistance

Thickener	%	200 µm layer	
		7 days	28 days
PUR thickener I	1.0	949 cycles	1020 cycles
Hydroxyethyl cellulose	0.30	344 cycles	474 cycles
Polyacrylate	0.35	412 cycles	593 cycles

### 3.2.2.8 Commercial Products

Borchigel L 75N (Bayer A.G.)  
 Coatex BR 100 (Coatex S.A.)  
 SER-AD FX 1010 (CONDEA Servo)  
 Primal RM 825 (Rohm & Haas)

### 3.2.3 Organic Thickeners for Solvent-Borne Coatings

*Johan Bieleman*

#### 3.2.3.1 Introduction

Organic thickeners are successfully used for the optimization of the rheological properties of solvent-borne coating materials. Suitable organic thickeners can inhibit sagging and sedimentation. Various products are available for coating formulations. The variations regarding the chemical composition of these thickeners are extraordinary versatile.

Organic thickeners differ from inorganic thickeners not only with regard to their composition (see Section 3.1), but also in their properties and performance. Most organic thickeners are surface-active; they may also be part of the polymeric film matrix during film formation. This explains, for instance, the excellent coating layer properties such as improved appearance, gloss, and flow. However, inorganic thickeners usually show a stronger thickening effect.

#### 3.2.3.2 Product Survey

The following organic thickeners are widely used in solvent-borne paints and coating materials:

- hydrogenated castor oil
- polyamides
- overbased sulphonates

The strengths and weaknesses of these thickeners are listed in Table 3.2-8. The typical characteristics are compared with the two widely used inorganic thickeners: organoclay and synthetic amorphous silicates.<sup>[3-14]</sup> Only generic properties are compared, but differences may also be possible within each group, depending on the specific grade and quality.

#### 3.2.3.3 Hydrogenated Castor-Oil-Based Thickeners

Hydrogenated castor oils (HCO) are the most widely used organic thickeners for non-aqueous systems. They belong to the group of fatty acid derivatives (see Section 3.2) and are made from hardened castor oil.

They may be further chemically modified: there are a number of amide-, ether-, and ester-modified hydrogenated castor oil derivatives available, which have improved temperature stability, so that some of these can withstand incorporation temperatures of 55 °C or even 65 °C. Moreover, these modifications may be of advantage for the specific usage, especially regarding the solubility or solvent-resistance of the coating.

**Table 3.2-8.** Comparison of typical thickener properties

Thickener	Advantages	Disadvantages
Hydrogenated castor oil	thixotropic rheology flow and levelling	heat-sensitive seeding solvent-dependency
Polyamides	stability universal	difficult incorporation effects intercoat adhesion
Overbasic sulphonates	easy incorporation high gloss temperature stability	low effectiveness water-sensitive
Organoclays	universal price heat-resistant	incorporation reduced gloss
Synthetic silicates	inert heat-resistant storage stability	incorporation reduced gloss

Chemically, hydrogenated castor oil thickeners are triglycerides of 12-hydroxystearic acid. This molecule has a three-dimensional structure and also contains a hydroxy functionality, which makes the formation of hydrogen bonds possible. Hydrogen bonds form in organic systems above a characteristic concentration. These interactions lead to the formation of networks by intermolecular associations between two neighbouring thickener molecules or between thickener and solvent. The network results in a viscosity increase of the coating material. However, the thickening effect is not only explained by the formation of hydrogen bonds. Thixotropy is also developed as the result of molecular chain entanglements. Externally applied shear disrupts the entangled molecules or hydrogen bonds, reducing the viscosity.

The waxy aspect of the hydrogenated castor oils also play an important role. The best thickening is achieved when the hydrogenated castor oil is only partly dissolved in the coating system. The organic solvents used in the coating formulation influence the thickening effect of the hydrogenated castor oils greatly.

Hydrogenated castor-oil-based thickeners are commercially available as a powdered material or as a paste.

The powder- as well as the wax form of hydrogenated castor oils have to be dispersed and activated in the coating system in order to get the full thickening effect.<sup>[3-42]</sup> During dispersal, the hydrogenated castor oil will be wetted and a colloid gel-like structure will be formed according to the following three steps<sup>[3-42]</sup>:

- Step 1: The thickener is dispersed into a strongly agglomerated substance in the binder/solvent.
- Step 2: The temporary influence of shear forces and heat leads to partial deagglomeration followed by swelling of the particles in the solvent medium.
- Step 3: If shear and heat transfer continues, the gelled particles will be further divided into primary particles, resulting in complete activation of the thickener.

The optimal incorporation temperature for hydrogenated castor-oil-based thickeners is generally between approx. 35 and 70 °C, depending on their modifications.

Hydrogenated castor oils may lose their rheological characteristics at high-temperature and/or when dissolved in solvents such as xylene after long dwell times. The dissolved thickener may crystallize when cooling down or after evaporation of the solvent during film formation; the crystals are visible as small particles in the dried layer. This phenomenon is known as “seeding”.

It is possible to recondition a partly dissolved organic thickener by dispersing the coating system during cooling again. This procedure transforms the swollen particles into their rheologically effective colloid structure again.<sup>[3-42]</sup>

The flow and levelling properties of hydrogenated castor-oil-based thickeners tend to be very good because these additives recover viscosity slower than, for instance, inorganic thickeners such as fumed silica or organoclays.

#### 3.2.3.4 Polyamides

Polyamide thickening agents are available in a variety of chemical compositions. They are produced from different carboxyl combinations and amines. Raw materials and conditions are chosen in such a way that high-molecular waxy polymers are formed with terminal amide groups.

The thickening mechanism is related to the specific composition of the applied polyamide. The thickening effect in coatings is partly explained by chelating. For other polyamides, it is mainly ascribed to the formation of micelles, as a result of their hydrophilic and hydrophobic ends, combined with association with the pigment particles. Formation of hydrogen bonds also appear to play a role, particularly in low polarity systems. These interactions typically result in the steep shear-thinning rheological properties.

Polyamides swell in some organic solvents, to increase the molecular volume of the thickener, with the result that the viscosity also increases. In the resting state, the swollen, partly looped molecular chains are arranged completely randomly, resulting in a highly viscous system.

As explained for cellulose thickeners in aqueous systems (see Section 3.2.1), the molecules are oriented parallel to the flow direction in case of increased shearing. Therefore, the molecules are able to slide by easier, with lower viscosity as the result. Coatings thickened with polyamides therefore show a steep shear-thinning curve, making them particularly well suited for industrial applications.

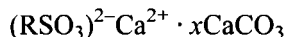
Polyamides have to be dispersed effectively during incorporation. Some types require, like hydrogenated castor oils, a minimal incorporation temperature as well. For some polyaminoamides the incorporation temperature may be as high as 150 °C and involve chemical reaction with the binder. These polyaminoamide-based products are mainly used in the production of thixotropic binders, notably thixotropic alkyd resins.

A major problem with polyamide thickeners is the negative effect these additives may have on the intercoat adhesion of coatings.<sup>[3-41]</sup> It appears that the polyamide molecules in the coatings migrate to the interface of the coating with the air, caus-

ing a reduced surface tension and consequently influencing the adhesion of the following layers negatively.

### 3.2.3.5 Overbased Sulphonates

One of the newest classes of thickeners for solvent-borne coatings are the overbased sulphonates. These liquid thickeners are derived from calcium sulphonates and are gelled in organic solvent; the neutral calcium sulphonates are subjected to a carbonization process to be transformed into basic calcium sulphonate, with the following structure:



where:

R = alkyl and/or aryl group

$x = 1-20$

In this formulation the amorphous calcium carbonate is colloiddally dispersed in the organic solvent.<sup>[3-43]</sup> The next step is the transformation of the basic calcium carbonate into a crystalline form. Typically the microcrystals have a size of 0.5 to 3  $\mu\text{m}$ .

Calcium sulphonate is adsorbed onto the calcium carbonate particles through the sulphonate groups. The nonpolar segments of the adsorbed sulphonate molecules form intermolecular bonds, particularly van der Waals forces. Therefore microstructures are formed, resulting in an increased viscosity.

The gel structure is strongly shear-thinning.

A particular advantage of these thickeners is their easy incorporation.

These overbased thickeners are liquid and function optimally simply through careful mixing of the thickener into the coating.

The gel structure, typically reached with basic sulphonates, is temperature stable. This is regarded as the main advantage of overbased sulphonates, which also have good sag resistance of freshly applied coatings onto vertical substrates, and also affect the gloss very little.

A disadvantage is their high alkalinity: these thickeners cannot be combined with acid catalysts.

The highest efficiency can be reached in highly pigmented systems.

### 3.2.3.6 Polyolefins

Polyolefins are typically dispersed in a solvent carrier and are mainly used as anti-settling- and sag-control agents in high-solids systems.

The thickening effect is relatively low, compared to other organic thickeners. However, when used at high concentrations they can behave as thixotropic agents. Polyolefins have a steep shear-thinning viscosity profile.

The thickening mechanism is based on association; polyolefins work best at high-pigment-volume concentrations.

**3.2.3.7 Commercial Products**

Thixcin R (Rheox Inc.)  
 Irgagel (Lubrizol Inc.)  
 SER-AD FX 2050 (CONDEA Servo B.V.)

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## 4 Surface-Active Agents

*Johan Bieleman*

Surface-active agents – also referred to as “surfactants” – are substances that are added to a liquid to increase its spreading or wetting properties by reducing its surface tension and by enriching the solution with interfaces. During the enrichment the surface-active compounds build molecular films, resulting in a reduction of the interfacial tension between the two adjacent phases.

Surface tension is the property of a liquid that makes it behave as if its surface is enclosed in an elastic skin. This property results from intermolecular forces: a molecule in the interior of a liquid experiences interactions from other molecules, equally from all sides, whereas a molecule at the surface is only affected by molecules below it in the liquid.

The surface tension or the more general expression, interfacial tension, is defined as the force acting over the surface per unit length of surface perpendicular to the force. Interfacial tension,  $\gamma$ , is defined as the energy required to increase the surface area isothermally by one square meter and is measured in  $\text{N} \cdot \text{m}^{-1}$  (equal to  $\text{J} \cdot \text{m}^{-2}$ ).

Interfacial tension results in the formation of liquid drops, foaming, defoaming, the ability of liquids to wet a surface, the rise of liquids in a capillary, etc. Interfacial tension always refers to forces in the border between two phases.

The interfacial tension  $\gamma$  is referred to as the free (or Gibbs) energy per surface area and is always positive. Enlargement of the interface area results in an increase in the free energy (expressed as enthalpy) for the defined surface area. Therefore, the enlargement of the interface will never take place spontaneously.

In the following equation:

$$\gamma = \frac{dG}{dF} > 0$$

$G$  represents the free enthalpy,  $F$  the surface area, and  $\gamma$  the interfacial tension

Surface tension is a special case of interfacial tension and is generally considered as interfaces with gas (air) as one of the two phases. Typical surface tensions of some solvents and binders are listed in Table 4-1 and surface tensions of some solid substrates are listed in Table 4-2 (see also Section 6.1.1.2).

Interfacial tension is essential for paint production, storage and processing and it directly influences some characteristics of the hardened paint. With respect to paints and coatings the following interfaces are differentiated:

- Liquid/air: Pigment wetting, levelling and film formation, defoaming
- Solid/air: Pigment wetting and stabilization, substrate wetting, coating film quality

**Table 4-1.** Surface tension of some solvents and binders

Solvent or binder	Surface tension in $\text{mN} \cdot \text{m}^{-1/20} \text{ C}$
Water	72.8
Ethylene glycol	48.4
Isobutyl acetate	25.5
Xylene	32
White spirit	26
Butyl acetate	27.6
<i>n</i> -Heptane	20.4
Silicone oil	18
<i>n</i> -Octane	21.8
Melamine resin	42–58
Alkyd resin	26–60
Polyacrylates	27–40

**Table 4-2.** Surface tension of some substrates

Substrates	Surface tension in $\text{mN} \cdot \text{m}^{-1/20} \text{ C}$
Glass	73
Phosphated steel	43–46
PVC	39–42
Polystyrene	36–42
Polyethylene	32–39
Polypropylene	28
PTFE (polytetrafluoroethylene)	19

- Liquid/solid: Pigment wetting
- Solid/solid: Adhesion, mechanical paint properties

The lower the interfacial tension is, the faster the wetting of a pigment by a liquid phase (binder, solvents, additives) will be. Another example of the importance of interfacial tension is that complete wetting of the substrate by the (liquid) coating material is a major requirement for optimal adhesion of the coating onto a substrate.

Surfactants have a relatively low surface tension and therefore little resistance to the formation of new surfaces. That means that any mechanical force brought onto a solution of surfactant may result in the creation of new surface area, examples of this are foaming, defoaming, wetting and adsorption onto solid surfaces by pigments or other substrates (adhesion).

In this chapter additives whose action greatly depend on interfacial activities will be described. Sections 5.1 and 6.1 also describe additives that have strong interface activity.

## 4.1 Wetting and Dispersing Agents

*Johan Bieleman*

### 4.1.1 Introduction

Dispersing is the homogeneous distribution of solids in a liquid medium. In the dispersing process the adhesive strengths between the finest solid particles must be overcome.

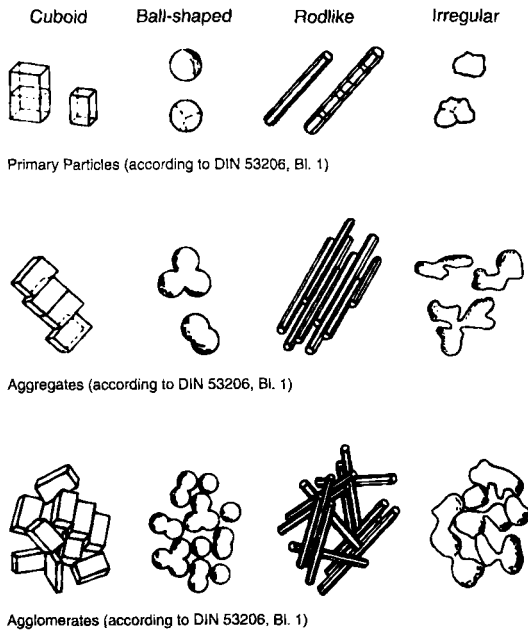
Pigments and extender fillers are typical examples of solids in paints and coating materials; typical liquid media are water, organic solvents, and binders or mixtures or solutions thereof.

The dispersion stage is extremely important. If the pigment is not correctly dispersed, this may result in various shortcomings in the paint or coating, such as low colour strength, poor colour development, coarse particles, sedimentation, separation of the phases, and poor application characteristics. That long dispersion time during the manufacturing process results in high manufacturing costs should also be considered. During the exposure of the coating, these unsatisfactory properties may lead to inferior opacity and gloss level, to surface defects, as well as to colour differences in the coating film. An additional disadvantage is that the properties of the expensive pigment are insufficiently used, and thus the raw material costs of the coating are unnecessarily increased. It is therefore extremely important to apply methods that enable an optimized pigment dispersion and stabilization against flocculation. For this, suitable pigment-dispersing agents are used.

In this chapter, processes are described that are very important for pigment and extender dispersion and stabilization in paints and coatings. Additionally, properties and application of dispersing agents will be explained in more detail.

### 4.1.2 Definitions

- **Agglomerates** consist of a loose arrangement of primary particles, aggregates, or a mixture of the two, e.g., a pigment or extender, that are connected (for example at their corners or edges) and held together by surface forces. The loose arrangement may be broken down during the manufacturing process of coatings or inks. The total surface area of the particles in an agglomerate is not substantially different from the total surface area of the individual constituents (Fig. 4.1-1).
- **Aggregates** consist of a cluster of particles rigidly joined together by partial fusion, i.e., by sintering or cementation or by growing together; they are not



**Figure 4.1-1.** Primary particles, aggregates, agglomerates

usually broken down by the dispersion techniques used in the paint industry (Fig. 4.1-1).

In practice it is not always possible to differentiate aggregates and agglomerates definitively.<sup>[4-1]</sup>

- **Brownian movement.** By microscope observable, continual, spontaneous movement of the finest particles suspended in a liquid. The movement of the particles is due to collisions with the fluid molecules.
- **Colloids** are very finely divided materials (particle diameter 0.01 to 1  $\mu\text{m}$ ).
- **Dispersibility** is the level of dispersion when it has become constant under the defined conditions; the dispersibility of a pigment depends on the liquid phase in which it has been dispersed, the method of dispersion, and the millbase composition.
- **Dispersing agents** are additives used in coating materials to facilitate the dispersion of the solid constituents in the liquid phase during manufacture, storage, and/or application of the coating.
- **The dispersion process** includes the total process and subprocesses, whereby solid material (pigments, extenders) is dispersed in the liquid phase. The purpose of this is to ensure the final even distribution of all particles in the liquid medium.
- **Flocculates** are loosely coherent agglomerates of pigment particles; in flocculates the attraction between the particles is weaker than in agglomerates and very much weaker than in aggregates.

- **Isoelectric point** is the pH value at which a substance or system is electrically neutral.
- **Milling** is the process during which the particle size of pigments and extenders is reduced. (It is really an outdated term, because practically all pigments are already offered in a final, flocculated, primary size, the so-called micronized pigments).
- **Milling paste** is a dispersion mix of solid and liquid constituents, it is also called “millbase”.
- **Primary particles** are the smallest particles obtained by the production of pigments and extenders; milling of the small crystals, of which pigments and extenders are built up, results in fractures within the crystal lattice (Fig. 4.1-1). During the drying stage of the pigment- or extender-manufacturing process, the primary particles form into agglomerates and aggregates.
- **Surfactants** are substances that reduce surface tension and enrich from a solution to interfaces. “Surfactant” is the contracted form of “surface-active agent”. Surfactants may form micelles and improve wetting (wetting agent), help to disperse pigments (dispersing agent), or inhibit foam or emulsify (emulsifier).
- **Wetting agents** are additives that belong to the group of surfactants; they consist of amphiphilic molecules, which facilitate the dispersion or adhesion process.
- **Zeta potential** is the potential across the diffuse layer of ions surrounding a charged colloidal particle, and is largely responsible for colloidal stability. Also known as electrokinetic potential.

### 4.1.3 The Dispersion Process

The paint quality is greatly determined by the dispersion status of the pigment particles in the liquid medium. Complete dispersion of the pigments is required for optimum colour-strength development, good opacity, high gloss, as well as good outdoor properties; it can also improve the mechanical characteristics of the coating film.<sup>[4-2, 4-3]</sup>

Dispersion – also referred to as milling or grinding – consists of physicochemical as well as mechanical actions in which the particle size is reduced when the pigment particles pass from the flocculated, agglomerated, or aggregated state to the nonagglomerated state. The purpose is to distribute the pigment particles in the liquid medium, so that the final product consists of fine primary particles distributed evenly throughout the medium, and to stabilize the particles in this state; stabilization refers to the maintenance of the disperse state in the finished coating material.

The dispersion process includes the wetting of the pigment particles, during which the solid/air interface on the agglomerated or aggregated particles will be changed to solid/liquid interfaces, as well as the disruption or breakdown of the agglomerates, and the stabilization stage.<sup>[4-4]</sup>

Stabilization of the obtained status, i. e., prevention of flocculation, is an important condition for optimal paint properties. An optimized dispersion status supposes therefore not only a good dispersion, but likewise an optimum dispersion stability. The following paint properties are largely related to the dispersion stability:

- stability during storage
- application properties of the liquid paint
- gloss level and stability during exposure
- opacity and colour development
- colour and colour stability

The maximum degree of dispersion, as a function of the energy expended, is expressed as follows:

$$D_{\max} = 1/E_{\min} \quad (1)$$

where  $E_{\min}$  is the minimum energy required theoretically, and  $D_{\max}$  is the maximum degree of dispersion.<sup>[4-4]</sup>

Dispersion is, consequently, expressed in units of mass per energy, and is therefore a direct measure of the quantity of powdered material that can be dispersed in the liquid medium by applying a defined amount of energy. As there is no practical procedure with 100% efficiency, an efficiency factor  $K_{\text{eff}}$  must be used for practical conditions:

$$D_{\text{eff}} = K_{\text{eff}}/E_{\min} \quad (2)$$

where  $0 < K < 1$ .

Theoretically,  $E_{\min}$  is the energy that must be applied to break down the interactions between the particles. However, it is very difficult to measure due to the different superimposed individual processes using or setting free additional energy. In fact, during the dispersion process only a small part of the applied energy is efficiently used;<sup>[4-5]</sup> in practice  $K$  has a value between ca. 0.001 and 0.04.

#### 4.1.3.1 Pigment Wetting

Pigment wetting is the replacement of a pigment/air interface by a pigment/medium interface.

Powdered pigment particles contain a layer of adsorbed water or air, depending on the hydrophilicity of the pigment surface. As commercial pigments are not supplied as primary particles, but as agglomerates and flocculates, there are various cavities between the pigment particles. These cavities are filled with air or water.<sup>[4-6, 4-7]</sup>

An average  $\text{TiO}_2$  pigment contains for every 4 parts (by volume) of the  $\text{TiO}_2$  pigment powder ca. 3 parts (by volume) of air! This means that the pigment is found in a pigment volume concentration of only 25%, distributed in air! During the wetting process these air/water quantities must be replaced by the liquid phase in which the pigment is dispersed. The adsorption energies of the solvents or resins are usually ineffective for obtaining a completely wetted pigment-particle surface.

### Wetting Theory

Wetting procedures used depend on the characteristic properties of the liquid phase and the pigment surface, as well as the size of the cavities within the agglomerates, and the mechanical process conditions for dispersing all the components.

The classical account of wetting starts with the geometry of a small amount of liquid placed on a solid. Fig. 4.1-2 represents a liquid in equilibrium with its vapour, where  $\theta$  is the equilibrium contact angle. The equilibrium relationship describing the system is given by the Young-Dupré equation:

$$\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cdot \cos \theta \quad (3)$$

or, differently expressed:

$$\cos \theta = (\gamma_{sv} - \gamma_{sl})/\gamma_{lv} \quad (4)$$

where:

$\gamma_{sv}$  = interfacial free energy of solid/air

$\gamma_{sl}$  = interfacial free energy of solid/liquid

$\gamma_{lv}$  = interfacial free energy of liquid/air

$\theta$  = the equilibrium contact angle between the solid and liquid phases

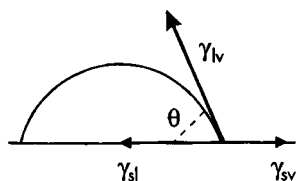
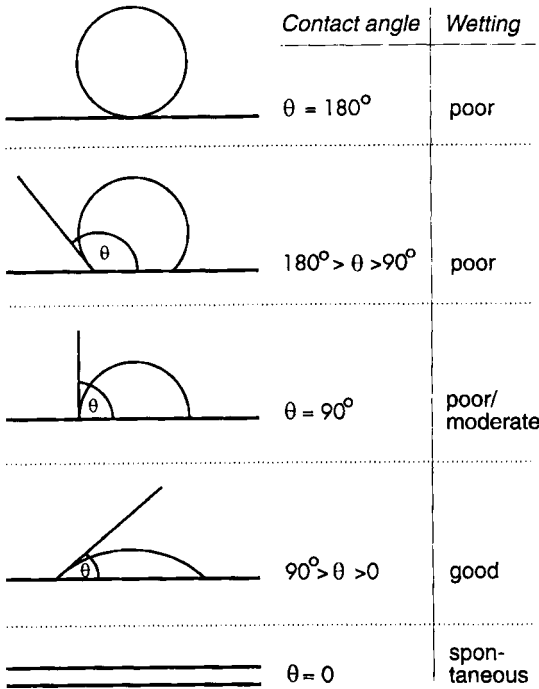


Figure 4.1-2. Contact angle according to Young

If  $\theta < 90^\circ$ , wetting is improved when  $\gamma_{lv}$  is reduced (Fig. 4.1-3). From this follows the conclusion that the use of wetting agents is to be recommended, since it reduces both  $\gamma_{lv}$  and  $\gamma_{sl}$ . Unfortunately, wetting is more complicated, and involves several important wetting processes.

A simplified picture of the wetting processes occurring when a particle is immersed in a liquid may be obtained by considering a cube. According to Parfitt,



**Figure 4.1-3.** Contact angle and wetting

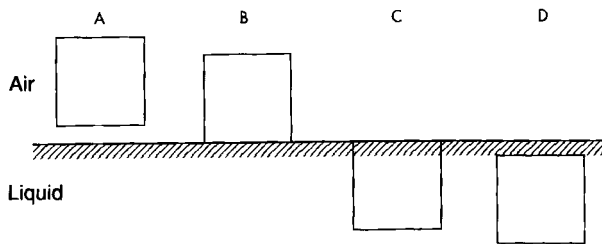
the wetting process of a solid surface in a liquid medium is divided in three stages<sup>[4-8]</sup> (Fig. 4.1-4):

- adhesion (a change from A to B in Fig. 4.1-4)
- immersion (a change from B to C in Fig. 4.1-4)
- spreading (a change from C to D in Fig. 4.1-4)

The work required to wet the surface of a 1 cm<sup>2</sup> area is indicated by the difference in the interfacial energy before and after the wetting:

$$W_d = \gamma_{sl} - \gamma_{sv} \tag{5}$$

$W_d$  = total work required for dispersion



**Figure 4.1-4.** The wetting process

The work of dispersion is the sum of the work of adhesion ( $W_a$ ), work of immersion ( $W_i$ ) and work of spreading ( $W_s$ ):

$$W_d = W_a + W_i + W_s \quad (6)$$

Although  $W_d$  could have been predicted in terms of total expenditure of energy, it is useful to split the process into three parts to enable the cause of poor wetting to be determined. With equation (3), and assuming that the solid surface is in equilibrium with the vapour of the liquid, it can be shown that the appropriate work of adhesion term is related to the energy changes as follows:

$$W_a = \gamma_{sl} - (\gamma_{lv} + \gamma_{sv}) = -\gamma_{lv} (\cos \theta + 1) \quad (7)$$

Exactly the same can be done for the work of immersion  $W_i$ :

$$W_i = 4\gamma_{sl} - 4\gamma_{sv} = -4\gamma_{lv} \cos \theta \quad (8)$$

and for the work of spreading  $W_s$ :

$$W_s = (\gamma_{sl} + \gamma_{lv}) - \gamma_{sv} = -\gamma_{lv} (\cos \theta - 1) \quad (9)$$

These equations may be used to predict whether or not any particular stage of the process is spontaneous, i. e., has a negative work term. Adhesional wetting is spontaneous ( $W_a$  negative) when  $\theta < 180^\circ$ , i. e., in all practical instances; the immersionsal wetting is only spontaneous at  $\theta < 90^\circ$ , and spreading only at  $\theta = 0^\circ$ . The total wetting process of outer surfaces is only spontaneous if the contact angle,  $\theta = 0^\circ$ . In all other cases a substantially larger amount of work is necessary to achieve complete wetting. By addition of surface-active substances, the contact angle is reduced and this reduces the amount of work required for the wetting.

The penetration process of the liquid into the agglomerate cavities is extremely complicated and highly dependent on the geometry of the solid. In the simplest case, a cylindrical tube with a homogeneous profile and in the absence of air, the penetration is only spontaneous if  $\theta < 90^\circ$ . However, in practice the cavities usually contain air and the air pressure increases substantially during the penetration of the liquid. If the liquid penetrates through the cavities only once, this would result in a higher air pressure inside the agglomerate, making complete wetting extremely difficult. With included air complete wetting only occurs when  $\theta = 0^\circ$ .<sup>[4-9]</sup>

It has been assumed that the solid (pigment) particle is available as discrete particles. However, when pigments are immersed in a liquid medium they enter as air flocculates, which contain a complex network of pores and channels between and inside the agglomerates. The permeation of the liquid medium into this structure is much more difficult than the wetting of a smooth surface.

For horizontal capillaries or in general cases where gravity may be neglected, the rate of penetration of a liquid into a tube is given by the Washburn equation:

$$l^2 = r \cdot t \cdot \gamma_{lv} \cdot \cos \theta / 2\eta \quad (10)$$

where:

- $l$  = the depth of penetration at time  $t$
- $\eta$  = the viscosity of the liquid medium
- $\gamma_{lv}$  = surface tension liquid/air
- $\theta$  = contact angle
- $r$  = pore radius

For a packed bed of pigments, the radius  $r$  from equation (10) may be replaced by a factor  $K$ , which contains an “effective radius” for the bed and a tortuosity factor taking into account the complex path formed by the channels in the pigment mass. Thus:

$$l^2 = K \cdot t \cdot \gamma_{lv} \cdot \cos \theta / 2 \eta \quad (11)$$

Equation (11) shows that the penetration of a liquid into the powder particles is easier for larger  $K$ . Therefore, loosely packed particles with macropores – typical for coarse pigment powder particles – will be wetted much faster than finely packed powder particles. The wetting of the finest pigment powder particles will therefore always be more difficult than the wetting of homogeneous pigments with coarse particles.

Penetration is also assisted by high surface tension of the liquid medium, low contact angle, and low viscosity. Unfortunately a high surface tension of the liquid medium and a low contact angle are usually incongruous but of the two a low value for the contact angle,  $\theta$ , is probably more important.

The surface tension is related to the individual surface tensions of the liquid components as well as the ratios of the components. A practical way to adapt the surface tension is to increase the resin concentration; in case of relatively polar resin solutions this may result in a higher surface tension of the liquid medium.<sup>[4-10]</sup> In practice it is necessary to find a compromise between binder concentration and surface tension.

The smaller the contact angle, the easier the penetration of the liquid into the pores takes place. Surfactants – here functioning as wetting agent – can reduce the contact angle significantly. Thus wetting agents strongly affect the breakdown of the flocculates, agglomerates, and aggregates, reducing the required energy for the dispersion process and increasing the dispersion speed.

Typical wetting agent used in practice are surface-active agents of low molecular mass and containing various (with different chemical compositions) anchoring groups in the same molecule. These various anchoring groups are required to offer adsorption sites for differently composed pigment surfaces (known as “multifunctional wetting agents”).

During the pigment-wetting process the wetting of the pigment particles leads partially to a spontaneous division of the pigment flocculates and most of the agglomerates. The remaining agglomerates and units are broken down mechanically.

### 4.1.3.2 Mechanical Disruption

After the pigment particles have been partially wetted, the next stage is the dispersion process where the pigment flocculates, agglomerates, and aggregates are broken up into smaller particles. The interactions between the solid particles can be overcome by mechanically induced force. As a rule, deflocculation is easy and can be accomplished by simple agitation, but the breakdown of aggregates and agglomerates requires a greater input of mechanical energy. Deagglomeration is brought about by shearing and comminution.

The type of dispersing equipment largely determines the milling conditions and the efficiency of the disruption process. For easily dispersible systems the dissolver is frequently used. Here the dispersion efficiency is related to the viscous drag of the millbase.

To disperse fine particles or to grind hard pigments in poor grinding medium it is not sufficient to simply disperse with the dissolver. In these cases, high-speed agitators, pearl mills or ball mills have been particularly successful as dispersion devices.<sup>[4-1]</sup>

The part played by additives such as wetting and dispersing agents is quite complex. Under suitable conditions a given degree of reduction of flocculated and agglomerated particles is achieved more rapidly. The additives function by improving the wetting and helping to maintain the stability of the dispersion; the just disrupted particles must be stabilized immediately to avoid reflocculation or reagglomeration.

### 4.1.3.3 Stabilization

In the absence of repulsive forces, freshly disrupted and suspended pigment particles will flocculate in response to attractive forces. The dispersed pigment particles must be protected from flocculation, not only during the production process of the coating material, but also during storage and application to avoid problems such as colour deviations, sedimentation, change in viscosity, etc. A main function of the pigment dispersing agent is to maintain the dispersed pigment particles in the deflocculated state.

Brownian movement results in continuous collisions between the pigment particles of dispersed systems. Insufficient stabilization of the particles can therefore result in reflocculation.<sup>[4-2]</sup>

During the approach between two dispersed pigment particles interactive forces, both attractive and repulsive, operate between the particles. Attractive forces between the dispersed pigment particles are:

- London–van der Waals forces, i. e., intermolecular forces with ranges equivalent to the diameters of a few molecules. These are electromagnetic attractions, resulting from interactions between the dipoles in the particles. London–van der Waals forces are the dominant attractive forces in colloidal dispersions. Colloidal dispersions typically have maximum particle sizes of 1  $\mu\text{m}$ . These London–van der Waals attractive forces are weaker than ionic or covalent bonds, but are effective when the distance between the particles is less than 1  $\mu\text{m}$ ; as the interparticle dis-

tance decreases the attractive effect increases rapidly to a maximum. The strength of this attractive force depends also on the typical properties of the particles as well as the dispersion medium. Usually the strength of this force is proportional to the particle size and inversely proportional to the distance between the particles:

- polymer bridging in the case of adsorbed polymers
- hydrogen-bonding; the range of this attractive force is shorter than that of the London–van der Waals force, however, the bonding strength is greater
- electrostatic attractive forces or Coulombic forces, associated with opposing charges on the pigment surfaces

In addition, the stabilization of pigment particles coarser than 1  $\mu\text{m}$  is largely influenced by gravitation forces.

Dispersing agents modify the electric charge on the surface and can introduce steric barriers that increase the stability. They can also alter the adsorption characteristics of the surface, to increase the adsorption of polymeric materials, thus increasing the barriers to flocculation.

Effective repulsive forces leading to stabilization effects are:

- Electrostatic repulsion between charged particles. This mechanism for stabilizing a dispersion, where ionic repulsive forces dominate, is known as “electrostatic” or also as “Coulombic stabilization” (Fig. 4.1-5).
- Steric repulsion between layers of adsorbed solvated polymers on adjacent pigment particles, creating a steric barrier (steric stabilization) (Fig. 4.1-6).

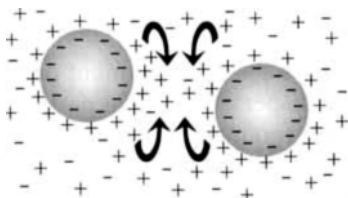


Figure 4.1-5. Electrostatic stabilization

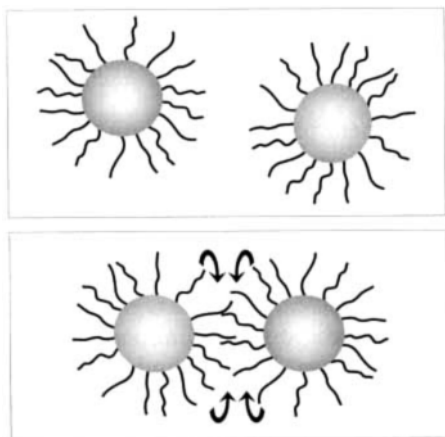


Figure 4.1-6. Steric stabilization

### Electrostatic Stabilization: DLVO Theory

Stabilization of dispersions by electrostatic repulsion is possible if the dispersed particles possess a homogeneous electrical charge. This charge can be developed in different ways. The following three mechanisms usually contribute:

- dissociation of ionic groups on the particle surface
- adsorption of only one type of ion or adsorption of oppositely charged ions of different dimensions
- when the dissolved counterions are present in uneven quantities

The classical theory that describes the interaction between London–van der Waals attractions and the electrostatic repulsive forces is known as the DLVO theory and was proposed independently by Derjaguin and Landau and Verwey and Overbeek.<sup>[4-11]</sup>

The DLVO theory is a quantitative concept of dispersion stability and can be summed up as follows: the dispersed particles are subject to three extended forces which influence the possibility of two particles meeting accidentally by random Brownian movement, to come into close contact. The forces considered are:

- London–van der Waals attractive forces
- electrostatic repulsion between electrical double layers of the same charge
- entropic repulsion

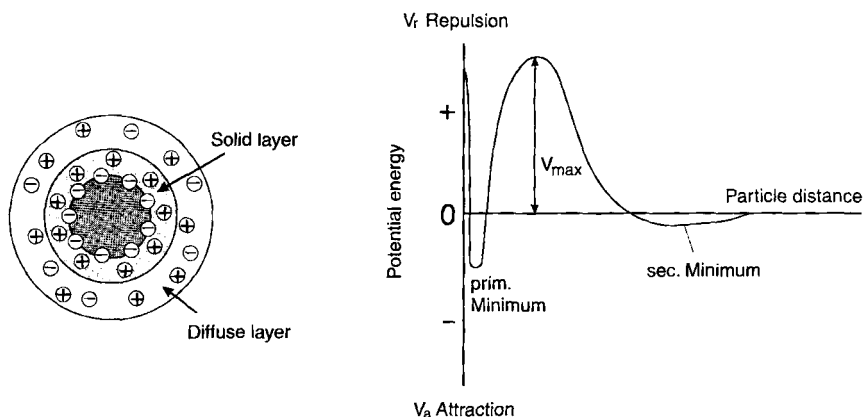
These forces arise from completely different sources and their values can be measured separately. Interaction between particles is the added total of the forces, divided by the distances between the particles. The interaction between two charged particles is determined by the overlap of their electrical double layers, which causes the repulsion. If the attraction exceeds the electrostatic repulsion, the dispersion will not be stable. If the electrostatic repulsion exceeds the attraction, and the level of the resulting energy barrier is larger than  $kT$  (thermal energy), then the rate of flocculation is nearly zero (Fig. 4.1-7).

Fig. 4.1-7 illustrates how  $V_a$  (attractive forces) exponentially decrease with increasing distance relative to the thickness of the electrostatic double layer. Nearly the opposite dependency of  $V_a$  in relation to the square of the particle distance<sup>[4-12]</sup> is found. The course of the curve for the total potential energy is largely determined by  $V_r$  (sum of the repulsive forces) and depends therefore greatly on the electrolyte concentration.

The total interaction of particles containing ionically adsorbed surfactant layers (with negligible contribution of entropic stabilization) is given by the DLVO theory as:

$$V_{\text{tot}} = V_r + V_a \quad (12)$$

The  $V_{\text{tot}}$  (sum of the attractive and repulsive forces) curve for dispersions in aqueous systems always contains two minima. The first minimum occurs for tightly connected particles, i.e., particles that are difficult to separate. The second minimum results from a more loosely connected structure (floculates), which can be



**Figure 4.1-7.** Electrostatic stabilization mechanism (DLVO theory)

destroyed by a relatively small energy input, such as low shear forces, since the particles are held together by relatively weak attractive forces. Under these circumstances the dispersion may form a three-dimensional gel network structure which can be deflocculated by shaking. When the shear forces are no longer applied, the structure will be regained (thixotropic system). A second minimum is theoretically not possible for colloidal particles in a solvent medium with a low dielectric constant, unless factors other than the charge involvement operate.

If  $V_{\max}$  is high and  $V_{\min \text{ sec.}}$  is shallow, a deflocculated dispersion is produced. This is the case when the surface charge is high (as a result of adsorbed dispersing agent molecules) and the electrical concentration is low.

On the other hand, if  $V_{\max}$  is low ( $<5-10 \text{ kT}$ ) or absent, the dispersion will flocculate, as the particles are able to surmount the energy barrier and enter the deep primary minimum. This is the case when there are only few dispersant molecules on the surface and/or if a high concentration of electrolyte is present. If the energy from collisions between the particles, induced by Brownian movements or mechanical influences, is large enough so that the repulsive energy maximum can be exceeded, the particles agglomerate or form aggregates. A large amount of energy is required to break these agglomerates apart again.

The zeta potential of the solid particles in the suspension determines the electrostatic stability of colloids. An effective dispersing agent would increase the zeta potential on the pigment/extender surface to a net negative charge so that the repulsive forces will exceed the attractive forces. If two mutually immiscible phases such as the liquid phase (solvent) and a solid phase (pigment) change their positions relative to each other, the ions of the diffuse part of the electrochemical double layer will participate in the movement of the liquid phase. However, the ions of the dense layer around the solid phase would keep its position relative to the solid phase. The participation of the ions of the diffuse layer in the relative liquid movement will not be indicated by the total interphase potential (thermodynamic potential), it is shown exclusively by the portion representing the potential decrease of the diffuse layer.

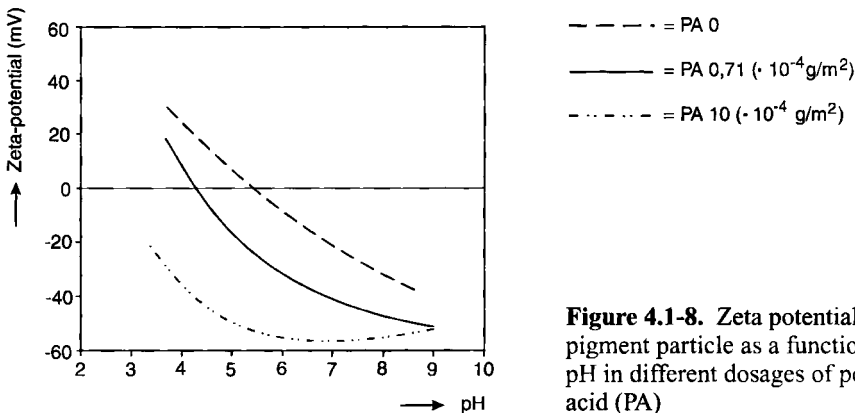
This potential is known as the zeta potential. The zeta potential is defined as the potential across the interface of all solids and liquids; it is the potential across the diffuse layer of ions surrounding a charged colloidal particle (see Fig. 4.1-7). The zeta potential is largely responsible for colloidal stability. The zeta potential is also known as the electrokinetic potential.

Surface potential cannot be measured directly, but its main component, involving repulsive forces, the zeta-potential, can be calculated from measurements of the suspended particle mobility in an electric field (i. e. from electrophoresis or moving boundary experiments):<sup>[4-13]</sup>

$$\zeta = 4 \pi \eta U / H \varepsilon \quad (13)$$

where  $\zeta$  is the zeta potential,  $\eta$  is the viscosity of the dispersion medium,  $U$  is the electrophoretic mobility,  $H$  is the electrical intensity of the external electrical field, and  $\varepsilon$  is the dielectric constant of the dispersion medium.

Because the zeta potential is measured some distance from the particle surface (e. g., 5 Å), this potential is the sum of the surface potential and the charges of adsorbed substances and charged adsorbed assistant materials or impurities. The zeta potential is therefore a result of all charges surrounding the particle and is a good measure for electrostatic stabilization. In Fig. 4.1-8<sup>[4-14]</sup> the zeta potential of a rutile titanium dioxide pigment ( $\text{TiO}_2$ ) is represented as a function of the pH, measured in different initial concentrations of the dispersing agent polyacrylic acid (PA). Without PA the  $\text{TiO}_2$  is positively charged at pH 5.7 and negative at a higher pH value. The zeta potential always becomes more negative when PA is used. The PA consequently also adsorbs on a surface with a (low) negative charge! This means that the adsorption of polyacrylic acid on the oxide surface is not exclusively the result of an electrostatic interaction. Surfactants based on strong acids like sulfonates or sulphates usually produce higher zeta potentials than polycarboxylates. For stable aqueous dispersions the zeta potential is normally in the range of -50 to -100 mV.



**Figure 4.1-8.** Zeta potential of a pigment particle as a function of the pH in different dosages of polyacrylic acid (PA)

### Steric Stabilization

Steric stabilization encompasses all aspects of stabilization of colloiddally distributed particles by non-ionic macromolecules and is applicable to both aqueous and nonaqueous systems.

The following factors are important for the effectiveness of the steric stabilization:

- structure of the adsorbed layer
- thickness of the adsorbed layer
- preferentially adsorbed segments and their adsorption density

The polymer molecule is adsorbed at the solid/liquid interface; it is connected to the solid-particle surface (e.g., pigment) by various anchoring segments in the polymer molecule. Other parts of the same molecule remain dissolved in the liquid phase. We consequently differentiate between “adsorbed” and “dissolved” segments.

The concentration of the solvated segments of the adsorbed layer is highest directly on the surface; this concentration decreases with the distance from the surface. If two particles with such adsorbed layers approach each other, the first contact is between the surfaces of the adsorbed layers. The relatively low polymer concentration first allows the diffuse polymer layers of both particles to be penetrated. This process also causes the polymer concentration in the overlap layer to increase.

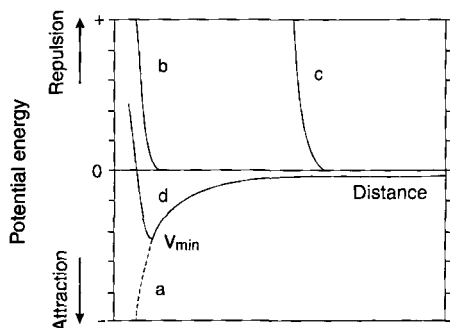
If the polymeric layers are superimposed, the free energy of the mixture of polymer and liquid medium increases. Due to the osmotic pressure difference between the overlap layer and the ambient liquid phase, the solvent tends to diffuse into the zones between the particles and to disperse the particles until the zones no longer overlap. This causes repulsion between the particles,<sup>[4-15]</sup> resulting in stabilization. This stabilization mechanism is called osmotic stabilization.

If the particles are pressed together until the distance between two particles is lower than the total thickness of the two adsorbed layers, this results in a compression of the layers. This reduces the number of configurations of the polymer molecules in these layers, in other words, the entropy is reduced.

Both the mutual penetration and the compression of the adsorbed layers result in repulsion between the particles. This repulsive force easily exceeds the London–van der Waals attraction. A minimum,  $V_{\min}$ , in the interaction curve (Fig. 4.1-9) is reached. This curve represents the influence of the distance between two sterically stabilized particles on their interaction energies.

The size of the minimum,  $V_{\min}$ , depends on the thickness of the adsorbed layer as well as on the van der Waals attraction at this distance. If a layer is not thick enough, the repulsion will only be significant at a distance where the van der Waals attraction already predominates; it results in a net attraction: the dispersion flocculates or agglomerates when the minimum of the interaction curve is reached.<sup>[4-16]</sup>

The thickness of the adsorbed layer therefore determines the stability; in order to obtain sufficient stabilization by adsorption of polymers, the nonadsorbed parts of the molecules must be well solvated and completely soluble in the liquid phase. If that is not the case, the adsorbed layer shrinks, the thickness of a layer decreases and the particles will flocculate.



**Figure 4.1-9.** Interactions between two sterically stabilized particles  
 a = Van der Waals attractive forces  
 b = Steric repulsion by adsorption of a thin layer  
 c = Steric repulsion by adsorption of a thick layer  
 d = Sum of a and b

As a general rule, the structure of the adsorbed layer and the medium should be relatively similar. This is the case for, e. g., solvated layers.<sup>[4-17]</sup> In practice this is very important and a major criterion when selecting pigment dispersants for coatings.

Dispersing agents that immobilize and solubilize the solvent molecules easily into the adsorbed layer of the dispersant should be chosen. On the other hand, this also shows that the solvent/binder composition is important for achieving optimum dispersing efficiency.

In polar systems, the salt concentration in the continuous phase also largely determines the stabilization effectiveness of the adsorbed polyelectrolyte layers. High salt concentration reduces the thickness of the adsorbed layer and thus the stabilizing effect. Next to steric effects the electrostatic effects also play a significant role under these conditions. Electrical effects of adsorbed layers contribute considerably to the stabilization of a dispersion, even in nonpolar media. However, this does not mean that adsorbed layers always lead to repulsion and thus an increase in the stability of two approaching particles. Adsorbed polymer layers can also cause the reverse, namely increasing attraction between two particles. Such phenomena are well known for particles coated with homopolymers.<sup>[4-12]</sup> This is because two particles may be bridged by one polymer molecule.

### Energetic Effects of Steric Stabilization

The core of the theory of steric stabilization is the interactions between the adsorbed polymer chains of two pigment particles approaching each other. An adsorbed layer has many features in common with a polymeric solution. Therefore, the interaction of two adsorbed layers on two particles approaching each other can be described by applying the characteristics of polymer solutions. If the polymer layers overlap, the free energy of the mixture of polymer and solvent increases, resulting in repulsion between the two particles. The repulsive energy becomes stronger if the particles continue approaching one another.<sup>[4-6]</sup> The free energy of this process,  $\Delta G_r$ , depends on the change in enthalpy ( $\Delta H_r$ ) and entropy ( $\Delta S_r$ ):

$$\Delta G_r = \Delta H_r - T\Delta S_r \quad (14)$$

The sign and absolute value of the free energy are determined by the contribution of both enthalpy and entropy. If  $\Delta G_r = 0$ , the flocculation behaviour is as if no adsorbed layers are present. If the free energy has a positive value, no flocculation takes place. One of the following three conditions must be fulfilled for a positive free energy and as a requirement for a stable dispersion:

- The entropy ( $T\Delta S_r$ ) and the enthalpy proportion are both negative, but the first term has a larger absolute value. This stabilization is known as entropic stabilization which means that the freedom and the number of configurations of the polymer molecules in the adsorbed layer is strongly reduced.
- Both terms are positive, and the enthalpy portion is larger (so-called enthalpic stabilization).
- $\Delta H_r$  is positive and  $\Delta S_r$  is negative. Both energies are then involved in stabilization (entropic/enthalpic or combined stabilization).

Electrostatic stabilization is a very effective in polar media, e. g., in waterborne paints. In nonpolar media, such as most organic-solvent-based systems, steric stabilization is the more effective way of stabilizing pigments against flocculation. Dispersing agents contribute for both stabilisation mechanisms significantly to the improved stability of dispersions.

#### 4.1.3.4 Stabilization in Polar Media: Practical Evaluation

The stability of dispersions in polar media is effectively improved if the adsorbed molecules make the particle surface electrostatically charged. A surface charge can be created, for instance, by adsorption of anionic dispersing agents onto pigment surfaces dispersed in water. When two particles with the same charge come into close proximity, they repel each other due to repulsive forces resulting from a charged electrical double layer surrounding the pigment particle (electrostatic or Coulombic repulsion, see Section 4.1.3.3 and Fig. 4.1-5).

Low-molecular-weight polycarboxylates have proved to be very effective dispersing agents in polar systems.<sup>[4-5]</sup> They are able to prevent flocculation by using both the stabilization mechanisms:

*Electrostatic Repulsion:* Polycarboxylates are negatively charged molecules in a polar medium and show a strong affinity for mainly hydrophilic pigments and extender surfaces. Upon adsorption onto the pigment surface, a diffuse double layer develops around the particle, increasing its total charge, and therefore also the repulsion.

*Steric Repulsion:* The polymeric structure enables the formation of a relatively thick layer around the pigment particle (depending on the molecular structure, the proportion of adsorbing groups and the molecular mass).

When an aqueous coating material forms a film, the polarity is generally decreased as the water evaporates; thus the contribution of the electrostatic repulsion to the stabilization diminishes as well. Especially when the water content in the drying film is strongly reduced, but the film is still liquid (and the ingredients are highly

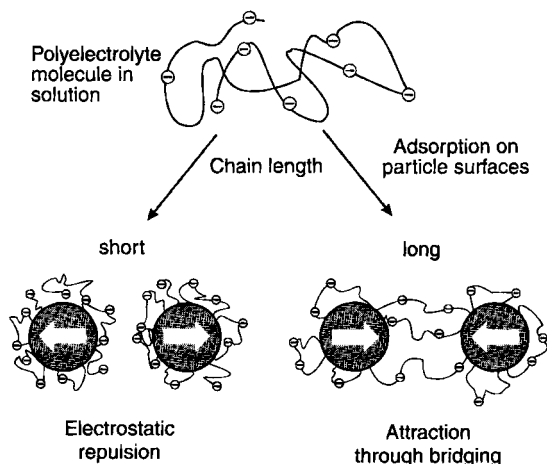
mobile), the dominating contribution to the stabilization shifts to the steric stabilization effect of the polymeric dispersing agent.

Polyelectrolytes such as the sodium or ammonium salts of homo- and copolymers of acrylic acid, methacrylic acid, or maleic acid have proved to be very suitable for this application. These polyelectrolytes are strongly adsorbed onto the pigment or extender surface; the high density of the carboxylate units per molecule presents strong anchoring for each molecule to the pigment or extender surface.<sup>[4-4]</sup>

The dispersion-stabilization effectiveness is related to the molecular mass of the polyelectrolyte dispersing agent; the optimum  $M$  is ca.  $8000 \text{ g mol}^{-1}$  for pigments and extenders that are commonly used in paints. Dispersing agents with this average molecular mass result in the lowest minimum viscosities for particular millbases (see Section 4.1.6.2), because they have the best deflocculating and stabilizing effects. Increasing the molecular mass of the polymer results in higher millbase viscosities and reduced stabilization. Larger quantities of such dispersing agents will also be necessary to reach the minimum viscosity. Moreover these high molecular mass polymers may act as flocculating agents (Fig. 4.1-10).

In practical applications, polyacrylate-based dispersing agents may be used in combination with polyphosphates. Polyphosphates are particularly useful in applications where the pigment is dispersed in an aqueous medium of very hard water; the polyphosphate complexes the calcium ions, thus reducing the electrolyte concentration in the aqueous medium and reducing the flocculation stage, to improve the stabilization of the dispersion. Under these conditions the polyphosphates assist the dispersing agents by supporting the electrostatic stabilization effect (see Section 4.1.4.1 for chemical compounds).

Polymeric dispersing agent with the lowest polydispersibility are the most effective. The lower molar mass fraction supplies insufficient quantities of counterions, whereas the higher fraction may function as a flocculant, bridging the distance between two particles and thus bringing about flocculation. For the optimum dispersing agent efficiency, the dosage is critical, and it may easily be determined by a titration procedure (see Section 4.1.6).



**Figure 4.1-10.** Polyelectrolytes as dispersing and flocculating agents

#### 4.1.3.5 Stabilization in Nonpolar Media: Practical Evaluation

The organic solvents used for coating materials are less polar and have smaller dielectric constants than water. Although the contribution of electrostatic stabilization in such nonpolar systems should not be neglected (a small charge can already cause a high surface potential<sup>[4-18]</sup>), dispersed pigment particles in these solvents are primarily stabilized against flocculation by steric effects, resulting from adsorbed polymer layers on the particle surfaces. The particles are mutually repulsed due to enthalpy and entropy changes owing to penetration or compression of the adsorption layers (Section 4.1.3.3). Because the repulsive forces are only effective in the adsorption layer region, steric stabilization requires an optimum adsorbed-layer thickness. London–van der Waals attractive forces have a large range, but the strength decreases strongly with increasing distance.

For effective steric stabilization several conditions need to be fulfilled, such as:

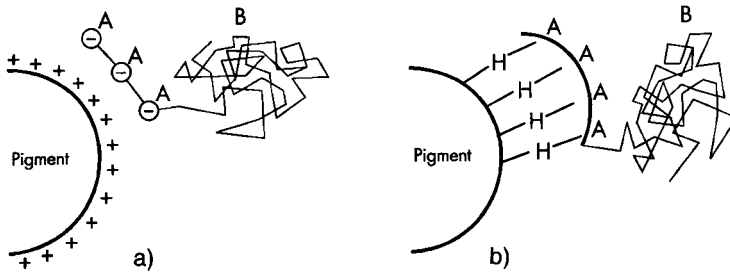
- complete coverage of the pigment surface with adsorbed molecules
- the adsorbed layer must be strongly anchored onto the surface and may not be desorbed during, e. g., collisions of the pigment particles or dispersion dilution
- the adsorbed layer thickness must be sufficient
- the adsorbed layer must consist of molecules that direct into the liquid medium in a stretched form and carry a solvated chain, in order to build up maximum layer thickness<sup>[4-3, 4-19]</sup>

Polymeric rather than monomeric dispersing agents are capable of meeting with these conditions. To cover the pigment particles completely and bind strongly, high adsorption energies are required per adsorbed molecule. This is best achieved with polymeric materials, as these offer a large number of adsorption contacts with the pigment surface per molecule. This results in a very high total sum of adsorption energies per molecule, even if they are low for the individual adsorption contacts. Statistically, the probability of complete desorption of the molecule is very low. This is in contrast to the adsorption of a monomeric surfactant, adsorbed with only one linkage per molecule to the surface.

Compared to copolymers, homopolymers are less effective steric stabilizers. A homopolymer chain tends to associate preferentially either with solvent molecules or with the pigment surface. For copolymers the structure can be designed in such a way that one segment of the polymer preferably adsorbs onto the pigment whereas the other segment is strongly associated to the liquid phase.

For nonaqueous coating materials, double-block-polymeric pigment dispersing agents of the AB type are particularly suitable. The A segment is made up of multiple short anchoring groups with many anchoring sites for adsorption.<sup>[4-20, 4-21]</sup> The composition of segment A may be chosen according to what gives the best interaction with the specific pigment surface. Segment A may adsorb by ionic- or hydrogen bonding (Fig. 4.1-11).

Typical anchoring functional groups for the A segment are carboxyl, amine, sulphate, and phosphate for ionic anchoring or polyether and polyamide for hydrogen bonds.

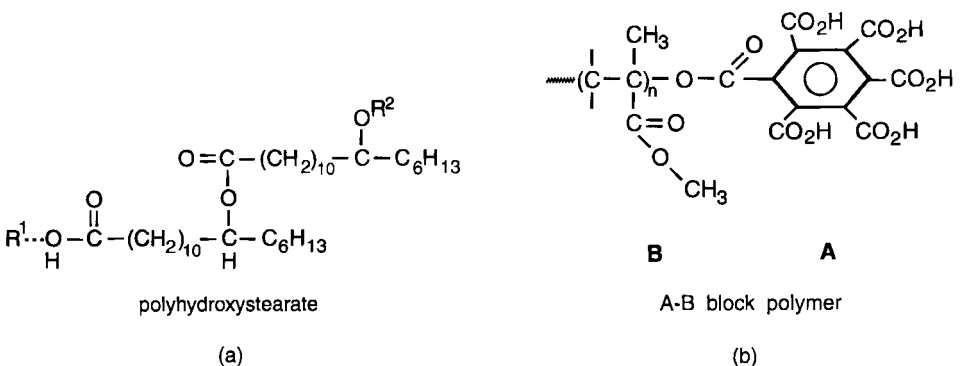


**Figure 4.1-11.** Adsorption of AB copolymers: (a) by ionic bonding, (b) by hydrogen bonding

The B segment represents the solvated side chain and is thus the stabilizing part of the molecule. A most important requirement for B is that it forms a sufficiently thick layer on the pigment particle, i. e., the B segment needs to dissolve thoroughly to be completely mobile in the liquid phase. The side chains on the pigment surface fold up with decreasing solubility. This decreases the thickness of the film and consequently also the stabilizing ability. This solubility is also important during the drying phase of the paint, because otherwise the pigments may flocculate in the drying layer.

To stabilize pigment particles with a standard particle size of 0.1 to 10  $\mu\text{m}$ , a film thickness of 5 to 20 nm is sufficient. Stabilization is possible with side chains with molecular masses of  $M = 1000$  to  $15000 \text{ g mol}^{-1}$ .<sup>[4-2, 4-19, 4-21]</sup>

The film thickness can be optimized further if the B segment and the dispersion resin are completely coordinated. In such a case, the dispersing resin will be strongly associated with the polymeric stabilizer molecules and it will be concentrated around the pigment particles. Suitable polymers for segment B are specially modified polyacrylates and polyhydroxystearates (Fig. 4.1-12).



**Figure 4.1-12.** Polymeric dispersing agents: (a) polyhydroxystearates, (b) AB mass polymer

#### 4.1.4 Chemical Composition of Wetting and Dispersing Agents

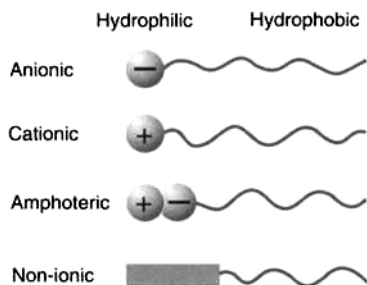
Wetting and dispersing agents are amphiphilic surface-active agents, also abbreviated as surfactants. Amphiphilic surfactants are defined as “chemical compositions, which, if dissolved or dispersed in a liquid phase, adsorb on the interfaces and cause there a number of physico-chemical properties or chemical properties, which are of practical importance.”

The adsorption on the interface results in a decreased surface or interfacial tension. This is the underlying property determining the action of surfactants as wetting and dispersing agents.

The characteristic amphiphilic structure refers to the presence of both one or several hydrophobic (lipophilic) groups as well as of one or several hydrophilic (lipophobic) groups in one surfactant molecule. Due to this structure, the surfactants are concentrated on the interface between a polar and a nonpolar phase, whereby the hydrophilic part of the molecule turns to the polar part at the interface and the hydrophobic part to the nonpolar part.

If the hydrophilic segment in the surfactant molecule dominates, the product will be water-soluble. If the hydrophobic part predominates, the compound will be less water-soluble or even water-insoluble. If the hydrophobic and hydrophilic parts are adjusted, the surface activity which is necessary for the system is achieved.



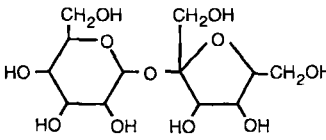
Schematically surface-active compounds may be represented by a tail-head model (0-). In this model, the tail (-) symbolizes the hydrophobic group and the head (0) the hydrophilic group (Fig. 4.1-13).



**Figure 4.1-13.** Surface-active compounds

Some typical compositions used for the hydrophobic and hydrophilic groups in surfactants as wetting and dispersing agents are represented in Fig. 4.1-14. Surfactants are characterized by the chemical structure of their hydrophilic groups. These groups can be either ionic or non-ionic.<sup>[4-22]</sup> The following classification is useful:

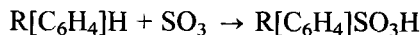
- anionic surfactants
- cationic surfactants
- non-ionic surfactants
- amphoteric surfactants

Hydrophobic group 	Hydrophilic group or compound 
$C_nH_{2n+1}^-$	$-COO^\ominus K^\oplus$
$C_nH_{2n-1}^-$	$-SO_3^\ominus Na^\oplus$
$C_nH_{2n+1}^- C_6H_4^-$	$-PO_3^\ominus 2Na^\oplus$
$C_nF_{2n+1}^-$	$-OSO_3^\ominus Na^\oplus$
	$-OPO_3^{2\ominus} 2Na^\oplus$
	$-(OCH_2CH_2)_nOSO_3^\ominus NH_4^\oplus$
	$-(OCH_2CH_2)_n-OH$
	$-CON[(OCH_2CH_2O)_nOH]_2$
	
	$-N(CH_3)_2$
	$-NR_3^\oplus Cl^\ominus$
	$-PR_3^\oplus Cl^\ominus$
	$-SR_2^\oplus Cl^\ominus$
	$-\overset{\ominus}{N}(CH_3)_2CH_2COO^\ominus$

**Figure 4.1-14.** Some examples of hydrophobic and hydrophilic groups or compounds

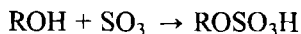
Anionic surfactants are amphiphilic compounds, in which the hydrophobic sections are connected to anionic groups. Examples for this are sulphates, sulphonates, phosphates, and carboxylates (soaps). The anionic group is neutralized with cations such as sodium, potassium, ammonium, or amine ions, which only influence surface-active property slightly.

In the sulphonates, the hydrophilic sulphonate group is connected to the hydrophobic part by a carbon-sulphur bond. Sulphonates, such as alkylarylsulphonates, are produced in practice by the reaction between sulphur trioxide,  $SO_3$ , with the alkyl-aryl compound, followed by neutralization of the formed alkylarylsulphonic acid.



Sulphonates are characterized by excellent thermal and chemical stability.

With sulphates, the sulphur of the hydrophilic group is connected to the hydrophobic residuals via oxygen.



Sulphates are stable under alkaline conditions, but more susceptible to hydrolysis under acid conditions and their thermal stability is poorer than that of the analogous sulphonates.

A common procedure for the manufacture of phosphate esters or phosphoric esters is to react an alcohol with phosphorus pentoxide,  $P_2O_5$ .



The number of hydrophobic compounds that may be sulphated, sulphonated, or phosphatized according to the mentioned methods is large and is not exclusively restricted to monomeric hydrophobic groups: polymers may also be sulphated, sulphonated, or phosphatized. Such polymeric surfactants are used as pigment-dispersing agents. The layer thickness obtained through adsorption of, for instance, a pigment-dispersing agent onto a pigment is influenced by the size of the molecule.

The specific properties and use of polymeric dispersing agents were discussed in the preceding paragraphs.

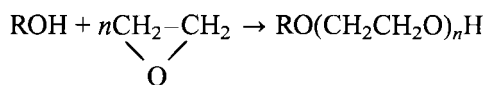
Polycarboxylates are widely used as dispersing agents. Polycarboxylates generally have a much lower surface activity than products like sulphates, sulphonates, or phosphate esters have. However, polycarboxylates are effective stabilizers for pigment dispersions, and effect both electrostatic and entropic stabilization.

Polyacrylates make up one of the most widely used groups of carboxylates for application as dispersing agents. Polyacrylic acid salts are among the primary representatives of the group of synthetic polymeric dispersing agents; they are discussed in Section 4.1.4.1.

Anionic surfactants are widely used as wetting and dispersing agents. In aqueous systems they may stabilize the dispersion electrostatically. However, depending on the structure and the thickness of the adsorbed layer, steric stabilization may also contribute or even dominate. The charged group also functions as an anchor for adsorption onto the pigment surface. This applies to both polar and nonpolar dispersions; the water adsorbed onto the pigment effects dissociation and stimulates the adsorption onto pigments in even nonpolar phases. Anionic dispersing agents generally effect good dispersion stability at low dosages and make the coating layer water resistant, however, they tend to stabilize foam and are pH-, electrolyte-, and temperature-sensitive.

Cationic surfactants are only of minor importance as wetting or dispersing agents in coatings. This is because of their high reactivity with the anionic components, which are widely applied. Amphiphilic compounds, mostly derivatives of fatty amines, with hydrophobic residues in the form of cations, are the main representatives of this group.

Non-ionic surface-active compounds – also known as “non-ionics” – are amphiphilic compounds that cannot dissociate into ions in aqueous solutions. Examples are alkyl polyglycol ether and alkylaryl polyglycol ether. Non-ionics are adducts (addition compounds), that are typically made from ethylene oxide (EO) and/or propylene oxide (PO). These adducts are produced by addition of the EO or PO to mobile protons, catalysed by bases or (Lewis) acids:



Several ethylene oxide molecules can be added to one base molecule such as a fatty alcohol, the polyether adduct formed this way still contains a hydrogen atom.

Hydrophilic (polyethylene) glycols are formed from ethylene oxide and hydrophobic (polypropylene) glycols are derived from propylene oxide.

The polyethylene glycol becomes water-soluble by hydration, e. g., through hydrogen bonds to the polar polyether groups. Upon heating of an aqueous solution of the polyethylene glycol derivatives, the hydrogen bonds break at a characteristic temperature. The solution becomes cloudy, because the molecule has become water-insoluble. The temperature associated with this effect is characteristic for the specific non-ionic compound and is directly related to the chain length of the polyether.

To compare the surface activities of a group of non-ionic ethoxylated compounds, the "HLB system", originally developed by Griffin, is useful. HLB stands for "hydrophilic-lipophilic balance". The HLB system indicates the ratio between the hydrophilic and the hydrophobic or lipophilic (water-repellent) segments in a non-ionic surfactant molecule. HLB is defined as:

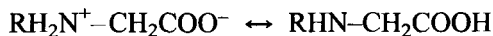
$$\text{HLB} = A/5 \quad (15)$$

where  $A$  = % polyethylene glycol, in weight %, in the molecule

When the user needs to choose an alternative for a specific non-ionic ingredient or mixture, the HLB system enables this to be done according to the characteristic number. However, the HLB value is only a tool for selecting non-ionic surfactants or wetting agents; generally the chemical composition must also be considered. The HLB method is developed and applicable only for non-ionic surfactants and too inaccurate to be used for ionogenic wetting agents. The influence of the charged group is neglected in the HLB system, but it is of decisive importance for the properties of anionic or cationic surfactants.

Non-ionic dispersing agents have the advantage over anionic dispersants of not being sensitive to pH changes. However, because the stabilization mechanism is largely based on steric stabilization, the dosages of non-ionics that are required are much higher than that of charged dispersants to reach a similar stabilization effect. This may result in higher water-sensitivity for the coating.

Amphoteric surfactants have both anionic and cationic groups in the same molecule. The pH value of the solution determines the predominant electrical charge state. Examples are aminocarboxylic acids and betaines:



#### 4.1.4.1 Polymeric Dispersing Agents

Polymeric compounds have been used for several centuries to improve the stability of dispersions. Natural polymeric products, such as protein and arabic gum, were already used in the Middle Ages to manufacture and stabilize waterborne artists' colours and paints. Completely synthetic polymers as dispersing agents have come

in use only in recent decades, and they have contributed significantly to the formulation of higher-quality coatings.

The following groups of polymers are distinguished according to the number of different monomers per molecule chain:

- Homopolymers: based on only one type of monomer
- Copolymers: based on two types of monomers
- Terpolymers: based on three types of monomers

The copolymers can be subdivided further according to how the monomers and monomer segments are distributed in the polymer chain:

Statistical polymers: A and B segments are distributed arbitrarily

.....AAABBABBBBBBAAAAAABB.....

Mass polymers: The segments are arranged into blocks

.....AAAAAAAAAABBBBBBBBBB.....

Graft polymers: These consist of a linear homopolymer backbone, on which side chains of other monomer blocks are grafted

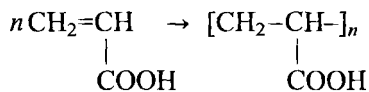
.....AAAAAAAAAAAAAAAAA.....  
                   B                  B  
                   B                  B  
                   B                  B

Polyelectrolytes are an important group of polymeric dispersing agents. In the dissociated state these offer a high density of charged monomeric units. One distinguishes between strong and weak polyelectrolytes. Strong polyelectrolytes are completely dissociated into their units in polar media and are pH-independent. Examples are polysulphates and polymeric quaternary amine compounds. The degree of dissociation of weak polyelectrolytes is related to the pH. Typical examples are polycarboxylates or polyamines. The dissociation of these polycarboxylates increase with increasing pH. Above a certain pH value, all groups that can be ionized, are present in dissociated form, and the properties of the polymer is then similar to that of a strong polyelectrolyte.

The electrostatic repulsion between the charged units in the molecule leads to a dissolved and dissociated polyelectrolyte that forms a stretched molecular structure; the nondissociated polyelectrolytes may form a coiled structure. Various ingredients in the medium influence the molecular structure as well, for instance, the salt or electrolyte concentration. Increasing the salt or electrolyte concentration in a polar solution leads to shrinkage of the polyelectrolyte molecule and finally to a conformation similar to that of an undissociated polymer molecule. The effect of the charged groups in the polymer molecule is compensated for by the electrolytes in the solution.

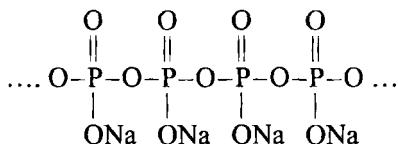
Polycrylate salts, also polycarboxylates, are successfully used as dispersants in waterborne coating materials (see Section 4.1.3.4).

Polyacrylates are synthesized by radical polymerization of acrylic acid:



For water-soluble polyacrylates the preferred cations are sodium or ammonium. Products that are used in practice typically have molecular masses of ca. 2000 to 20000 g mol<sup>-1</sup>. The optimum molecular mass for dispersants of pigments and extenders in coatings is ca. 8000.

The polyphosphates, discussed in Section 4.1.3.4, are produced from orthophosphates in a melting process. Only linear (no cyclic) structures are formed.<sup>[4-23]</sup> The term hexametaphosphate, which is often used, is therefore not correct. The connecting bonds between the phosphate units are -P-O-P-:

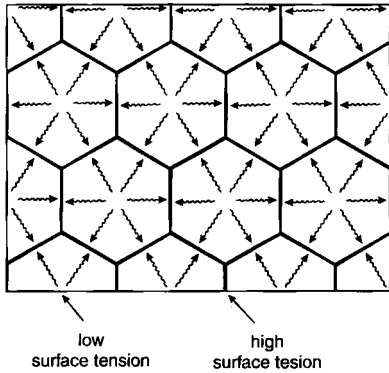


Highest water-softening efficiency is obtained with polyphosphates of middle chain length (range  $n = 6$ ). Polyphosphates of higher chain lengths have the disadvantage of a low solubility in water.

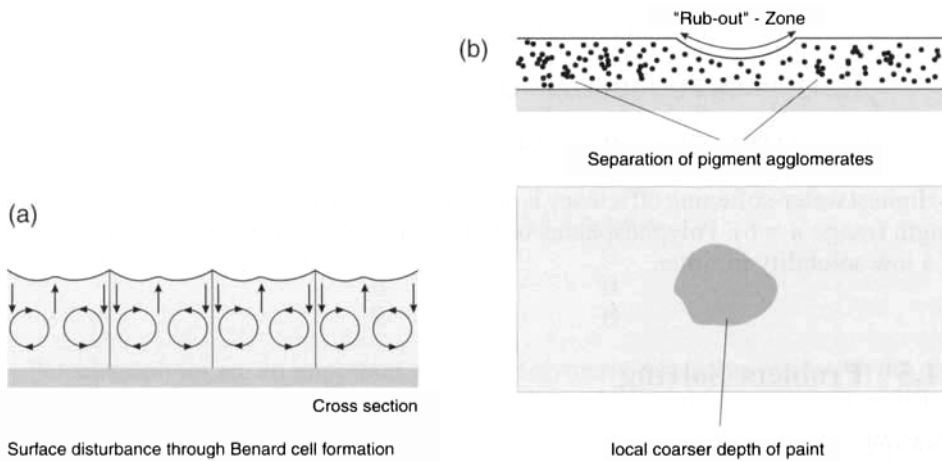
### 4.1.5 Problem-Solving

#### Floating

A well-known problem in practice is the phenomenon of “floating”. Floating is a defect found in coloured paints containing one or more pigments. During drying or storage one or more of the pigments separate or float apart from the others, producing an inhomogeneous surface effect with so-called Benard-cells, patches, or streaks. The paint has a smudged appearance. This phenomenon often occurs in coatings that containing pigments of differing natures. The pigment separation is connected to the different pigment mobilities. During solvent evaporation a circular flow occurs in the drying coating layer, which lead to the formation of Benard cells. These cells are often associated with the evaporation of the solvent during paint drying, irrespective of whether the paint is pigmented or unpigmented.<sup>[4-24]</sup> These cells form as a result of small local temperature-, density-, viscosity-, and surface tension gradients during the solvent evaporation. These gradients form when the solvent, by evaporating on the paint surface, forms local areas of lower temperature. This area has, for example, a different surface tension to that of the film layer beneath it. The resulting circular current results in the transfer of material, e. g., pigment particles, in the coating layer. Ideally, the material transfer should lead to the formation of hexagonal cells, which remain in the dried or cured coating layer (Figs. 4.1-15 and 4.1-16).



**Figure 4.1-15.** Paint surface: Benard cells



**Figure 4.1-16.** (a) Circular flow in each cell, with upward movement in the centre of the cell; (b) Dispersion check in the rub-out test

If the coating material contains various types of pigments, with large differences in particle size or density, the convection currents will transport the individual pigment particles at different speed, according to their structure. The different mobilities result in separation of the pigments. This is particularly apparent on the edges. The addition of suitable additives can prevent such a separation of pigments.<sup>[4-25]</sup>

Floating may be avoided or reduced by influencing one or more of the following factors:

- mobility of the pigments
- particle size of the pigments
- flow in the drying coating film

The mobility of the pigment particles depends on particle size, specific gravity, morphology, physical properties of the surface, as well as on the degree of flocculation of the pigment.

In addition to the effects influencing the movements of the particles via the flow properties, the contribution of gravity should be considered. Gravity influences the movements of the particles in the drying coating layer. According to Stokes' law, the sedimentation speed of spherical particles and their particle size are related as follows:

$$V = 2D(d_{pi} - d_{bi})r^2g/9\eta \quad (16)$$

where:

- $V$  = sedimentation speed
- $D$  = proportionality factor
- $d_{pi}$  = density of the solid particle
- $d_{bi}$  = density of the liquid medium
- $r$  = radius of the solid particle
- $\eta$  = viscosity of the liquid medium
- $g$  = gravitational acceleration

According to equation (16), the sedimentation speed increases strongly with increasing particle size. Calculations show that the sedimentation speed of  $TiO_2$  particles is faster by a factor of 1000 than that of the smaller carbon black pigment particles.<sup>[4-25]</sup>

Equation (16) is valid for spherical particles of colloidal dimensions.

For the pigments typically used in coating materials not all requirements for Stokes' law are fulfilled, nevertheless, equation (16) shows that an increase in particle diameter leads to an increase in the sedimentation speed. The particle's diameter affects the sedimentation speed more than specific gravity does.

Flocculation results in larger particles and thus to an increase in the sedimentation speed and different mobility. Coating materials usually contain combinations of various pigments, e. g.,  $TiO_2$ , made up of relatively large particles, and organic pigments with small particle sizes. When  $TiO_2$  in this mixture flocculates, the sedimentation speed of the  $TiO_2$  particles increases, and faster separation between the pigments occurs. The opposite is also possible: the smaller-sized pigment particles may flocculate, resulting in big particles that may separate faster than the originally bigger  $TiO_2$ -pigment particles!

Additives such as pigment dispersants avoid flocculation, thereby reducing the possibility of floating.

Flow influences material transfer; increasing the viscosity results in decreased flow. Increasing the viscosity is another way in which pigment floating may be avoided or reduced. Additives that cause a degree of pseudoplasticity to increase the viscosity in the low-shear range are particularly suitable.

### 4.1.6 Procedures for Determining Dispersion Efficiency

The dispersion properties may be investigated by various methods. The measurement of surface charge and methods that have found widespread application will be summarized in this section.

#### 4.1.6.1 Surface-Charge Measurement

Section 4.1.3 shows that pigment particles may be stabilized by electrostatic repulsive forces if the density of the interfacial charge is sufficient. The electrical interfacial charge on the pigment particles is compensated for by counterions in the dispersion medium, to form a diffuse electric double layer around the particle. To characterize the charged state, the speed of charged particles within an electric field needs to be determined (for instance using laser techniques, ESA).<sup>[4,13, 4-26]</sup>

#### 4.1.6.2 Dispersant Demand

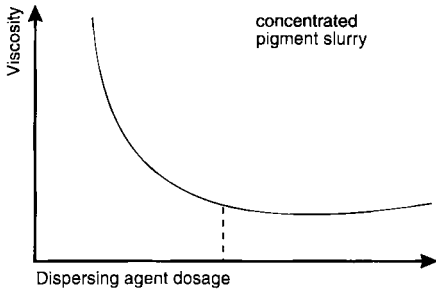
During the dispersion process, the proportions of the different components – pigment/extender, solvents, binders, and additives – need to be optimized. An optimum result depends strongly on the qualities and quantities of the wetting and dispersing agents used. The following method is a simple process for determining the dispersing agent demand in aqueous millbases that contain hydrophilic pigments and extenders.

The first part of the procedure is the “water-demand titration test”, which determines the required quantity of water: a defined amount of pigment and/or extender (usually the same composition that is used for the particular millbase) is simply moistened.<sup>[4-18]</sup> Water is titrated onto a small quantity of pigments/extender while being continuously mixed. The end point, defined as the wetting point, is reached when the mixture is completely wetted and forms a homogeneous paste.

The water-demand number is expressed in ml water per 10 g pigment and/or extender.

This composition is used as follows for the determination of the dispersant-demand curve: A mixture of water and pigment/extender, corresponding to that used for the water demand test, is titrated stepwise with a concentrated aqueous solution of the dispersant. After it has been mixed with a spatula, the viscosity is measured. The viscosity values are plotted against the amounts of dispersing agents used; the resulting diagram is known as the “dispersant-demand curve”. The viscosity minimum is identical to the minimum demand of dispersing agent for the used pigment/extender mixture under the mixing conditions used!

However, in practice the pigment surface is substantially increased by deflocculation and deagglomeration during the dispersal. This results in a larger demand for dispersant in order to cover all surfaces. It has been shown experimentally that the



**Figure 4.1-17.** Viscosity-demand curve: determination of the minimum viscosity for a millbase

amount of dispersant used needs to be ca. 50% more than the minimum amount found with the dispersant-demand-curve test (Fig. 4.1-17).

#### 4.1.6.3 Monitoring the Dispersion Process

Dispersion of pigments in liquid media or in dried coating layers may be studied by several methods.

A basic test, for both laboratory experiments and production control, is the determination of the grinding fineness, as it is a rapid and favourable measuring method. Several methods are available, most based on the same principle: the determination of the size of the coarsest particles. The Hegman gauge is a widely used device to measure the fineness of dispersions: a (milling) paste or paint is drawn down over a channel of tapered depth; the minimum depth at which pigment particles are observed to interfere with the smooth wet surface of the paint is noted. The ASTM gauge (D 1210) is almost identical to the Hegman gauge. This test is fast, cheap, and reproducible. A disadvantage of this method is the fact that only the coarsest particle sizes are registered and the particle size distribution is not measured. Additionally, the measurement results may be interpreted in different ways.

#### 4.1.6.4 Degree of Dispersion

The degree of dispersion of a pigment influences the optical characteristics of a coating material. Properties such as colour development, opacity, hue, light scattering, and gloss are all related to the particle size and can be regarded as a measure of the particle size.

When white pigments are present, the whiteness strength can be used for measuring the degree of dispersion. The whiteness strength is determined as the colour-reducing power. The white-test sample is mixed with a small quantity (usually 10%) of a black pigment paste; the whiteness strength is directly related to the degree of "whiteness" of the mixed sample. The degree of dispersion of the white pigment is related to the light scattering and brightness of the paint sample. Improving the de-

gree of dispersion of the white pigment results in a shift to a bluish hue as the light scattering, within the blue range of the natural light, increases.

The gloss level is also a tool for determining the degree of dispersion. The gloss level of a dried coating layer is affected by the refractive index of the layer, the texture of the surface, and the light angle. Defects in the surface of the coating film, even as low as  $0.1\ \mu\text{m}$  deep or high, result in lower gloss values. As this value corresponds to the size of a pigment particle, it follows that the status of the pigment particle is significant for gloss.<sup>[4-6]</sup>

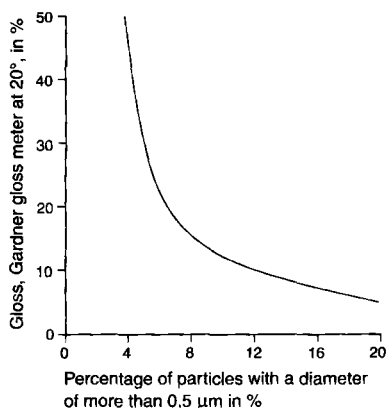
The determination of rheological properties is also a useful way of determining the degree of dispersion. However, the interpretation of the observed phenomena is often difficult, and various factors, others than the degree of dispersion, may also have a strong effect on the rheology.

#### 4.1.6.5 Degree of Flocculation

The degree of flocculation is directly related to the gloss value of a coating film. Gloss is related to the particle size: the higher the degree of coarse particles, the lower the gloss. This is demonstrated in Fig. 4.1-18, in which the gloss is plotted in relation to the percentage of coarse particles, i. e., those larger than  $0.5\ \mu\text{m}$ .

Determining the hiding power (covering ability or opacity) is another practical method for establishing the degree of flocculation. The hiding power generally decreases at increased degree of flocculation. This is valid for pigments with particle sizes of  $0.3\ \mu\text{m}$  and more. Exceptions are fine-particle-sized pigments, with particle sizes typically below  $0.3\ \mu\text{m}$ , smaller than the visible-light spectrum, whose hiding power can even increase after flocculation. To evaluate the hiding power, a defined layer thickness of the coating material is applied on a contrast substrate.

Determining the speed of sedimentation of undiluted dispersions is a method that only gives qualitative information on the degree of flocculation.



**Figure 4.1-18.** Gloss level of a stoving enamel in relation to the particle-size distribution

All the above-mentioned methods have the advantage that they can be executed without diluting the pigment suspension.

The rub-out test is another method for determining the degree of flocculation; it is carried out on the drying coating film (see next section, Section 4.1.6.6).

For many other methods the material must be diluted strongly, e. g., for the determination of statistical particle-size-distribution curves with the Coulter counter or microscopic evaluation. Dilution may result in flocculation and may therefore lead to misinterpretations.

#### 4.1.6.6 Flooding: Rub-Out Test

The term flooding is used to describe the effect caused by concentration of one of the pigments at the surface of a coating film; a change in colour at the surface results. Flooding is related to floating (Section 4.1.5). However, flooding refers to uniform colour changes, whereas floating refers to local excess of one colour.

Flooding is greatly affected by differences in pigment sedimentation rates, and is therefore strongly influenced by flocculation.

The “rub-out” test is an extremely practical and simple test to make pigment flooding visual and measurable. For the rub-out test, the drying coating layer needs to be rubbed. Flocculated particles will be re-dispersed by rubbing, as a result the colour strength of these particles increases. The colour difference between the rubbed and the unrubbed area indicates the degree of flocculation as well as the flooding extent.

Flooding is mainly caused by flocculation. However, flooding may also be found in nonflocculated dispersions, if the pigments are not statistically homogeneously distributed.<sup>[4-27]</sup> To quantify the colour difference, the colour strengths of the rubbed and the nonrubbed areas are measured.<sup>[4-25]</sup>

According to Kubelka-Munk:

$$F = K/s = (1 - R_{\infty})^2/2R_{\infty} \quad (17)$$

$F$  = colour strength

$K$  = coefficient expressed in  $X^{-1}$

$s$  = scattering coefficient expressed in  $X^{-1}$

$R_{\infty}$  = remission factor of a nontransparent layer

From this the “rub-out number” is calculated by the following equation:

$$RN = \{F_r/F_{nr} - 1\}100 \quad (18)$$

$RN$  = rub-out number

$F_r$  = colour strength of the rubbed area

$F_{nr}$  = colour strength of the nonrubbed area

The sign of the rub-out number,  $RN$ , may be positive or negative. A positive  $RN$  means that the colour strength of the rubbed area is higher than the colour strength of the nonrubbed area. The opposite applies to a negative  $RN$ . No rub-out effect is present if  $RN$  is zero.

In practice, the term rub-out effect is often equated with the term flocculation. The terms are only interchangeable if flocculation was detected by other suitable techniques (e. g., microscopy).

## 4.1.7 Biological and Toxicological Properties

The biological and toxicological properties depend on the specific composition of the product. Very diverse chemical compositions are found in the group of wetting and dispersing agents. The information in this section is therefore limited to general data on the wetting and dispersing agents known as “surfactants” and “polymers”.

### 4.1.7.1 Surfactants

Hydrophobic wetting and dispersing agents that belong to the group of surfactants, may result in degreasing. Skin contact may lead to degreasing of the skin and irritation, shown by red spots and inflammation. These compounds are predominantly classified as irritating with  $R$ -classifications of 36/38 (see Section 9.4).

The presence of other components such as additives or solvents may result in another classification.

The acute oral toxicity of surfactants that are typically used as coating additives are generally within the region of greater than  $2000 \text{ mg kg}^{-1}$  and does therefore not pose a material danger.

Alkyl phenol derivatives may have an endocrinic effect.

The biodegradability of most additives used as dispersants is very good (>90% OECD Confirmatory). In this case other ingredients may also influence the degradability negatively.

### 4.1.7.2 Polymers

Polyacrylates that are used as pigment dispersants in waterborne paints are basically nontoxic materials. However, polymers, especially powdered products, should always be regarded as chemical compounds.

Polymers are well-known to be mostly poorly biodegradable; in general they remain relatively long in the receiving water of a clarification plant. Sodium polyacrylates, for example, biodegrade to 15 to 30% after 28 days.

### **4.1.8 Commercial Products**

Disperbyk (Byk Chemistry)  
Efka (EFKA Chemicals)  
Tegospere (Tego Service)  
Borchigen (Borchers)  
SER-AD FX (CONDEA Servo BV)  
Nuospere (CONDEA Servo BV)

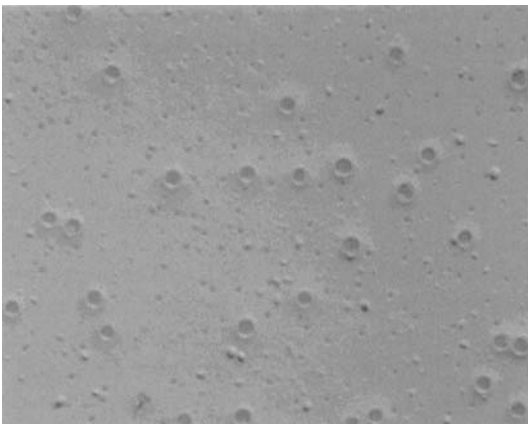
## 4.2 Defoaming of Aqueous Paint Materials

*Wernfried Heilen and Stefan Silber*

### 4.2.1 Introduction

Surface-active chemicals such as emulsifying agents for the stabilization of the binder or, on the other hand, agents for wetting the substrates (Section 4.4), as well as pigments and extender substances (Section 4.1), are nearly always added to aqueous paint materials. The most important property of the surface-active-agent substances is their ability to accumulate on interfacial surfaces and to orientate themselves according to their chemical structure, to reduce the interfacial surface tension. An unwelcome side effect is that these surface-active agents may stabilize air, which has entrapped during the manufacture or application of the paint, in the form of foam bubbles.

The stabilization of foam bubbles begins with the development of orientated monomolecular layers of surface-active substances on the surface of the air bubbles in the paint material. If the air bubbles, which are loaded with surface-active-agent molecules, rise upwards in the coating material, further such steps lead to the agglomeration of air bubbles in the upper section of the liquid phase, initially with retention of the spherical structure of the air bubbles. This spherical foam has, generally, a lamellar thickness of several  $\mu\text{m}$ . Gravity then causes draining off of the liquid (drainage) from this border area and the deformation of the formerly spherical bubbles into a polyhedral foam.<sup>[4-28]</sup> This lamellar discharge ends when the layer thickness amounts to between 10 and 100 nm. Very thin foam lamellae, which enclose relatively high air volumes,<sup>[4-29]</sup> are stabilized



**Figure 4.2-1.** Macrofoam on the surface of a pure acrylate emulsion paint

in the polyhedral foam by the formation of double layers of surface-active agents, as a result of the further convergence of the gas bubbles towards one another, as well as through the increase in the concentration of the surface-active agents due to the drainage.

If the bubbles burst during drying of the film of paint, then both the polyhedral foam and the spherical foam lead to unwelcome surface defects in the aqueous paint materials, such as craters or pinholes (Fig. 4.2-1). Although the tendency towards foam stabilization can be limited during formulation through suitable component selection and composition, the only really effective way of avoiding such defects is the addition of suitable defoamers and foam inhibiting agents.<sup>[4-30]</sup>

## 4.2.2 Foam Formation in Aqueous Paints

Foam formation in aqueous paint materials has various causes:

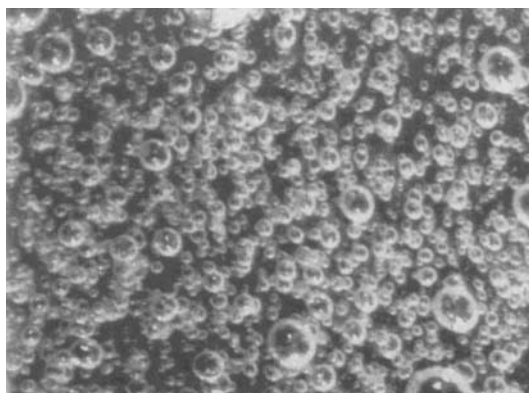
Air enters not only during manufacture, but also during the application of aqueous coatings. It can also be released from porous substrates. Additionally, gases may be released as a result of chemical processes (reaction of isocyanates with moisture) during paint hardening.

Avoiding the entry of air, or at least breaking down the foam which has formed, is easy during manufacturing. It is more difficult to reduce bubbles effectively during application, as the air which has entered must be eliminated extremely quickly, before the coating dries. Particularly critical application methods are, for example, the curtain coater application and airless-spraying. Naturally, however, air also enters into a coat of paint when a roller or a paint brush is used.

During the curtain coater application paint material flows from a narrow slit onto a substrate which is moved through the paint curtain. Excess quantities of paint are fed back from a collection container into the storage container by means of a pump, with the result that considerable quantities of finely dispersed air enter into the paint material. If this air is not removed quickly enough, continuing the painting will result in the formation of a faulty coating.

Considerable foam problems also occur during airless-spraying; these problems are only partly caused by the air which enters during the agitation of the paint before its application. An additional cause is the air dissolved in the paint under the pressure conditions within the pump. After pressure reduction, which occurs after the paint material has passed through the nozzle, the paint is oversaturated with dissolved air. This formerly dissolved air is then released into the paint film during drying. In addition, air is incorporated during the impact of the sprayed viscose material onto the substrate on which is to be coated.<sup>[4-31]</sup> Both processes lead in the end to (micro) bubbles in the film (Fig. 4.2-2).

For bubble-free coatings it is therefore extremely important to avoid completely the stabilization of air bubbles in paint materials as far as possible.



**Figure 4.2-2.** Microfoam in a wood coating based on acrylate

Before the possible solutions for obtaining bubble-free coatings can be discussed further, the physical-chemical influencing factors which determine foam stabilization and foam suppression in aqueous systems will be discussed.

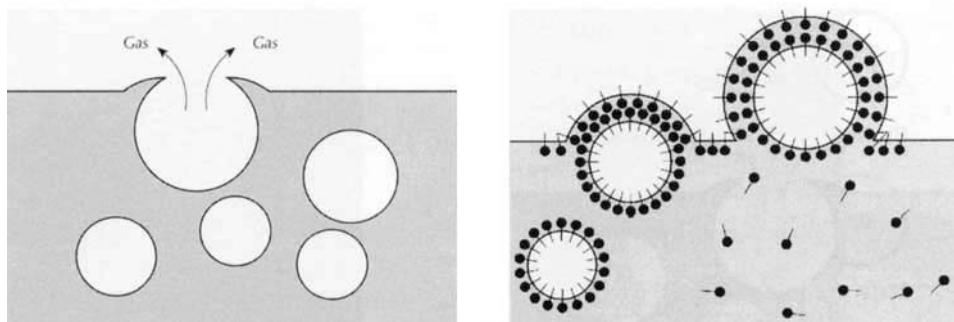
### 4.2.3 Causes of Foam Stabilization

If an air stream is fed into a liquid, the bubbles generally take on a spherical shape. As spheres possess the lowest surface area at a given volume of a body, this means that the lowest possible surface energy has been achieved.

The presence of surface-active substances within the liquid is, to begin with, not necessary for the generation of these spherical bubbles. However, the absence or presence of surface-active substances determine whether “naked” spherical bubbles or foam bubbles with a surface active-agent coating, which are more stable, form.

The spherical bubbles rise upwards in the surrounding liquid; this movement can be described by Stokes’ law. According to this law, the larger bubbles rise faster than the smaller bubbles as, at constant viscosity, the ascending velocity,  $v$ , is proportional to the square of the bubble radius,  $r$ . Therefore, if the coating has a high viscosity,  $\eta$ , and if paint drying is accompanied with a swifter viscosity increase, then ventilation is counteracted.

When the gas bubbles reach the surface of the liquid and penetrate the surface then their behaviour differs depending on whether they are “naked” bubbles or bubbles which are coated with a surface film (Fig. 4.2-3). The “naked” bubbles tear open, the enclosed gas can escape, the liquid flows together. The bubbles with a surface-active-agent coating remain enclosed by a lamella during penetration of the surface. Lamellar bubbles therefore form a foam crown.<sup>[4-32, 4-33]</sup>

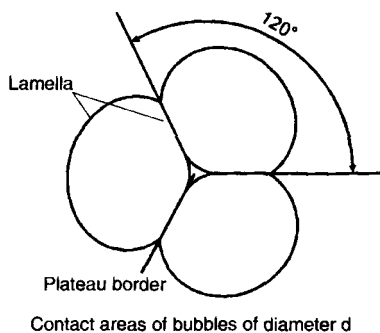


**Figure 4.2-3.** Ascension and stabilization of air bubbles in liquids which are free of surface-active agents (left) and liquids which contain surface-active agents (right)

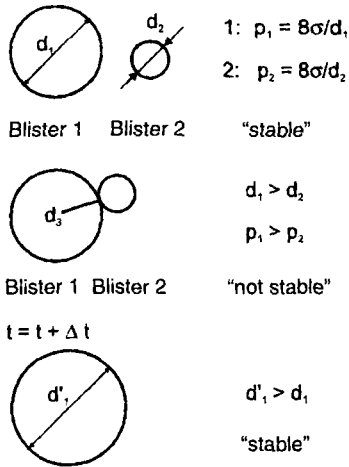
### 4.2.3.1 Stability-Reducing Parameters

The volume of a foam crown becomes smaller immediately after it has developed, mainly because of drainage and bubble coalescence. Along the boundary surface between the foam and the environment, the liquid evaporates and the upper foam blisters burst. This disperses the liquid onto the lamellae and the plateau border areas. The curvature of the surface (Fig. 4.2-4) in the plateau zone indicates under-pressure: a suction effect occurs which extracts liquid from the lamellae. Foam drainage causes the thickness of the walls of the liquid lamellae to become continuously smaller until the bubble bursts.

Two separate bubbles with diameters  $d_1$  and  $d_2$  (whereby  $d_1 > d_2$ ) will have different pressures  $p_1$  and  $p_2$  ( $p_2 > p_1$ ). Both bubbles represent isolated stable systems. If, however, the bubbles are brought into contact, a new system arises which, due to the different inner pressures, is not stable.<sup>[4-29]</sup> The gas in the small bubble, because of its higher inner pressure, diffuses into the large bubble through the contact area between the two bubbles. The small bubble consequently disappears with time and the large bubble takes on a larger diameter  $d_1^*$ . At the same time, the pressure in the new bubble changes to  $p_1^*$ , which is smaller than the pressure  $p_1$  (Fig. 4.2-5). The



**Figure 4.2-4.** Basic principles of the drainage effect



Influence of the blister size on the foam stability

Figure 4.2-5. Bubble coalescence

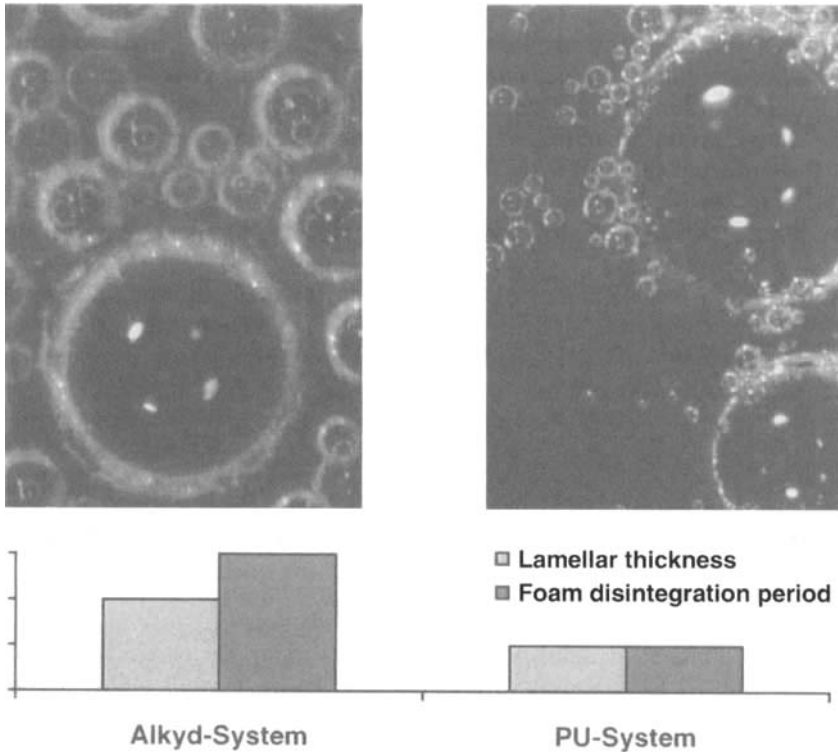
time it takes for the bubble to disappear depends on the wall thickness of the contact area. When the wall is thin, diffusion is more rapid than with a thicker wall (Fig. 4.2-6).

Diffusion-controlled solvation of air into the liquid phase is especially important for dissolved spherical bubbles in highly viscous coatings, and should also be regarded as a further destabilization mechanism. According to Epstein and Plesset,<sup>[4-34]</sup> the time it takes for a spherical bubble, which is surrounded by the liquid phase, to dissolve, increases with the cube of the sphere's radius. This means that, in particular, small spherical bubbles (<5 μm) can preferentially disappear via solution processes.

These basic processes cause the foam volume to become smaller with time. On the other hand, there are several parameters that promote foam stability thereby hindering the reduction of the foam volume.

#### 4.2.3.2 Parameters That Promote Foam Stability

According to Gibbs,<sup>[4-35]</sup> the foam lamellae behave like elastic membranes, in particular when they are subjected to short-term strain and loads. If a surface-active-agent film is expanded, then the surface tension is increased as a consequence of the reduction in the equilibrium concentration of surface-active substances. This so-called Gibbs elasticity only occurs when the deformation proceeds quickly enough, so that no time remains for the surface-active substances to diffuse into the enlarged lamellar boundary surface or to diffuse out of the smaller lamellar boundary surface. If, however, there is sufficient time between the deformation of the boundary surface and the occurrence of a new equilibrium then the Marangoni effect also occurs.<sup>[4-36]</sup> As long as equilibrium is not achieved, then an additional re-



**Figure 4.2-6.** Influence of lamellar thickness on foam stabilization (picture detail corresponds to  $1.2 \times 0.9$  mm)

set force, which decreases with time, has a stabilizing effect. This results from diffusion-controlled transport of the surface-active-agent molecules from the liquid into the lamellar boundary surface and vice versa. The Marangoni effect therefore results from variations in surface tension. The interaction between the Gibbs and Marangoni effects thus stabilizes the foam against fluctuations in the film thickness and sphere size.

Especially polymeric surface-active agents (also ethoxylates) can also become embedded in the gas/liquid phase-boundary surface of a bubble. This layer then has a higher viscosity than the ambient liquid. Also, as a result of this higher surface viscosity, the drainage of the water is delayed.

A further mechanism of foam stabilization is of an electrostatic nature. When the surface-active substances are ionic, then like charges form not only along the inner surface but also along the outer surface. The electrostatic repulsion of the lamellar boundary surfaces counterbalances further drainage or thinning out.

The often rapidly increasing viscosity of a coating when it begins to dry hinders, moreover, the convergence of gas bubbles towards one another. However, this is necessary for larger bubbles to develop from smaller bubbles, which would then have a swifter ascending velocity. If two small bubbles should nevertheless come close,

then the high viscosity additionally hinders the drainage, i. e., the draining off of the liquid from the lamella and thus also the coalescence.

Moreover, during drying, the viscosity increase in the coating cross-section does not develop uniformly, but appears much faster in the outer layers of the film than it does in the deeper layers. Then the outer layers of the film take on a sealant layer function. If the diffusion is excessively hindered by this sealant layer, particularly with thermodrying, further bubbles, filled with solvent fumes as well as film-forming substances may appear. This undesirable phenomenon is known as cooker formation.

Apart from the viscosity phenomenon, the migration of bubbles during the flow of the paint within the film through surface tension gradients should also be considered. During the development of Benard cells, air bubbles enter into the areas of lower surface tension and consequently to the surface of the substrate.<sup>[4-36]</sup>

## 4.2.4 Composition and Effect of Defoamers and Foam Inhibiting Agents

### 4.2.4.1 Defoamers

Defoamers are added when the foam already exists and, amongst other things, counterbalance the above-mentioned Gibbs and Marangoni effects. In order to be efficient they must have a lower surface tension, be insoluble in the phase that needs to be defoamed, and have a high evaporation enthalpy in order to guarantee a long-lasting effect.

On the other hand, no surface defects such as craters may be generated, so that also sufficient compatibility of the defoamers in the binder system must be ensured.

In accordance with the efficacy mechanisms accepted in literature,<sup>[4-37-4-39]</sup> the defoamer-active substances which are dispersed as fine droplets must enter into the foam lamellae. There the defoamers must penetrate into the layer of surface-active agents, which requires a high spreading activity. It has been recognized that this can also be expressed as the demand for positive penetration coefficients ( $E$ ) and spreading coefficients ( $S$ ).<sup>[4-40, 4-41]</sup>

$$S = g_m - g_d - g_{md} > 0$$

$$E = g_m - g_d + g_{md} > 0$$

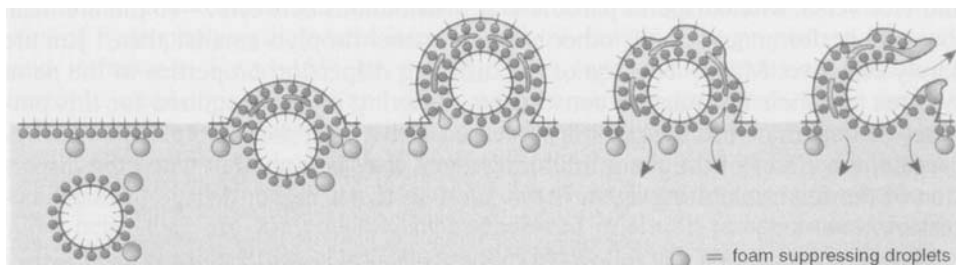
where:

$g_m$  = surface tension of the medium

$g_d$  = surface tension of the foam-suppressant oil

$g_{md}$  = interfacial surface tension between the medium and the defoamer oil

The tension gradients which are created through the spreading, lead to the lamellae breaking apart. If the penetration coefficient is positive, then the defoamer droplets penetrate into the surface-active-agent layer to stabilize the lamella. The resulting film shows a lower cohesion than the thin surface-active-agent film which stabilized the lamellae previously, with the lamellae breaking as a result (Fig. 4.2-7).



**Figure 4.2-7.** Model showing how the defoaming effect takes place

Commercial defoamers of this type are often based on silicon oils with  $g_d = 20 \text{ mN m}^{-1}$ , which for most foams leads to positive penetration and spreading coefficients. Through the addition of special, hydrophobic particles, such as hydrophobic fumed silica<sup>[4-42]</sup> or amino derivatives,<sup>[4-43]</sup> the effectiveness of foam-suppression-active substances is increased. This effectiveness is explained best through a de-wetting process.<sup>[4-44]</sup> The surface-active-agent film which stabilizes the foam lamellae cannot wet the hydrophobic particles. The resulting low adhesion force causes the foam bubbles to burst so that the enclosed air escapes.

A further function of the hydrophobic particles is to hinder the carrier oil from distributing itself completely onto the lamellar surface, which would reduce the de-wetting process. Suitable fumed silicas have very large specific surfaces of between 50 and 500  $\text{m}^2 \text{g}^{-1}$ . The average particle size should be less than 10  $\mu\text{m}$ , preferably 0.2–5  $\mu\text{m}$ . The best defoaming effect is achieved when the hydrophobic fumed silica reaches the effective layer thickness of the lamellae.<sup>[4-42]</sup>

#### 4.2.4.2 Foam Inhibiting Agents

Foam inhibiting agents are added to the system which is to be defoamed before foam formation. During the manufacture of a product which has a foam-formation tendency, the foam inhibiting agent is added as early as possible during the production process, ideally to the millbase. The breaking of the lamellae here also follows the mechanisms described above. The mentioned insolubility of the defoamer oil in the foaming system and the demand for positive spreading and penetration coefficients are indeed necessary, but are not adequate conditions for the suitability of defoamers as foam inhibiting agents.

In practice, the droplet-size distribution and the boundary surface tension  $g_{md}$  of dispersed defoamer droplets determine the applicability of defoamer and foam inhibiting agents. Recent results<sup>[4-45]</sup> showed that a higher and longer shearing action  $G$ , a low interfacial surface tension  $g_{md}$  between the defoamer oil and binder matrix, a lower viscosity of the defoamer droplets  $\eta_d$ , as well as a high viscosity  $\eta_m$  of the systems to be defoamed tend to lead to low particle sizes of the defoamer oils and vice versa. Monodisperse particle-size distributions between 2–10  $\mu\text{m}$  are ideal for good performance; on the other hand, defoamer droplets smaller than 1  $\mu\text{m}$  are barely effective. Mainly because of the differing dispersion properties of the paint systems and their formulation constituents, differing oils are required for this purpose. Particularly when the paint is processed with a high shear force dispersion aggregate, the effect of the foam inhibiting agent may be impaired when the dispersion of the foam inhibiting agent is too good, so that a higher dosage becomes necessary.

The recommendation that follows from these physical considerations is that the user and the formulator should use defoamer compounds as foam inhibiting agents, above all for applications with high- to medium-shear forces: due to their pre-set particle-size distribution o/w defoamer emulsions should preferably be used for applications with low-shear forces – deflagration substances or with subsequent addition.

The particle-size distribution is decisive for the characteristics of paints shortly after their manufacture, and after renewed application-related shearing action. Particularly polyether siloxane oils with a low boundary surface tension are often found to have a considerably finer droplet dispersion after a longer storage period, consequently resulting in poorer effectiveness. Polyether siloxanes with a high interfacial surface tension  $g_{md}$  are therefore more stable towards storage. On the other hand, low interfacial surface tensions are more favourable for the reduction of surface defects. Through the structural variation of polyether siloxanes, as well as through suitable formulation, an appropriate defoamer can be found for each paint system, with the parameters discussed taken into consideration.

#### 4.2.5 Formulation of the Active Substances

Defoamers on the whole consist of:

- water-insoluble, to a large extent hydrophobic, organic liquids; for example, mineral, vegetable, and animal oils as well as polydimethyl siloxanes or mixtures thereof
- hydrophobic particles
- emulsifying agents for easier dispersion
- water, if required

To date, of all the numerous defoamer-active formulations for aqueous paint systems, mineral oil defoamers and silicon defoamers have become the most important.

Aromatic or increasingly aliphatic mineral oils are applied as classic, spreading-active substances in foam-suppressant formulations. The aromatic oils which were often applied in the past are associated with physiological and ecological risks. Aliphatic suspending oils are indeed safer, however, as with the aromatic oils, they reduce the degree of gloss in emulsion paints, often due to their incompatibility.

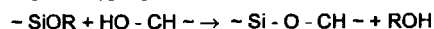
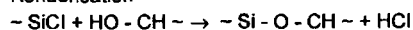
Mineral oil defoamers are manufactured as a rule through the addition and dispersion of hydrophobic silicic acid into mineral oil. For this, the proportion of silicic acid is between 5 and 15% by weight. Often further substances are added, for example, emulsifying agents and solids such as metal soaps, waxes, or fat amides.

Simple silicon oils are often used as foam inhibiting agents due to their high evaporation enthalpy and low surface tension. Here the addition of fumed silica also has a positive influence on the defoaming behaviour. Fumed silicas can also be applied here; they are subsequently hydrophobized in situ at temperatures of 150–200 °C and reaction times of one to several hours.

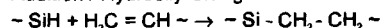
A class of highly efficient defoamers is made available through the modification of functionalized polydimethyl siloxanes with hydrophobic polyethers. This leads to active spreading substances which show their strength in particular in modern aqueous paint systems. Besides the advantage of not reducing the gloss, such defoamers are distinguished through good compatibility.

Various reaction methods can be applied<sup>[4-46]</sup> for the synthesis of polyether siloxanes. Through condensation reactions between polyether- and siloxane blocks, combined copolymers<sup>[4-47, 4-48]</sup> with SiOC bonds result; when catalysed by transition-metals, hydrosilylation reactions result in polyether siloxanes with SiC bonds (Fig. 4.2-8).

#### Kondensation



#### Addition / Hydrosilylierung



**Figure 4.2-8.** The synthesis of polyether siloxanes

The siloxane block is responsible for the surface activity, while the degree of compatibility is mainly regulated by the polyether block. The copolymer segments may be designed in such a way that suitable defoamers may be obtained for practically all application cases. Hydrophobic polyether siloxanes are generally distinguished by the fact that, although they are highly incompatible with foaming media, they are also selectively compatible in a dry film. This means that high defoaming activity can be combined with low crater-forming tendency. As polyether siloxanes defoam well even in the absence of hydrophobic solid matter, defoamers without solid matter, which have a particularly low tendency towards paint defects, can also be formulated. Often defoamers are formulated on the basis of polyether siloxanes as o/w gloss paints with pre-set droplet-size distributions.

### 4.2.6 Test Methods for the Evaluation of Defoamers

For the practitioner it is necessary to determine the efficiency of suitable defoamers in laboratory tests. Despite the fact that results of laboratory tests cannot always be transferred easily to industrial scale, a series of practice-related test methods exist. We shall confine ourselves here to only a few methods that we believe permit the measurement of defoaming effect during manufacture and when the paint is filled into containers, as well as the foam-formation prevention during application, with sufficient precision.

A method often used is the agitation test (Fig. 4.2-9), in which air is dispersed in the dispersion or formulated paint under defined conditions by means of a turbine agitator. The dispersion or paint which has thus been processed is then, immediately after switching off the turbine, filled into a graduated cylinder up to the calibrating mark and then weighed. The density is reduced through the quantity of air that has been stirred in and is a gauge for the efficiency of the defoamer (Fig. 4.2-9).

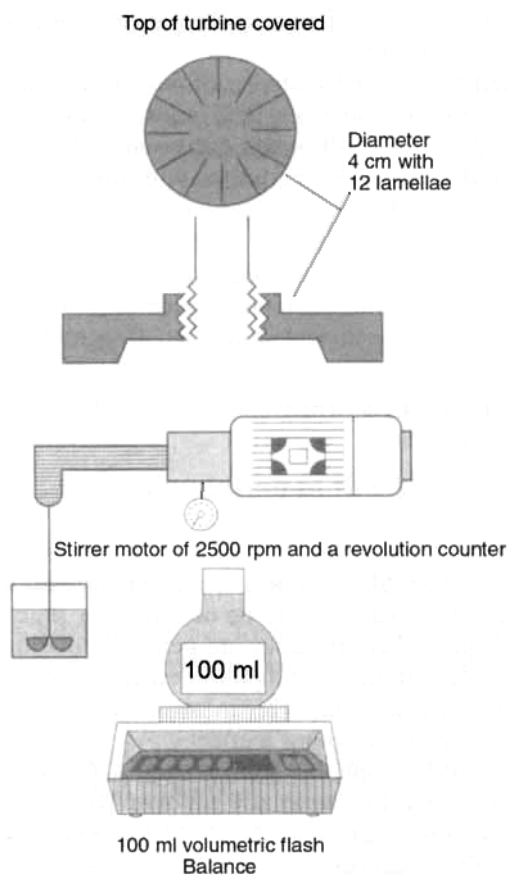


Figure 4.2-9. Agitation test

Many defoamers cause surface defects, of which, in particular, craters are as unwelcome as those defects which are caused by foam bubbles. To investigate this aspect, the foamed-up specimen from the agitation test can be poured onto a sheet – ideally fixed onto a slanted surface. In addition, after the film has dried, the ventilating effect of the defoamers can be evaluated – if required, with the assistance of a microscope. Experience has also shown that the (final) selection of defoamers should be based as far as possible on application-related factors.

The necessary dosage, or effectiveness, of a defoamer depends, in principle, on the formulation. The type and stabilization of the binder, the level of pigmentation, as well as the composition and ionogenic properties of the surface-active substances used for pigment and substrate wetting have a particularly strong effect.

## 4.3 Adhesion Promoters

*Martina Ortelt*

### 4.3.1 Definition

The concepts of adhesion and adhesive strength are nowadays part of the accepted vocabulary of anyone concerned in whatever way with producing bonding. These bonds can be between materials that are the same or different, and can be produced by, for example, adhesive bonding, brushing, coating, or filling.

Whenever the terms adhesion and adhesive strength are used, a certain bonding strength is associated with it.<sup>[4-49]</sup> For coatings, the adhesive strength is defined by DIN 55945. This defines the adhesiveness in terms of the resistance of the coating against mechanical separation from the substrate.

The adhesive strength of a coating on exposure to water and moisture is termed its wet adhesion.<sup>[4-50]</sup>

One of the ways in which the adhesion can be improved is by the use of adhesion promoters. This is a general term for all those substances that improve the adhesive strength of the materials that are to be joined.<sup>[4-51]</sup>

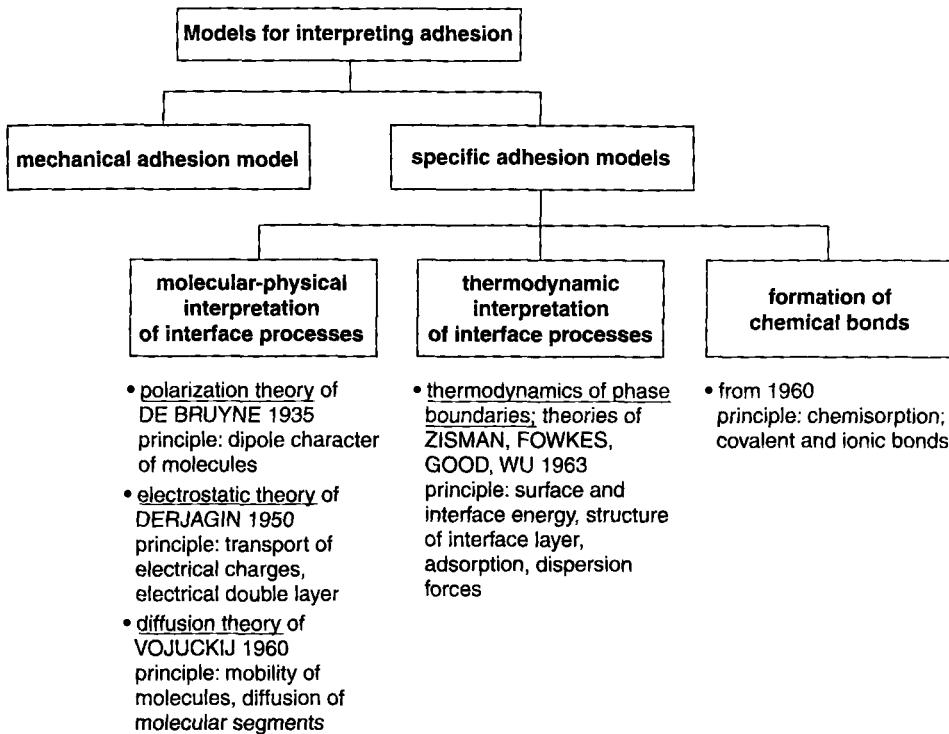
### 4.3.2 Models for Interpreting Adhesion Phenomena

Because of the complexity of adhesion phenomena, there are many models for it (Fig. 4.3-1). None of them, on its own, can fully explain adhesion. However, each model describes a part of the complex processes involved in adhesion.<sup>[4-49]</sup>

The core concept of mechanical adhesion is that the liquid coating material hardens within the hollows or pores of the surface of the substrate, where it is mechanically anchored as with dowels or press-studs. The established view nowadays is that this effect, although certainly present to a greater or lesser extent, is only of limited importance. This is being increasingly replaced by the opinion that the greater adhesion observable when the “roughness” of a substrate surface is increased, can be attributed to the increase in the effective surface area.<sup>[4-49]</sup>

Adhesion is almost always due to physically and chemically induced intermolecular interactions in the interface or interface layer. The physical interactions include the formation of:<sup>[4-52]</sup>

- permanent dipoles (bond energy  $< 20 \text{ kJ mol}^{-1}$ )
- induced dipoles (bond energy  $< 2 \text{ kJ mol}^{-1}$ )
- London dispersion forces (bond energy  $< 40 \text{ kJ mol}^{-1}$ )



**Figure 4.3-1.** Models for interpreting adhesion phenomena

The bond energies for hydrogen bonds, which are also of importance, are less than  $50 \text{ kJ mol}^{-1}$ .

If bond energies are considered, then chemical bonds between the coating and the substrate must result in high adhesive strengths. A distinction is made<sup>[4-52]</sup> between:

- covalent bonds (bond energy  $60\text{--}700 \text{ kJ mol}^{-1}$ ), and
- ionic bonds (bond energy  $600\text{--}1000 \text{ kJ mol}^{-1}$ )

In addition to the formation of specific bonds at the phase boundary, an important part is also played by the wetting of a surface. W. A. Zisman therefore arrives at the general finding that a substance can only be adsorbed by a surface when the surface energy is less than (or at most equal to) the critical surface energy of the solid.<sup>[4-49]</sup>

The wetting of a surface by a liquid is expressed by the equilibrium contact angle. The prerequisite for wetting is a contact or wetting angle of less than  $90^\circ$ .

### 4.3.3 Adhesive Strength in the Bond

The factors which influence adhesion are diverse. They are depicted below, by way of example, for a bond between strip steel and a coat of paint containing an adhesion promoter (Fig. 4.3-2).<sup>[4-49]</sup>

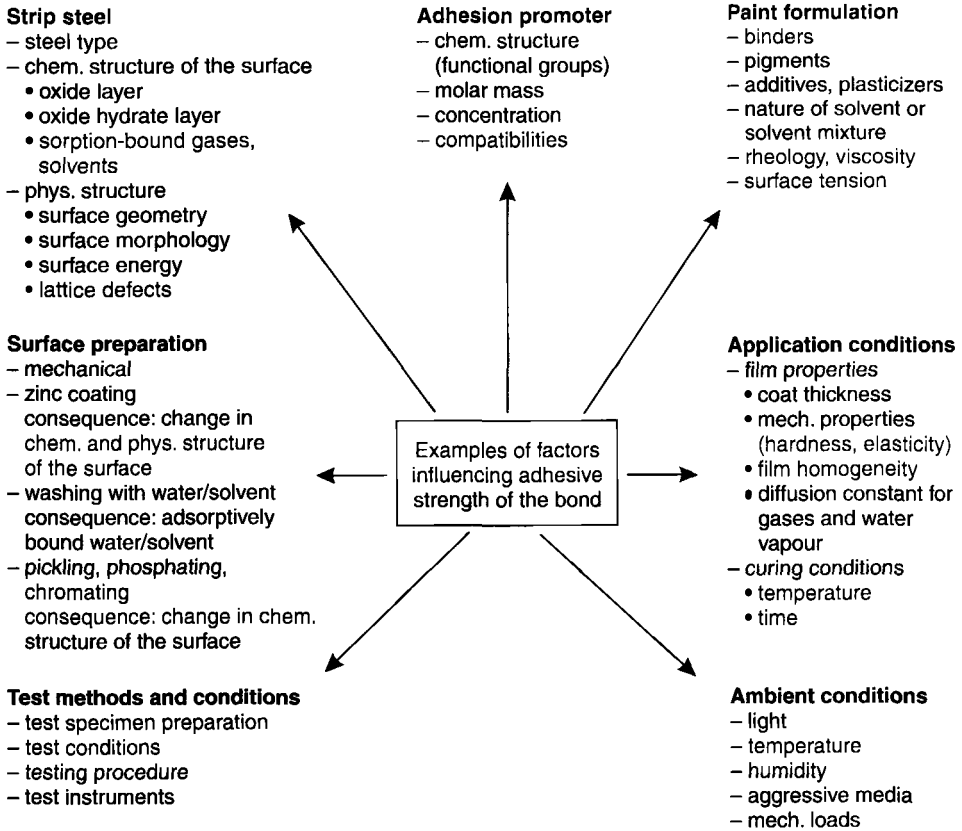


Figure 4.3-2. Possible factors influencing adhesion: painted strip steel (example)

Effective protection of substrates is possible only if the coating adheres sufficiently. The requirements for a paint formulation often include specifications for the use of specific types of binder, so that adhesion problems are often programmed in from the outset. In such cases, the addition of adhesion promoters is often the only remedy.

### 4.3.4 Adhesion Promoters

#### 4.3.4.1 General Remarks

Because of the great diversity of coating systems, the various types of surfaces that are to be coated (wood, metal, paper, leather, plastic, etc.), the diverse surface structures (flat, porous, homogeneous, etc.), and the many possible stresses to which it may be exposed (temperature, extensibility, hygroscopicity, etc.), it is impossible to find a single additive which can be used universally to improve adhesion.<sup>[4-53]</sup>

The market offers a large number of different chemical varieties of adhesion promoters. The range of chemicals available includes silanes, silicones, titanium compounds, zirconates, amides, imines, phosphates, and specially modified polymers. Furthermore, there are binders, plasticizers, and additives (e.g., wetting agents) which, though intended for other purposes, have the secondary effect of providing good adhesive strength. In terms of adhesive strength, it is in many cases the overall formulation of a paint or other coating material which is decisive. For instance, it is known that viscosity-reducing additives such as solvents, for example, improve the adhesive strength by improved mechanical anchoring of the film. In this context, the partial dissolution and/or swelling of the substrate (plastic substrates, undercoat) may also contribute to an improvement in adhesion.<sup>[4-53]</sup>

It is generally assumed that the mode of action of adhesion promoters is based partly on the formation of chemical bonds with the substrate surface and the binder, and partly on an increase in the wettability of the surface or on the formation of an interlayer between substrate and binder.<sup>[4-54]</sup>

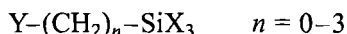
Silanes, titanates, and zirconates have similar activity, which is tied to the similarity of their substituents. They generally include three identical or different substituents in the form of alkoxy groups, and a linkage to the substrate is formed by way of these groups. The fourth substituent is an organic radical which has the capacity to interact with the binder.

Some adhesion promoters can be used as additives to the formulation in question, or can be employed in the form of a surface pretreatment. The advantage of the latter procedure is that the adhesion promoter is located directly in the boundary layer and so is best able to exert its effect. The additional working step, however, is a disadvantage.

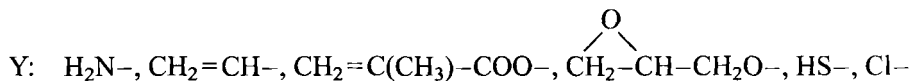
### 4.3.4.2 Organofunctional Silanes

#### Structure and Difference from Alkylsilanes

Organofunctional silanes have the general structure:<sup>[4-55]</sup>



with the organofunctional group

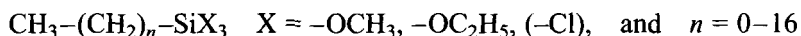


and the silicon functional group

X: usually  $-OCH_3$ ,  $-OC_2H_5$  (generally alkoxy groups, sometimes also  $-OCOCH_3$ ,  $-Cl$ )

Difference from alkylsilanes:

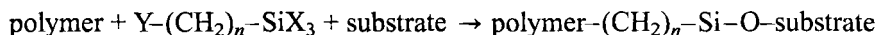
In addition to the functional organosilanes there are also so-called nonfunctional organo- or alkylsilanes. These are silanes of the general structure:



However, the alkyl group is unable to form a bond to the polymer, and so alkylsilanes are inactive as adhesion promoters. They are used merely to make inorganic materials water-repellent and organophilic.

#### Mode of Action

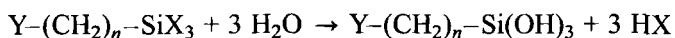
In very general terms, their mode of action is explained by the alkoxy groups or silicon functional groups (X) interacting with the substrate, while the organofunctional group (Y) establishes the bond to the polymer:<sup>[4-55]</sup>



The mode of action of organofunctional silanes consists of a number of possible substeps:

##### 1. Reaction of the Silicon Functional Group

By reaction with the surface moisture of the inorganic substrate (glass, metal, fillers, pigments) or when an aqueous solution is prepared, the alkoxy groups hydrolyse to form reactive silanols:



The rate of hydrolysis decreases according to the following series:



The process is accelerated by acid or base catalysis and by catalysis with certain organometallic compounds, such as tin compounds (dibutyltin dilaurate). Except for the aminosilanols, the resultant silanols are unstable. Condensation with OH groups of the inorganic surface produces a firm bond to the substrate.

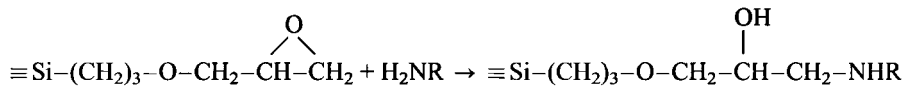
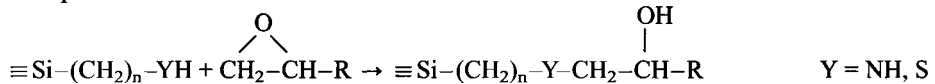
Also of great importance for a good bond in this context is the formation of hydrogen bonds. Different inorganic materials possess different surface activity with respect to silanes. Glass, quartz/sand and mica are regarded as good. Magnesium oxide, kaolin, talc, silicatic fillers, iron oxide, titanium dioxide, and inorganic pigments possess moderate activity, while carbon black, chalk, barium sulphate, and calcium sulphate (gypsum) are of poor activity. Metals with good affinity include iron, aluminium, zinc, and copper. Good bonding can also be established with mineral building materials such as natural stone, concrete, lime sandstone, bricks, and roof tiles. When using silanes as adhesion promoters it must be remembered that, depending on the silane concentration and the pH, water-insoluble polysiloxanes may be formed and that the resultant silanols and the coating binder may also react.

## 2. Reaction of the organofunctional group

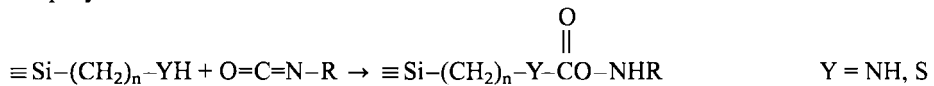
The organofunctional radical, on the other hand, forms a connection with the organic polymer. Examples of the possibilities are:

- free-radically, grafting (vinylsilane),  
e. g., for unsaturated polyesters, EPDM rubber

- for epoxides:



- for polyurethanes:



- for phenolic resins:

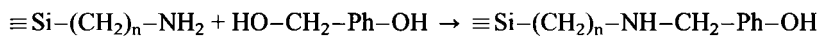


Table 4.3-1 lists silanes which may be suitable as adhesion promoters for the various types of binder.<sup>[4-53]</sup>

**Table 4.3-1.** Selection of silane adhesion promoters

Organofunctional group of the silane adhesion promoter	Recommended for the following polymers
Amino	Epoxy, phenol, melamine, furan, urea, PVC, urethane, polyvinylbutyral, polyimide, polychloroprene, nitrile rubber, etc.
Vinyl, methacryl	Unsaturated polyesters, EPDM, polyolefins, urethane, alkyd
Epoxy	Epoxy, phenol, epichlorohydrin, PVC, polyester, urethane, polysulphide
Mercapto	All elastomers, urethane, polysulphide, PVC
Urea	Phenol, urea or melamine resins, epoxy resins
Chloro	Epoxy resins, polyurethane, thermoplastics

### Properties and Use

Organofunctional silanes are soluble in the usual organic solvents, are flammable, are sensitive to hydrolysis, and have favourable toxicological properties. They are highly effective adhesion promoters when the task at hand is to improve the adhesion of inorganic materials (glass, minerals, metal) to organic partners (thermosets, thermoplastics, elastomers).<sup>[4-55]</sup> The use of organofunctional silanes as adhesion promoters was patented in the mid-1940s for glass-fibre-reinforced plastics, its first major application. Vinylsilane- and methacrylsilane-treated glass fibres are state of the art for polyester laminates. The use of aminosilanes and epoxysilanes has become established for phenolic and epoxy resin laminates.

For use in coatings, varnishes, and paints their particular advantages are:

- the improvement in adhesion, especially after exposure to water, when coatings often separate automatically from the substrate
- the improvement in chemical resistance
- the hydrophobization
- the improved corrosion protection

The adhesion of coatings and sealants to organic substrates is, in some instances, improved by silanes, although there is no satisfactory explanation for such activity. In these applications the silane adhesion promoter is also selected according to the possible reaction of the organofunctional group with the binder used.

The silane adhesion promoter can be employed either as an additive or in the form of a primer (silane content 1–2%) for pretreating the substrate. When introduced as an additive, larger quantities are required than for the primer form. The competitive effect of mineral components present in the mixture may have to be borne in mind. Added silane is absorbed by inorganic compounds and is then no longer available to effect external adhesion.<sup>[4-56]</sup>

The primer is produced by preparing a dilute silane solution (silane content 1–2%) and then applying it thinly. Suitable solvents are organic ones such as alcohols, ke-

tones, or aromatics; small amounts of water may also be present. Aqueous solutions can also be employed; the silane is hydrolysed when water is present in concentrations of 0.2–2%, when acid has been added (usually acetic acid), and the pH is between 3 and 4. Depending on the type of silane, the result after 5 to 60 minutes is a clear, aqueous solution which, however, remains stable for a limited period only, owing to the formation of oligomeric siloxanes. For the amino-functional silanes, no acid needs to be added to prepare the aqueous solution. In comparison to the other types, moreover, their aqueous solutions are stable for a substantially longer period. Aqueous silane solutions develop their full activity about 30 minutes after preparation. Table 4.3-2 shows examples of important organofunctional silanes.

**Table 4.3-2.** Examples of silane-based adhesion promoters

Name	Structure
(3-Aminopropyl)trimethoxysilane	$\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$
(3-Aminopropyl)triethoxysilane	$\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$
(3-Aminopropyl)diethoxymethylsilane	$\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{CH}_3)(\text{OC}_2\text{H}_5)_2$
( <i>N</i> -Aminoethyl-3-aminopropyl)trimethoxysilane	$\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$
( <i>N</i> -Aminoethyl-3-aminopropyl)dimethoxymethylsilane	$\text{H}_2\text{N}(\text{CH}_2)_2\text{NH}(\text{CH}_2)_3\text{Si}(\text{CH}_3)(\text{OCH}_3)_2$
Triethoxy-(3-ureidopropyl)silane	$\text{H}_2\text{NCONH}(\text{CH}_2)_3\text{Si}(\text{OC}_2\text{H}_5)_3$
Trimethoxy-(3-methacryloxypropyl)silane	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$
(3-Glycidyloxypropyl)trimethoxysilane	$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CHCH}_2\text{O}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3 \end{array}$
(3-Mercaptopropyl)trimethoxysilane	$\text{HS}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$
(3-Chloropropyl)trimethoxysilane	$\text{Cl}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$
Trimethoxyvinylsilane	$\text{CH}_2=\text{CHSi}(\text{OCH}_3)_3$

Examples of commercial products:

Dynasilan	(Degussa-Hüls AG)
Prosil	(PCR Incorporated)
Silquest	(OSi Specialties)
Additive grades	(Dow Corning)
GF grades	(Wacker-Chemie)

#### 4.3.4.3 Organometallic Compounds

##### Titanates and Zirconates

Organotitanates and zirconates have been used successfully for many years as additives for promoting adhesion in coating materials and printing inks. In addition, they are employed as catalysts for esterification and transesterification reactions, polyaddition reaction, and addition polymerization. Titanates and zirconates are

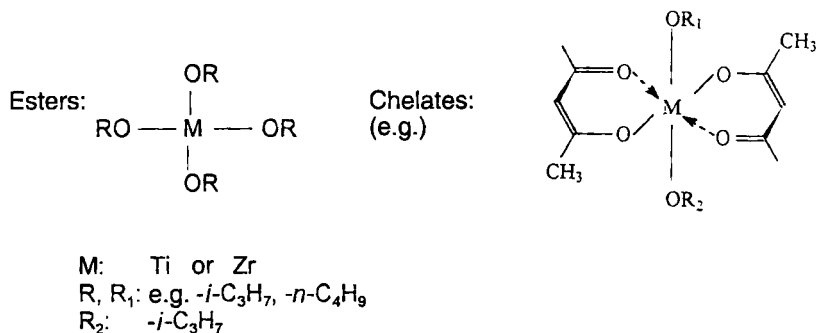


Figure 4.3-3. Structure of organotitanates and organozirconates

highly reactive compounds. With  $-\text{OH}$  and  $-\text{COOH}$  groups they form stable bonds and so are also used as crosslinking agents in industrial coatings, wire enamels, printing inks, and emulsion paints. Within such systems they speed up the curing rate and at the same time improve water and chemical resistance and thermal stability.<sup>[4-57]</sup> They are likewise of importance as dispersing auxiliaries.

Adhesion promoters based on organotitanates and organozirconates have the general structures shown in Fig. 4.3-3.

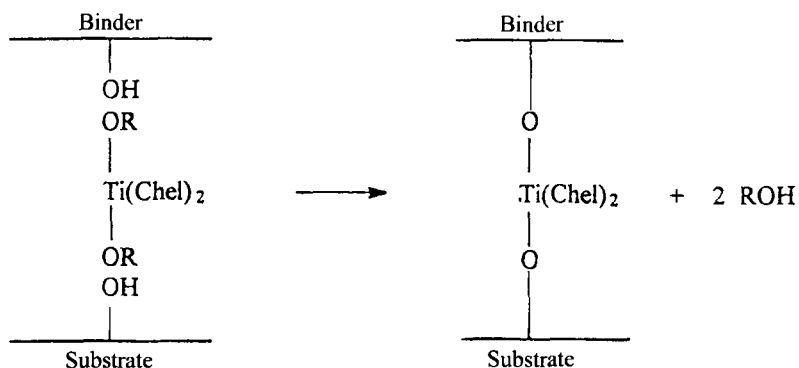
Acetylacetonate is used predominantly for chelation. Table 4.3-3 shows a number of examples of titanates and zirconates that are employed as adhesion promoters.<sup>[4-54, 4-57]</sup>

Table 4.3-3. Examples of titanate- and zirconate-based adhesion promoters

Name	Structure
Tetraisopropyl titanate	$\text{Ti}(\text{O}-i\text{-C}_3\text{H}_7)_4$
Tetra( <i>n</i> -butyl) titanate	$\text{Ti}(\text{O}-n\text{-C}_4\text{H}_9)_4$
<i>n</i> -Butyl polytitanate	$n\text{-C}_4\text{H}_9\text{O}-[\text{Ti}(\text{OC}_4\text{H}_9)_2\text{O}]_n\text{-C}_4\text{H}_9$
Isopropyl triisostearoyl titanate	$(\text{CH}_3)_2\text{CHOTi}(\text{OC}_{17}\text{H}_{35})_3$
Titanium acetylacetonate	$(i\text{-C}_3\text{H}_7\text{O})_2\text{Ti}(\text{C}_5\text{H}_7\text{O}_2)_2$
(various possibilities)	$(i\text{-C}_3\text{H}_7\text{O})(\text{C}_4\text{H}_9\text{O})\text{Ti}(\text{C}_5\text{H}_7\text{O}_2)_2$ $(i\text{-C}_3\text{H}_7\text{O})(\text{C}_2\text{H}_5\text{O})\text{Ti}(\text{C}_5\text{H}_7\text{O}_2)_2$
Isopropyl tri( <i>N</i> -ethyl-aminoethylamino) titanate	$(\text{CH}_3)_2\text{CHOTi}(\text{OCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2)_3$
Citric acid diethyl ester zirconate	$(n\text{-C}_3\text{H}_7\text{O})_2\text{Zr}(\text{C}_{10}\text{H}_{15}\text{O}_7)_2$

As with silanes, titanates and zirconates are employed either in the form of a pre-treatment (primer), or are added as additives. Through pretreatment they enhance wetting and adhesion of coatings on substrates such as glass, metal and plastics (pretreated).

Their mode of action is comparable to that of the silanes by virtue of their similar reactivity towards, for example, water,  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{NH}_2$ , and  $-\text{CONH}-$  groups.



**Figure 4.3-4.** Mode of action of titanium acetylacetonate as an adhesion promoter

Lindall and Duncan's description of the mode of action of titanium acetylacetonate in printing inks is depicted in Fig. 4.3-4.<sup>[4-58]</sup>

Chelates are less reactive than the pure esters. For printing inks in particular, the high reactivity of the esters causes unwanted premature reactions with the binder, therefore chelates are predominantly employed for this purpose. Titanium acetylacetonate is the most important in this respect.

Titanium acetylacetonate is especially important in improving the adhesion of solvent-based printing inks on difficult substrates such as pretreated polyethylene and polypropylene foils.<sup>[4-57]</sup> In this case the attachment is, for example, to OH groups formed in a corona pretreatment.

Lindall and Duncan describe the use of titanium acetylacetonate for packaging printing inks. In addition to providing effective adhesion, the advantages are good toxicological properties and the enhanced water, solvent, and heat resistance. However, the strong intrinsic colour and marked intrinsic odour limit the use options to some extent, although new developments are accompanied with improvements in these respects.<sup>[4-58]</sup>

Neoalkoxy organotitanates and -organozirconates are described by Kenrich Petrochemicals as suitable adhesion promoters with adequate thermal stability at 200 °C for a broad range of different polymer substrates such as polyurethanes and polypropylene.<sup>[4-59]</sup>

Examples of commercial products:

TYZOR	titanates and zirconates	(DuPont)
Ken-React	titanates and zirconates	(Kenrich Petrochemicals Inc.)
Tilcom	titanates	(Tioxide Chemicals)

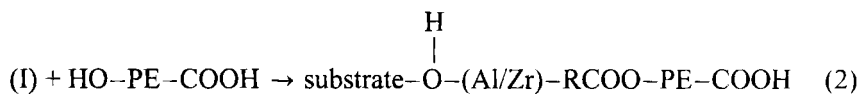
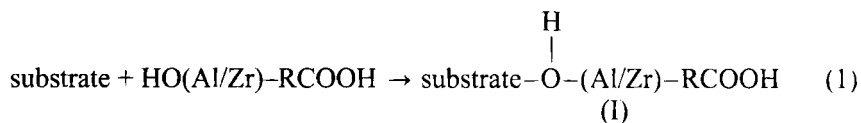
### Zirconium Aluminates

Sathyanarayana and Yaseen describe zirconium aluminates as a new class of organometallic adhesion promoters with efficient action on metals and difficult substrates.<sup>[4-60, 4-61]</sup>

Applications include:

- solventborne and aqueous coatings (high-solids polyesters and epoxies, alkyd resin systems)
- rubber applications

Zirconium aluminates interact with the metal surface via OH groups. The carboxyl groups of the zirconium aluminate then undergo condensation reactions with OH groups in the resin:



Compared to silanes, the zirconium aluminates are hydrolytically stable.

They are suitable as adhesion promoters for a number of substrates (metals, difficult substrates). In addition, they improve wet adhesion and thus the corrosion protection afforded by solventborne and aqueous coatings.

Zirconium aluminates are highly polar and are difficult to incorporate into the resin/solvent system. In order to incorporate them, the user has to exert high shear forces in order to bring about their optimum fine distribution within the system.

Example of commercial products:

Manchem (Rhône-Poulenc)

#### 4.3.4.4 Chlorinated Polyolefins

Examples of these are chlorinated polyethylene and polypropylene, which are obtained by chlorinating the corresponding polyolefins.<sup>[4-62]</sup> They are used in particular for improving the adhesion of polyolefin substrates without pretreatment.

They are employed, on the one hand, as adhesion primers, in film thicknesses of 2–5 μm. To improve the adhesion of printing inks, these primers are usually sufficiently active. Nevertheless, pretreatment by, for example, corona discharge or flame treatment is not always avoidable, especially in the case of polyethylene. These adhesion primers are, however, highly effective on untreated or EPDM-modified polypropylene. Here, the activity is dependent on the film thickness. Film thicknesses of between 2 and 4 μm, and somewhat higher drying temperatures are regarded as favourable. In practice, however, it is not always easy to consistently reproduce the film thickness and surface wetting with the required accuracy.<sup>[4-63]</sup>

Chlorinated polyolefins are also suitable for improving the adhesion of coatings on other plastic substrates or metals such as galvanized steel or aluminium.

Other than in the form of adhesion primers, they are, secondarily, used as coating additives. In this case, it must be borne in mind that basic pigments such as zinc oxide and lithopones promote decomposition and so may have an adverse effect on the stability. Another disadvantage is that, under certain conditions, chlorinated polyolefins have a tendency to give off HCl. They can be stabilized by adding “scavengers”, such as epoxides.<sup>[4-62]</sup>

Examples of commercial products (chlorinated polypropylene):

Chlorinated polyolefin CP (Eastman Chemical)  
Hardlen (Toyo Kasei)

#### 4.3.4.5 Special Condensates

##### Polyesters

Products that improve adhesion also include special polyester resins, which differ in flexibility/hardness and in their compatibilities/solubilities. Generally speaking, they improve adhesion on various metallic, mineral, and plastic substrates, to some extent on particle board with a melamine resin coating, and they enhance intercoat adhesion. There are also specific variants which can improve adhesion even on olefinic substrates such as, for example, PP/EPDM (pretreated). Such adhesion promoters are used in coating materials (can/coil coating, solventborne and aqueous industrial coatings), conventional and radiation-curing printing inks, adhesives, floor paints, roadmarking paints, etc.

Examples of commercial products:

Adhesion Resin (Degussa-Hüls AG)  
Borchigen (Gebr. Borchers AG)  
Plusolit (Pluess-Staufner AG)  
Alresat (Hoechst)  
WorleeAdd (Worlee)

##### Rosin Esters

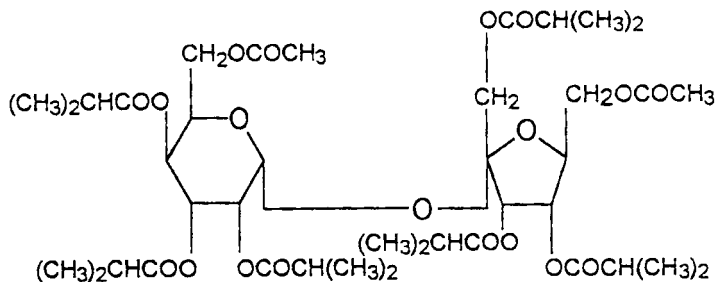
Rosin is obtained by extraction and subsequent processing from a variety of woods (mostly pine species). Rosin consists of a series of what are known as resin acids, the principal constituent being abietic acid. Others represented include neoabietic, palustric, pimaric, isopimaric, and dehydroabietic acid. The carboxyl group of the resin acids can be reacted, inter alia, to form esters. Such esters may act as adhesion promoters for metals.<sup>[4-62]</sup> They are used, for example, in flexographic printing and in the printing of foils and packaging.

Example of a commercial product:

Rokrasin (Robert Kraemer GmbH)

### Products Based on Sucrose

Products based on the disaccharide sucrose (saccharose) are also significant as adhesion promoters. Sucrose acetoisobutyrate (SAIB) is available commercially:



Sucroseacetoisobutyrate

The highly viscous liquid not only raises the solids content with no loss of film hardness, but also improves the adhesion of coatings for wood, paper, plastics, and metals. The good pigment wetting is also an advantage.<sup>[4-64]</sup>

Sucrose benzoate has also been described to be used in the same way as SAIB.<sup>[4-65]</sup>

Example of a commercial product:

SAIB sucrose acetoisobutyrate (Eastman)

#### 4.3.4.6 Phosphates

To improve adhesion on metallic substrates and to improve intercoat adhesion as well, special phosphates are used. Another important point favouring the use of such products is their enhanced corrosion protection (passivation of the metallic substrate).

Examples of commercial products:

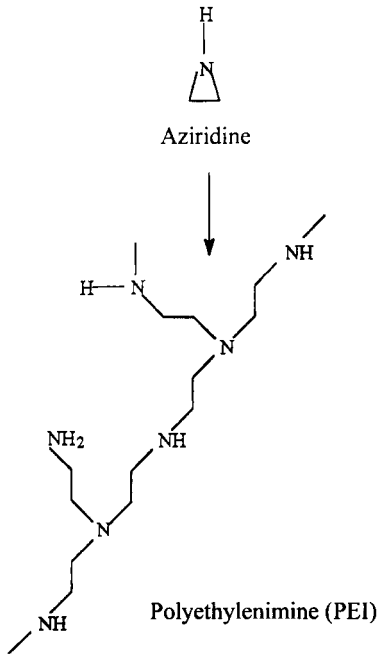
Lubrizol (The Lubrizol Corporation)

Additol (Hoechst)

#### 4.3.4.7 Polyethylenimine

Polyethylenimines (PEIs) are branched, spherical, polymeric amines prepared from aziridine (with a free aziridine content of < 1 ppm). Each two carbon atoms are followed by a nitrogen atom. No other class of cationic polymer has so many cationic

amine functions within such a restricted space. The ratio of primary to secondary to tertiary amines is approximately 1 : 2 : 1.



The cationic character can be raised by protonation. Polyethylenimines are highly soluble in polar solvents and partly soluble in apolar solvents. They are infinitely miscible with water.

In varnishes, paints, and adhesives they generally improve adhesion to porous and nonporous surfaces. They are employed, furthermore, as hardeners for epoxy resins. In inks, they increase water resistance.

Further areas of use are in papermaking (aggregation of paper fibres), the complexation of heavy metals (in effluent treatment, for example), wood preservation, textiles, etc.

Example of a commercial product:

Lupasol (BASF)

#### 4.3.4.8 Silicones and Silicone-Modified Polymers

Silicones and polyorganosiloxanes are polymeric organic silicon compounds in which the silicon is attached directly to carbon and in which there is at least one bond to oxygen. Because of the presence of reactive silanol groups and surface activity, silicones and, correspondingly, silicone-modified polymers generally provide

good adhesion to metals, mineral substrates and, in some cases, glass. Moreover, such adhesion promoters may also improve the water resistance.<sup>[4-60]</sup>

Example of a commercial product:

Dow Corning additive (Dow Corning)

#### 4.3.4.9 Miscellaneous

##### **Platelet-Shaped Fillers and Pigments**

A mechanical improvement in adhesive strength can be achieved with platelet-shaped fillers and pigments. Talc is often used in this context. The forces of adhesion between the platelet-shaped particles and the substrate, however, are determined by the paint formulation itself. Their effectiveness is, moreover, limited almost solely to mineral substrates, including glass.<sup>[4-53]</sup>

Example of a commercial product:

Talkum SM-M10 talc (Scheruhn Talkum-Bergbau GmbH)

##### **Others**

Sathyanarayana and Yaseen described a range of further classes of chemical compound which may promote adhesion.<sup>[4-60]</sup>

They include:

- amides/imides as adhesion promoters for vinyl-based adhesives for metals, wood, and plastics
- naphthenates (metal soaps) as adhesion promoters for bitumen, antifouling paints, and some printing inks as well, amongst others
- organophosphorus enamines as a new class of adhesion promoters for glass
- silyl-functionalized polymers for improving adhesion to metallic substrates

#### 4.3.4.10 Summary

Coatings are only able to fulfil their purpose if they adhere sufficiently. Adhesion promoters play an important role in this context, to possibly improve adhesion. The adhesion promoter most suitable for a given application is a function, *inter alia*, of the application, the composition of the coating, and the substrate. In conclusion, Table 4.3-4 gives an overview of suitable adhesion promoters as a function of coating and substrate.

**Table 4.3-4.** Application fields for the different classes of adhesion promoters

Adhesion promoter	Coatings system	Substrates
Silanes	In general for coatings based on epoxy-, phenol-, urea-, or melamine resins, furans, PVC, urethanes, PVB, polyimides, polychloroprene, rubber, polyesters, polyolefines, alkyd resins, primer	Glass, mineral substrates, (concrete, bricks, natural stones), partially for metals (Fe, Al, Zn, Cu); glass-fibre-reinforced plastics
Titanates, zirconates	Printing inks (based on, e. g., nitro-cellulose, PVB, CAB, CAP), Industrial paints (resins with OH-, COOH-, NH <sub>2</sub> groups, e. g., polyesters, polyamides), wire enamels (polyesters, polyesteramides, polyesterimides), primer	Critical polyolefinic substrates, e. g., pre-treated PP, metals (e. g., Al, steel), glass
Zirconium aluminates	Solvent- and waterbased coatings, adhesives, rubber, high-solid polyester/epoxide systems, alkyd resins	Metals, critical substrates
Chlorinated polyolefins	Plastic substrates, primer	Above all nonpolar plastics (PP, PE), functions partially without any pre-treatment, metals
Special polyesters	Paints (CAN/COIL coating, solvent- and waterbased industrial paints), conventional and radiation-curing printing inks, adhesives, floor paints, roadmarking paints	Metals, mineral substrates, plastics; enhance intercoat-adhesion
Rosin esters	Flexo-, foil-, and packaging-printing inks	Metals
Sucrose derivatives	Paints, printing inks, hotmelts	Wood, paper, plastics, metals
Phosphates	Coatings, e. g., on the basis of alkyd resins, polyesters, acrylates	Metals, enhance intercoat-adhesion
Polyethylenimines	Paints, adhesives, primer	Improvement in adhesion to porous and nonporous surfaces
Silicones	Organic coatings	Metals, mineral substrates, sometimes glass
Talc	Organic coatings	Mineral substrates

## 4.4 Additives to Improve Substrate Wetting

*Wilfried Scholz*

When a liquid coating is applied to a substrate, it is expected that it will wet that substrate easily and evenly. Good wetting is necessary for a good optic appearance, good adhesion to the substrate, and full functioning of the coating (substrate protection).

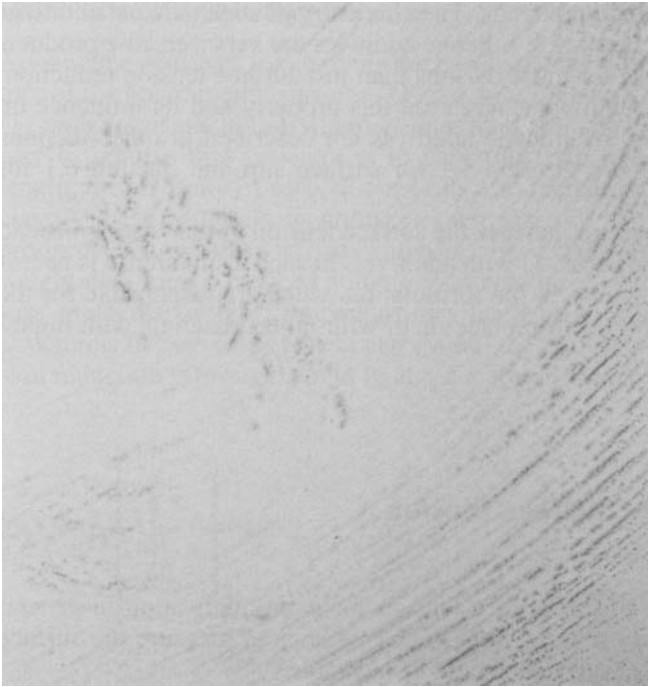
### 4.4.1 Importance of Surface Tension for Substrate Wetting

The surface tension values of the involved materials, the (in most cases) liquid coating and the solid substrate, are most important for substrate wetting. In general, for good substrate wetting the surface tension of the coating material ( $\sigma_p$ ) should be lower than the surface tension of the substrate ( $\sigma_s$ ), or they should at least be equal.

$$\sigma_p \leq \sigma_s$$

If the surface tension of the coating material is higher than that of the substrate, poor wetting may occur (Fig. 4.4-1). The real reason for insufficient substrate wetting is the too high surface tension of the liquid coating, however, other factors will also influence how strongly this defect shows up. Film thickness is, for example, quite important: wetting problems are easily seen in thin coating layers; a high film buildup may cover the defects. The viscosity/rheology of the coating plays, in a similar way, an important role: low-viscous systems with more Newtonian flow behaviour will show substrate wetting problems at once, whereas highly viscous systems will not show the defects at all.

The situation is further complicated by the fact that the polarity of the substrate and possible surface structures (porosity, roughness) will also influence the final appearance. Furthermore, specifically with “natural” surfaces such as wood, the surface tension will not be the same across the whole surface but will vary. Additional surface tension irregularities can be due to contamination of the surface, which will then cause wetting problems in the form of craters in some areas. Finally, there is also a time aspect. Immediately after application, the liquid paint film may have a surface tension that is lower than the surface tension of the substrate, and therefore substrate wetting is perfect. But this situation can change until the film formation process is finished, and dewetting effects may occur. The surface tension of the substrate is constant, but the surface tension of the liquid phase changes due to solvent evaporation and crosslinking reactions. If, in this process, the surface tension of the liquid exceeds that of the substrate, dewetting can occur, if the film viscosity is still low enough.



**Figure 4.4-1.** Poor substrate wetting of an aqueous baking enamel on a metallic substrate. In this specific case the dewetting effect is due to contamination of the substrate (residual traces of oil) and the relatively high surface tension of the aqueous coating system

#### 4.4.2 Influencing the Surface Tension of Coatings

The surface tension of the liquid coating is primarily defined by the selection of the resins and the solvents; the pigments have no influence. In practice, however, selection of these raw materials is normally not based on their surface tension but on other properties. Resins are selected for, for example, their crosslinking mechanism, the required chemical resistance, and the mechanical properties of the dry film. For the solvents it is important that they can easily dissolve the resins in questions; other important properties are evaporation behaviour, flash point, and – more and more important these days – their ecological performance.

Therefore it is very convenient to control the surface tension of the liquid paint independently from other raw materials by suitable additives. It was shown above that improvement of substrate wetting requires a reduction of the surface tension of the coating. Additives which can do exactly this are polysiloxanes and fluoro surfactants. Polysiloxanes modified in many ways (“silicone additives”) have found

broader usage than the fluoro compounds. The chemistry of such silicone additives is discussed in detail in Section 4.4.4. Silicone additives are very versatile products and they are used in coatings for more reasons than just surface tension reduction. However, in this section we will concentrate on this property and its influence on substrate wetting. Other uses of silicone additives are described in other sections (see Section 4.2 for defoamers, Section 5.1 for surface slip and Section 6.1 for levelling).

In some cases it is necessary to increase the surface tension of the coating instead of reducing it; this cannot be achieved with additives. In such a situation it is necessary to identify those components in the formulation which are responsible for the low surface tension and then try to replace them with other materials with higher surface tension.

### 4.4.3 Measurement of Surface Tension

Because of the importance of the surface tension for paint application in general and specifically for substrate wetting, convenient methods to measure the surface tension of liquids and of solid surfaces should be available.<sup>[4-66]</sup>

The *static* surface tension of liquids can easily be determined with the *ring detachment method* of Nouy. For higher-speed application processes (printing, roller coating) the *dynamic* surface tension needs to be measured, for example, with the *bubble method*.<sup>[4-67]</sup> For both methods and other similar methods, suitable instruments are commercially available.

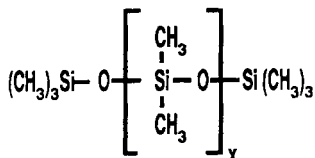
The determination of the (critical) surface tension of solid surfaces is possible with the *contact-angle method*. It is quite time-consuming, but automatic instruments are available nowadays, which have made this method routine.<sup>[4-68]</sup> A procedure is derived from the contact-angle method, which allows a qualitative estimation of the surface tension of the substrate by the application of different test liquids.<sup>[4-69]</sup> For systematic and scientific investigations it is absolutely necessary to measure the exact surface tension, but for many practical purposes, however, a quick application test is often faster and – due to the fairly complex interrelations – often gives more reliable results.

### 4.4.4 Chemistry of Silicone Additives

The term “silicones” is used for a wide variety of different chemical products, which are used in many different technical application areas. Only a small number of these chemicals are suitable as additives for paints and coatings.

### Unmodified Polydimethylsiloxanes

All silicone additives for coatings are based on the relatively simple chemical structure of the polydimethylsiloxanes (Fig. 4.4-2). The backbone consists of several Si–O– units (siloxane units), where each silicon atom carries two methyl groups. One way to modify this structure is to vary the chain length. With increasing chain length, the viscosity of such silicone oils also increases, and therefore it is useful to classify these materials according to their viscosity. Some commercially available products even use this viscosity value as part of their trade name. Higher molecular weight also means reduced solubility in coating systems and lower compatibility. Low-molecular-weight compounds may have, besides linear structures, also cyclic structures. In both cases (linear and cyclic) the typical silicone effect of surface tension reduction is brought about by the dimethyl structures.

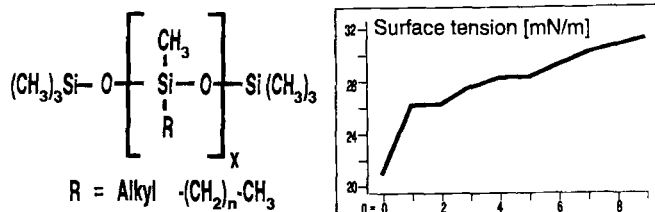


**Figure 4.4-2.** Chemical structure of polydimethylsiloxanes (silicone oils)

Polydimethylsiloxanes with low molecular weight (number of dimethyl groups  $x < 60$ ) and cyclic products ( $x = 3$  to  $6$ ) reduce surface tension and also improve levelling of coatings. Their viscosity is in the range from 1 to 50 mPa · s. The cyclic products (as well as the linear products with  $x < 6$ ) are volatile and therefore their usage is not without problems: they evaporate from the coating film during the baking process and may then later, for example, in the baking oven, condensate chemically to very high molecular products which can then contaminate other paints and substrates and cause severe cratering. Products with a higher molecular weight ( $60 < x < 100$ ; viscosity between 50 and 100 mPa · s) additionally give a better surface slip to the dry coating film (see Section 5.1). Polydimethylsiloxanes with  $x \approx 1200$  (viscosity  $\approx 60\,000$  mPa · s) have, for many commonly used binder systems, just the right balance between compatibility and incompatibility to be effective as defoamers. Products with an even higher molecular weight ( $x > 1400$ , viscosity  $> 100\,000$  mPa · s) are so incompatible and insoluble in most coating systems, that they create craters in a very defined and reproducible way, and therefore can only be used for special effect coatings like hammertone finishes.

### Polymethylalkylsiloxanes

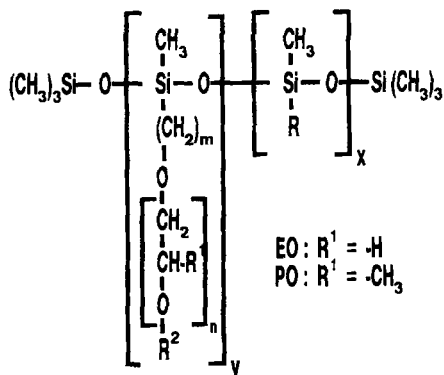
To modify the properties of the polysiloxanes it is possible, apart from varying the chain length, to replace the methyl groups (partly) by other side chains. Polysiloxanes with methylalkyl groups still have the typical silicone properties, but the surface tension of such materials increase with increasing alkyl chain length (see Fig. 4.4-3) and therefore their surface-tension-reduction effect is less pronounced.



**Figure 4.4-3.** Structure of polymethylalkylsiloxanes and influence of the length of the alkyl side chain on surface tension

### Organically Modified Polysiloxanes

More important for coating applications is the possibility of replacing some of the methyl groups by chemically completely different groups; the resulting products are termed “organically modified” polysiloxanes. This organic modification is a very elegant method to control the compatibility of these structures with coating systems. These organic side chains improve the compatibility, and the above-mentioned influence of the molecular weight of the polysiloxane backbone becomes less important. In most cases, the polysiloxanes are modified with polyether chains (see Fig. 4.4-4). This way of modification offers so many possibilities, that silicone additives with very specific property profiles can be synthesized and be tailor-made for the various requirements of many application areas.



**Figure 4.4-4.** Polyether-modified polysiloxane. The polyether side chains can be built up from ethylene oxide units (EO) or propylene oxide units (PO)

The dimethyl groups give the silicone additives a low surface tension, and variation of the ratio dimethyl groups to polyether modifications ( $x:y$ ) therefore offers an ideal way of adjusting the surface tension to specific values. As described above, there still is the additional possibility of influencing the surface tension by replacing some of the remaining dimethyl structures by methylalkyl groups. This further increases the surface tension of the silicone and the surface tension reduction effect of the additive is reduced accordingly.

Furthermore, the structure of the polyether chain itself can be modified. These polyethers are basically made up of ethylene oxide units (EO) and propylene oxide units (PO). Polyethylene oxide is quite hydrophilic (polar), whereas polypropylene oxide is hydrophobic (nonpolar). The EO/PO ratio therefore controls the overall polarity of the silicone additive: high EO amounts increase the polarity and the additive becomes more compatible in polar coating systems and the additive may even become water-soluble. However, its foam-stabilization tendency also increases at the same time. High PO amounts, on the other hand, reduces water-solubility and increases defoaming properties.

Besides the EO/PO ratio and the number of the polyether modifications, it is also important to know where in the polysiloxane backbone these modifications are located: statistically distributed along the backbone (comb structure), as block structures, or only at both ends of the polysiloxane chain.

Another detail is the way in which the polyether chain is linked to the polysiloxane backbone. Fig. 4.4-4 shows that the polyether is not linked directly to the silicone atom but by a (short) alkyl chain. Such a linkage is hydrolytically stable. In case of a direct linkage, the resulting products are prone to hydrolysis: polyether groups are easily split off and the remaining polysiloxanes react to high molecular weight structures by condensation reactions (compatibility is lost, cratering very probable).

### Other Modifications

In most cases, modification of the silicones is made with polyether chains, but other modifications are also possible and are also used in practice. Most interesting are modifications with polyester chains and arylalkyl groups (Figs. 4.4-5 and 4.4-6). Silicones modified in this way also reduce surface tension of coatings and, in addition to this, such additives are much more thermostable. Polyether-modi-

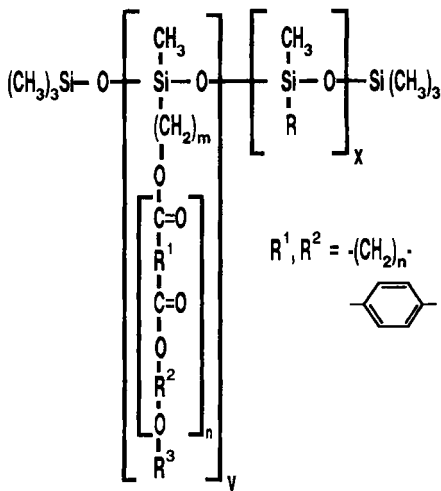


Figure 4.4-5. Polyester-modified polysiloxanes

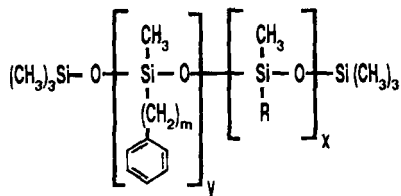


Figure 4.4-6. Arylalkyl-modified polysiloxanes

fied polysiloxanes undergo thermal degradation at temperatures above approximately 150 °C; polyester- and arylalkyl-modified polysiloxanes are stable up to temperatures of 200 °C and above. The thermal degradation of the silicone additives should be avoided because it can cause problems with overcoating and intercoat adhesion.

### Silicone Surfactants for Aqueous Coatings

As shown above, it is possible, by adjusting the polarity, to synthesize silicone additives that are compatible with aqueous coating systems. However, the efficiency of such additives is often not sufficient, especially when low-energetic substrates (plastics) have to be wetted. The water content in these coating systems creates a relatively high surface tension (higher than in solvent-based coatings) which is reduced by the silicone additives, but often is still too high for good wetting. For such cases, a special class of silicone additives was created: silicone surfactants.<sup>[4-70]</sup> Chemically, these additives are also polyether-modified siloxanes, but their molecular weight is much lower, resulting in a pronounced surfactant-like structure. Due to this structure, these additives strongly reduce the surface tension in aqueous systems; they are nearly as active as fluoro surfactants. Compared to the fluoro surfactants the silicone surfactants, however, have one important advantage: foam stabilization by silicone surfactants is nearly absent, whereas fluoro surfactants are not always unproblematic in this respect.

### 4.4.5 Usage of Silicone Additives

Very small amounts of polysiloxanes in a coatings system can already have very pronounced results. To avoid problems, several points have to be observed for their successful application.

#### Dosage

Due to their high surface activity, the dosage of the undiluted polysiloxanes (100% active substance) are typically between 0.01% and 0.2% of the total formulation. To be able to handle such small amounts, the additives are in most cases used as (strongly) diluted solutions. If the dosage is too high or the silicone additive in gen-

eral is too incompatible, crater formation may result. Overdosing can also reduce the recoatability of the coating film and create adhesion problems of the second layer. In principle, silicone-containing coatings are recoatable, as long as the surface tension of the second paint layer is low enough. If the silicone content in the first coating, however, is too high, then the surplus silicone practically separates the two paint layers and intercoat adhesion is reduced.

Therefore, the lowest possible amount of silicone that gives the required effect (substrate wetting in this case) should be used.

In many practical situations it is not possible to completely isolate one coating system from other coatings. In many cases, several paints are used in the same spray booth at the same time or in short succession. Overspray of one coating then may cause craters in the freshly applied paint film of another coating when the spray dust has a lower surface tension. This example shows that, in many situations, surface tensions of different coatings must be adjusted to roughly the same value.

### **Incorporation and Testing**

Incorporation of the silicone additives in the coating formulation is, in most cases, not critical. Normally they are added during the let-down phase and mixed into the coating. Homogeneous distribution of the additive in the coating has to be assured; otherwise locally high concentrations can cause cratering. To evaluate the effectiveness of the additives, it is possible to measure the surface tension reduction (see Section 4.4.3) or to directly check the influence on substrate wetting by an application test.

### **Side Effects**

Silicone additives do not only influence surface tension of the coatings, as mentioned above, they also influence other properties. In each case it has to be checked if these influences are desirable (acceptable) or undesirable. In most cases, an influence on levelling and surface slip will be deemed positive. Negative side effects are primarily problems with recoatability (wetting and adhesion problems) and foam stabilization. As shown above, for problem-free recoatability, the correct dosage and the right baking temperature are essential. Correct dosage is also important with regard to foam stabilization. Furthermore, the chemistry of the silicone additive itself is relevant: if a coating under defined application conditions has a tendency to foam, the use of a more suitable silicone (less compatible, higher surface tension) can avoid the foam or reduce it at least in such a way that a defoamer will work successfully.

It is possible to make use of the desired effect of the silicones to improve substrate wetting without creating other negative side effects.

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## **5 Additives for Surface Modification**

*Wilfried Scholz*

The mechanical and optical properties of a coating surface are primarily defined by the resin system, and in the case of pigmented systems, the dispersed pigment and extender particles also have an influence.

The resin binder controls the mechanical hardness, scratch resistance, and scrub resistance of the coating surface as well as the surface slip. All these properties are closely connected. The use of polysiloxane-based and wax-based additives makes it possible to control these surface characteristics independent from the coating binder.

One of the important optical surface properties is gloss. With this, the resin system also has some influence, but more important are the dispersed pigment particles and extenders, in particular the particle size, shape, and state of dispersion: small and well dispersed, deflocculated particles are necessary for the highest gloss readings. Partly flocculated systems have larger particles and therefore less gloss. Flocculation is, however, not the recommended method for controlling the gloss level, the use of matting agents is preferable.

## 5.1 Additives to Improve Surface Slip

*Wilfried Scholz, Wernfried Heilen, and Johan Bieleman*

### 5.1.1 Introduction

The term surface slip describes the slip resistance in the coatings surface (friction), which is a mechanical property. Additives to control this property are described in this section. Another, closely related property, is the surface smoothness, which describes the geometry of the surface structure and which can be influenced by leveling additives (see Section 6.1).

### 5.1.2 Important Terms

A few terms related to surface slip are defined here:

- **Sliding or slipping** is the relative movement of two objects that are in contact with each other.
- **Scratch resistance** is the resistance of a surface against visible, linear injuries caused by moving, hard objects that make contact with the surface; during scratching, the scratching object moves relative to the surface.<sup>[5-1]</sup>
- **Mar resistance** includes scratch resistance as well as the resistance against the development of streaks as a result of friction/rubbing of sharp objects against the paint surface.<sup>[5-2]</sup>

### 5.1.3 Practical Importance of Surface Slip

Depending on the usage of the coating system, it is either the surface slip itself that is of interest, or other properties that are closely related to the slip resistance.

With, for example, floor coatings or parquet lacquers, the slip properties directly control the appropriateness of the coating. Too much slip can be dangerous: floors in gyms, for example, have very narrow requirements regarding slip. With paper coatings, the slip properties have a strong influence on the handling of the coated paper material: too much slip will cause problems when the paper has to be stacked. Surface slip also controls the “feel” of a material and can bestow a “soft-feeling” effect.

In many cases greater surface slip is welcome, because this also means better surface protection. A surface with less slip resistance is not really harder, but it gives that impression. Due to the higher slipping ability, it is not so easy to damage the surface mechanically. Thus, the scratch- and scrub resistance is improved, and metal- and black-heel marking is reduced. In all these cases, an increase in slippage leads to an accompanying enhancement in the effect. A scratched surface has lost not only its optical appeal, but also, at the same time, the protective function of the coating has been reduced.

### 5.1.4 Factors Influencing Scratch Resistance

The scratch resistance of a coating is made up of a complex mixture of factors:

- hardness
- elasticity and viscosity of the dried material
- slip properties

The hardness or toughness is the resistance of the object against penetration by another object.<sup>[5-1]</sup> The penetration resistance has a great influence on the scratch resistance of a surface, although the hardness of a coating is never enough to make it automatically scratch-resistant. A complication is that increasing hardness is accompanied by marked deterioration in properties such as flexibility and adhesion.

The hardness of the surface greatly determines the appearance of developing scratches. The harder and more brittle a surface is, the more it tends to crack. At every scratch, irregular pieces break off. A softer surface results in regular scratches that come about through the plastic deformation of the paint material.

Both “soft” and “hard” surfaces can be scratch-resistant. The decisive factor is the elastic toughness of the coating. The ideal scratch-resistant coating is completely elastic, that is, the surface should be deformable, and the polymer matrix should be able to recover from the deformation, and get back to the original state. An example of this is the relatively soft rubber which is, on the basis of its dominating elasticity, very scratch-resistant.

The third factor that influences the scratch resistance is the properties of the surface – its smoothness or slipperiness, this determines the sliding or slip properties.

### 5.1.5 Slip Ability

For two surfaces to slide past one another, frictional force needs to be overcome.<sup>[5-1, 5-2]</sup> If the two surfaces were originally in a resting state, the first force to overcome is the adhesive friction, and the next force the lesser slip friction. Friction may be

regarded as a force operating in the direction opposite to the movement and velocity. The main origin of the friction is the uneven surface of the object. Microscopic analysis will show even carefully prepared surfaces to be rough and fissured.

For a solid object: The frictional force,  $F$ , is directly proportional to the applied load,  $G$ . The ratio of these values is the unitless coefficient of friction,  $m$ . The frictional force is independent of the contact surface of the sliding objects.

When a surface with a defined applied force slides past another surface, the resulting frictional force is determined only by the frictional coefficient,  $m$ , which depends on the properties of the surface, i. e.:

$$F = m G \text{ (at constant speed)}$$

Large friction means that there are many microscopically small surface unevennesses that are colliding. These uneven parts rub off onto the other surface, or even penetrate it to cause scratches. This can be lessened by careful polishing. With polishing, a fine unevenness is transferred to the coating surface, to reduce the number of possible exposed sites. A more effective way of reducing the susceptibility to scratching is to apply a lubricant layer.

### 5.1.6 Influencing the Surface Slip

To reduce friction in technical processes in general, lubricants are employed, which form a thin film between two surfaces and thus separate these surfaces. A similar approach can be used in coatings: additives are added to the coatings formulation which migrate after application to the surface and create a sliding effect very similar to that of a lubricant film without, however, creating a real macroscopically visible film. Two types of additives are successfully used in this way: silicone additives (polysiloxanes) and waxes.

### 5.1.7 Silicone Additives

The chemistry of the modified polysiloxanes (silicone additives) is discussed in detail in Section 4.4.4. These products are all surface-active, i. e., they migrate to the surface of the coating film. The organic modifications (which were introduced to control compatibility) are orientated inside the paint film, while the dimethyl units (and longer alkyl groups) stick out of the paint film and are responsible for the surface slip. The larger the dimethyl structures of the additive, the stronger its slip-increasing properties. As when it is used to influence the surface tension, only minor amounts of a silicone additive (starting from approximately 0.01% active sub-

stance) is necessary to reduce slip resistance considerably. Increasing amounts increases the effect, until, finally, a plateau is reached. More silicone then no longer increases slip, because the surface is already completely covered with polysiloxane molecules. More silicone only increases the danger of possible negative side effects (foam stabilization, loss of intercoat adhesion). It is therefore quite important in practice to find out the right silicone dosage to achieve the required slip effect.

Suitable silicone additives with different compatibilities for solvent-based, solvent-free, and aqueous systems are commercially available. The silicone surfactants described in Section 4.4.4 which result in very strong surface tension reduction in aqueous coatings have practically no influence on the surface slip because of their very short dimethyl structures. If in an aqueous systems a higher surface slip is also required, the silicone surfactants have to be combined with polymeric silicones.

The silicones which are usually employed to improve surface slip are, as the structures appearing in Section 4.4.4 show, nonreactive molecules. The additives contain no chemical groups which may take part in the cross-linking reactions of the binder resin. Therefore, although these additives may be found on the surface of the coating after film formation, they have not reacted with the resin matrix. The silicone additives may therefore be removed (at least partly) from the coating surface relatively easy, e.g., by cleaning the surface with solvents. Improvement of slip- and scratch resistance by silicones is therefore only a temporary effect which gradually wears off as the silicone concentration in the surface diminishes. If a more permanent effect is desired, this can be achieved with reactive silicones. Such products contain chemically reactive groups incorporated in their molecules, which can cross-link with the resin system (e.g., primary OH- groups for two-pack polyurethane systems or double bonds for UV systems). If the silicone additive is fixed in this way in the coating surface it can not be removed easily from the surface and therefore the slip improvement is more permanent. When such a coating is exposed to UV radiation (outdoor exposure), normal weathering processes will cause the slip additive to be lost from the coating fairly rapidly, because it had reacted with the topmost layer of resin molecules. Under such conditions, a reactive silicone additive is effective for longer than a nonreactive additive is, but the effect is still not permanent. If the coating is for inside use only (no or only little UV radiation), the reactive silicone will stay active for much longer. One general remark on the use of reactive silicones: recoating and good adhesion on a layer of paint that contains a reactive silicone is only possible after careful and extensive sanding.

### 5.1.8 Waxes

Waxes are not defined by their chemistry, but by their technological property of waxiness. Among other things, that means that their melting point is above 40 °C (differentiating them from oils and fats) and that they have a very low melting visc-

osity (differentiating them from resins and other polymers). The first wax was beeswax, later other animal waxes and vegetable waxes such as Carnuba wax and fossil waxes (paraffin wax, Montan wax) became known. Apart from these natural waxes, modified waxes are also available, i. e., chemically modified natural waxes. The waxes that are most important today are synthetic waxes such as polyethylene, polypropylene, Fischer-Tropsch waxes, or ethyl vinyl acetate waxes.

In coatings, waxes can only be used in the form of wax preparations which allow easy and problem-free incorporation. Dispersions in water and organic solvents, as well as micronized types are typically used. Waxes with different degrees of hardness, different melting points and polarities are used in these preparations in order to fulfil the various requirements of different application areas. Wax mixtures are also quite common.

Depending on the particle size, waxes can also influence the gloss of the coating. Wax dispersions with very fine particles can be used even in high gloss coatings without gloss reduction and waxes with coarse particles can be used for matting.

In most cases, waxes are employed for slip increase and in general for surface protection. To improve surface slip, waxes must be used at higher dosages than the silicones described in Section 5.1.4; typical dosages are between 1% and 2%. The slip increase of waxes is much more permanent than the effect from the silicones, also in outdoor applications. Problems with recoatability of wax-containing surfaces are normally not observed.

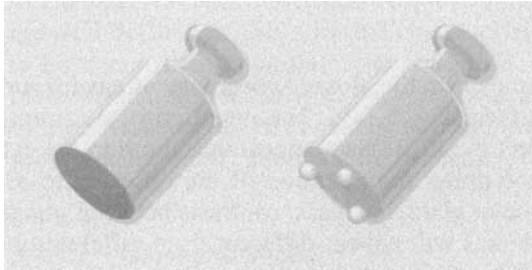
Besides improving surface slip, waxes also can increase sanding ability, improve the “soft-feeling” effect, and create hydrophobic surfaces. Some types can even be used as rheological modifiers. The usage of very soft waxes also brings about surface slip reduction, i. e., slip resistance is increased instead of reduced. The additional possibility of gloss reduction and matting was already mentioned above.

### 5.1.9 Measuring Surface Slip

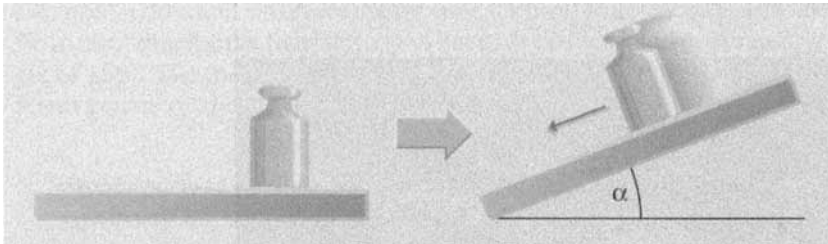
Paint technicians easily evaluate surface slip with their fingers. Passing the hand over painted surfaces will reveal differences in their slip property. This is, of course, only a very subjective evaluation and not a real quantitative measurement. The evaluation becomes more objective, when a defined probe is moved across the coating surface and the necessary force for this movement is monitored. A specialized weight, with a felt-covered contact area is used for planar surfaces; for uneven (structured) surfaces, a weight with three spherical contacts is preferred (see Fig. 5.1-1).

In a very simple test set-up, the weight is put onto the horizontal surface and the panel is then slowly tilted by raising it on one side. At a certain angle the weight starts sliding downwards; the smaller this angle the better the surface slip (Fig. 5.1-2). More precise results can be obtained when the weight is pulled gradually across the (horizontal) surface. The force for this movement is then measured by a simple

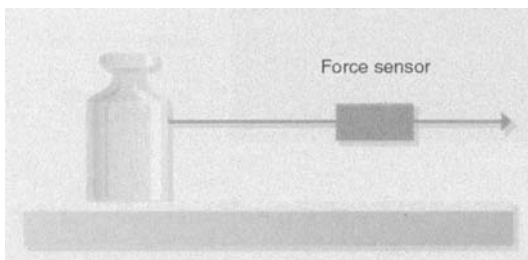
spring balance or, more comfortably, with an electronic force sensor and recorder (Fig. 5.1-3). One also has to distinguish between the static friction and the sliding friction. To start the movement of the weight, the static friction must be overcome, to then keep it in motion, only a force which equals the sliding friction is necessary. The sliding friction is always lower than the static friction. Differentiating between these two types of friction is only possible with the method shown in Fig. 5.1-3.<sup>[5-3]</sup>



**Figure 5.1-1.** Two different probes to measure surface slip on planar (left) and structured (right) coating surfaces



**Figure 5.1-2.** Slip angle as an indication of surface slip



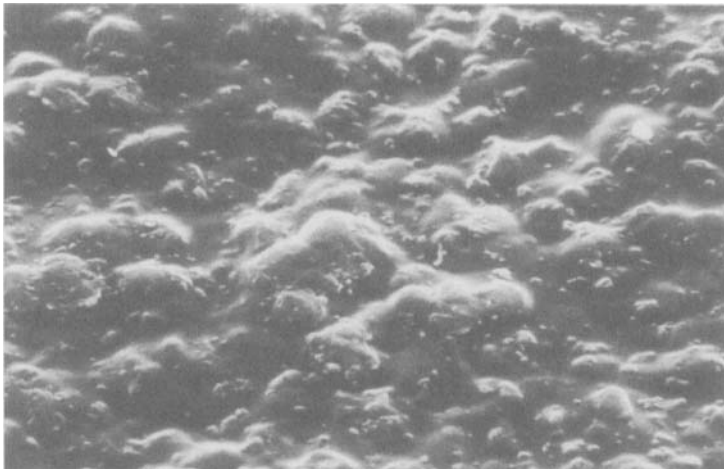
**Figure 5.1-3.** Evaluation of surface slip by measuring the force required to drag a weight gradually across the coating surface

## 5.2 Matting

*Uwe Ferner and Georg Lüers*

### 5.2.1 Basic Physical Principles of Matting

The function of a matting agent is to transform the glossy appearance of a paint surface into a diffuse light-scattering surface (Fig. 5.2-1). The intention is to impress on the observer the quality of the object by its pleasant appearance, both to the eye and to the touch. A glossy appearance draws the attention of the observer to reflected images in terms such as sharpness, glare, haziness, contrasts between image elements, etc. The gloss of moving objects will appear different from different observation angles. The visual quality of the surface will be assessed in such terms as evenness, absence of residual brush marks, and waviness. For a closer inspection the fingers of the investigator will provide a tactile assessment, for qualities such as smoothness and roughness. For a clear-coat film, the observer will assess the clarity and haziness of the substrate.



**Figure 5.2-1.** Matt paint surface

### 5.2.1.1 Methods for the Characterization of Surfaces

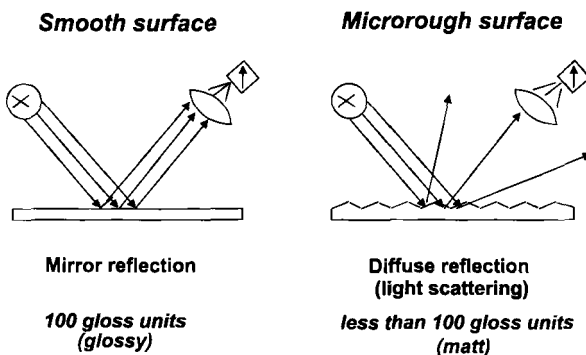
The perceived attributes of a surface can be divided into three classes of characteristics:

- colour impression
- surface reflection
- surface structure

The last two characteristics are often summarized under the term gloss. While there are well-defined methods for the characterization of the impression of colour, there is no conclusive quantitative measurement of the psychological impression of a matt surface. Various sensorial impressions are recognized and determine the value of the assessed subject. For many of these important impressions, such as waviness, grey-blue haze, etc., there are no measuring methods available.

### 5.2.1.2 Gloss and Sheen

Normally the gloss is measured according international standards, with the aid of film surfaces, which are applied on smooth, non-adsorbing substrates. The light reflected in an angle of  $60^\circ$  from the normal is simply termed gloss. The light measured at an angle of  $85^\circ$  from the normal is defined as sheen. For some applications an angle of  $20^\circ$  is also used. Gloss and sheen are appropriate for most routine cases. However, for scientific measurements, the light reflection needs to be measured continuously across an angle of  $180^\circ$ . The measuring results depend on the equipment used, because of the different geometrical conditions and the calibration methods (Fig. 5.2-2).

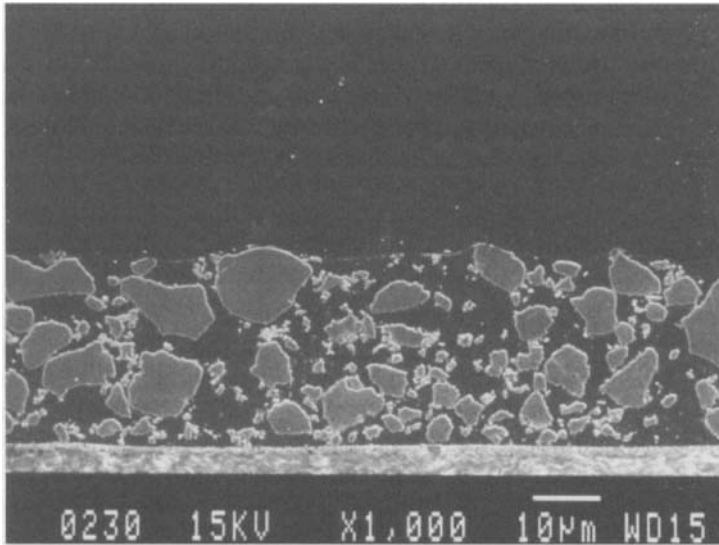


**Figure 5.2-2.** Gloss measurement principle

### 5.2.1.3 Surface Roughness

The microroughness of the film, caused by the matting agent is primarily responsible for the reduction of gloss and the matt appearance of the coating. The correlation between roughness and degree of matt appearance is still not completely un-

derstood. When a matt surface is examined microscopically, a clear microroughness is apparent. There are no obvious regularities. Particles or aggregates below the surface seem to be responsible for causing the microrough surface structure of the film. Cross-sections of such a matt film show randomly distributed particles throughout the cross-section of the film. Usually the thickness of the film is much greater than the thickness of the largest particle (Fig. 5.2-3).



**Figure 5.2-3.** Cross-section of paint film

Several statistical methods have been used to characterize the surface roughness of a paint or lacquer film. Besides sophisticated characteristics such as height distributions and gradient distributions, the performance of autocorrelation and Fourier transformations, the following common characteristics are used:

- $R_{\max}$ : the maximum difference between the highest and the lowest level
- $R_z$ : the average difference between the highest and the lowest level of several measured distances

#### **5.2.1.4 Properties Not Influenced by the Matting Agent**

Paints and lacquers are formulated to fulfil several functions, for example, protection against water, light, mechanical influences, etc. The matting agents are often added in the last step of the formulation and, as a consequence, should therefore exhibit the following characteristics:

- no influence on transparency and haze
- no sedimentation during storage
- no influence on the drying properties of the paints and lacquers
- no negative influence on the intercoat adhesion
- uniform surface roughness
- improvement of the wear resistance of the film
- stability against shear stress during incorporation of the particles
- no negative influence on the mechanical properties of the film
- good scratch resistance and protection against polishing of the film
- no negative influence on the weatherability.

### 5.2.1.5 Mechanism of Matting

#### Shrinking Paint and Lacquer Systems

As described in Sections 5.2.1.2 and 5.2.1.3, the observer gets the impression of a matt surface, if the incoming light is reflected in a diffuse manner at the surface of the film. The microrough surface necessary for this process is created by the matting agent which is evenly distributed in the paint film.

“Traditional” paint systems contain a relatively high content of volatile components or solvents. Due to the surface tension of the wet paint or lacquer, the appearance of a wet film is a glossy surface. The matting agent particles are evenly distributed in the film. Because of the evaporation of the solvents, the volume of the applied film is reduced. This phenomenon is known as “film shrinkage” and up to 70% reduction in the film volume can occur. An additional chemical reaction of paint components also contribute to this process. There is an intermediate step, described by Feig<sup>[5-4]</sup> as the “gelling step”, where the matting-agent particles are fixed in the film. Parameters that influence this step are critical for the creation of a matt effect. The continuous shrinkage process during curing creates the necessary microroughening of the surface.

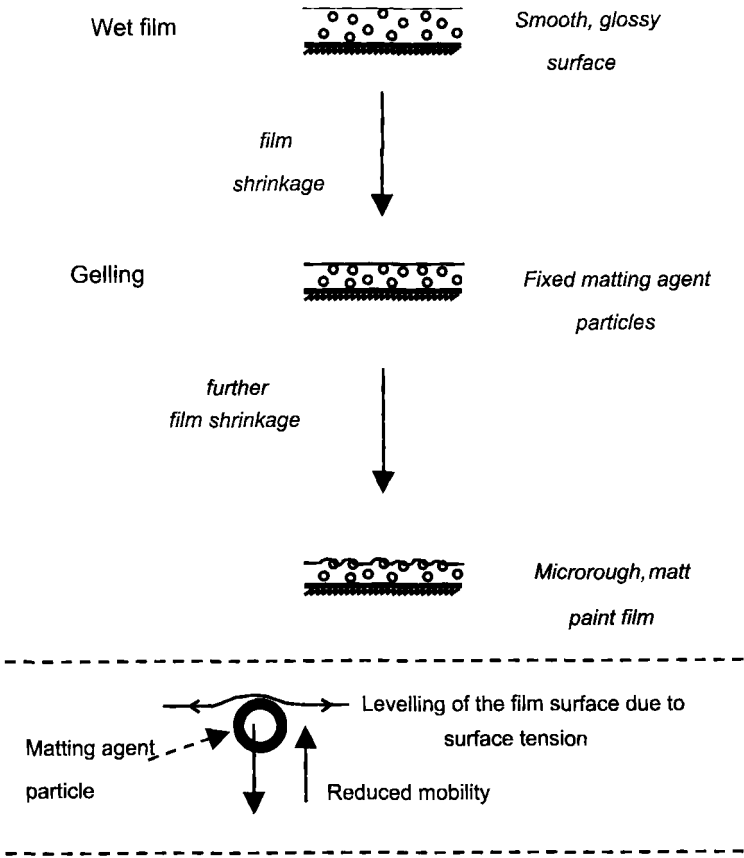
This process is demonstrated in Fig. 5.2-4. The mechanism also demonstrates that for the creation of a microrough surface, the film has to be filled with particles. This means particles with a low density, e. g., guaranteed by a high pore volume of silica gel matting agents, are very effective matting agents (see Sections 2.4 and 3).

#### “Low-Shrinkage” Paint Systems

In the recent years there has been a tendency to reduce the emission of solvents into the atmosphere. This tendency has been initiated by the legislative pressure in different European countries and has resulted in the development of VOC-compliant coatings that meet the legislative requirements.

Such coatings are:

- powder coatings
- radiation-curing systems
- high-solids systems
- waterborne systems



**Figure 5.2-4.** Schematic representation of drying of solvent-containing paints

With the exception of waterborne systems, all the paint types are formulated with a minimum of or totally without volatile components or solvents.

During the drying step there is therefore no distinct shrinkage process; this makes it difficult to provide matt paint systems. Matting is now mainly influenced by the reactivity of the system. First of all this is obvious for radiation-curing systems (see Section 5.2.3.4)

In some systems, besides pigments, chemical reactions or incompatibilities are used for matting (powder coatings). By influencing the surface cure through oxygen inhibition or combinations of different curing aggregates, the necessary shrinkage is obtained.

Another fundamental possibility is to fit matting agents with a controlled steep particle size distribution to the given dry film thickness proposed by Field and Kent<sup>[5-5]</sup> to matt UV lacquers. The particle size is selected to create a rough surface in the liquid film prior to curing. A large portion of the particles or agglomerates should be slightly coarser than the dry film thickness. The particle size distribution should,

however, be controlled not to create an unpleasant rough surface. This method is very dependent on constant film thickness and is therefore only recommended when consistent film thickness can be guaranteed, e. g., roller coating application.

On the other hand, only relatively coarse silica matting agents are effective in high-solids systems. This is due to the high-solid content of these formulations, because a greater matting agent concentration than in standard systems is necessary. As a result, the rheology or viscosity is strongly influenced, with a potentially negative effect on the application of the coating.

In practice, a compromise between gloss and rheology is very often necessary. A combination of silica matting agents and waxes or organic matting agents is the solution in most cases.

These compliant coating systems generally present a great challenge in the development of new effective matting agents.

## 5.2.2 Matting Agents

### 5.2.2.1 Introduction

Matt surfaces are preferred for many different reasons. They provide an elegant and luxurious appearance, hide imperfections of the surface caused by dust particles or other small irregularities. In addition, matt surfaces can improve safety, e. g., when dazzling roofs and sides of buildings are avoided and the gloss in the dashboards of cars is reduced. The improvement of other general product properties, such as abrasion resistance, can also be a justification for the use of matt paints.

In the past, a matt surface was created by sanding a glossy paint surface with a pumice stone or steel wool. In the course of time these methods became uneconomical and consequently the use of matting agents in paint became state of the art. First of all, the possibility to produce synthetic silica in an industrial scale after the second world war resulted in its wide use in different coating systems.

The easiest way to matt a paint is to increase the pigment or filler ratio. However, this is only possible in pigmented paints and can strongly influence other paint properties.

For this reason, organic and especially inorganic products with defined particle size distributions have come to dominate the market.

### 5.2.2.2 Economical Importance

The market for synthetic silica (silica gel, precipitated silica) that are used as matting agents consisted of about 11 000 ton in Europe in 1994. These products are used in the following applications, ranked in order of importance:

- wood and furniture lacquers
- trade paints
- coil-coating lacquers
- thin-film systems such as foil or leather lacquers
- printing inks
- industrial paints

Natural silicas such as diatomaceous earth are used together with pigments and fillers in wall paints mainly for economic reasons. However, there is a current trend towards replacing such products with synthetic silica because these products have no crystallinity.

Waxes used as matting agents are mainly micronized polyolefins, and are less important because of inferior matting efficiency compared to silica. Very often waxes and silica in combination are used if special surface characteristics are required or when the influence on the rheology of the paint system should be minimized. Table 5.2-1 gives an overview of current matting agents, suppliers, and trade names.

**Table 5.2-1. Matting agents**

Synthetic silica gels	Natural silica gels	Waxes		Fillers	Polymers (micronized urea-formaldehyde resins)
<b>SILICA GELS</b>	<b>Diatomaceous earth:</b>	<b>Micronized:</b>	<b>Precipitated:</b>	- Talcum	- Pergopak
- <b>Grace-Davison</b>	- Celite	Types:	Types:		(Ciba Geigy)
SYLOID	Manufacturer:	- Polyethylene	- Dispersions		- Deuteron
- <b>Crosfield</b>	- John Manville	- Polypropylene	- Pastes		(Schöner)
Gasil		- Polyamide			
- <b>SCM-Glidden</b>		- Teflon (PTFE)			
Silcron					
<b>PRECIPITATION SILICA GELS</b>		<b>Manufacturers:</b>	<b>Manufacturers:</b>		
- <b>Degussa</b>		- Langer	- Byk & Cera		
Acematt		(Lancowax)	- Hoechst		
- <b>PPG</b>		- Hoechst	- Bader		
Lovei		(Ceridust)	- Daniel		
- <b>Rhône-Poulenc</b>		- Micro Powder	- Langer		
Flatosil		Inc.			
- <b>Langer</b>		- Allied Chem			
Lanco Matt					
- <b>Zeofinn Oy</b>					
Zeomatt					
<b>AGGLOMERATION- PRECIPITATION SILICA GELS</b>					
- <b>Degussa</b>					
TS 100					

### 5.2.2.3 Requirements for Modern Matting Agents

The formulation of paints and lacquers is very demanding and requires a high extent of knowledge with respect to chemical and physical relationships between the coating components and the surface of the substrate. Modern matting agents fulfil the requirements to create a matt surface without negatively influencing other important properties of the liquid or dried paint film. The incorporation even in the finished lacquer is possible without any problems.

Traditionally, different products are used to matt clear and pigmented paint systems, e. g.:

- synthetic amorphous micronized silicas
- natural micronized silicas
- micronized and precipitated waxes
- natural minerals such as, e. g., chalk

Synthetic amorphous silica is found to be cost-effective in a broad range of coating applications. The main reasons are the high matting efficiency, high transparency of the matted films and the ease of incorporation. These properties are combined with totally inert behaviour in nearly all coating systems.

### 5.2.2.4 Amorphous Silica

#### Chemical and Physical Properties

The manufacturer has a variety of possibilities for influencing the performance of the silica particles in the wet and the final dried coating film.

The health risk attached to amorphous synthetic silica is less than that of crystalline natural silica (quartz). Composed purely of  $\text{SiO}_2$  with very stable OH groups covering the surface, the particles do not react, with exception of some known adsorption reactions, with the ingredients of the paint and lacquer system. The high surface energy causes the easy dispersion of the agglomerates in the wet paint.

The efficiency of the particles, i. e., the concentration of matting agent necessary to achieve a certain gloss, depends in the first instance on the *density of the particles*. The manufacturer has the possibility to add a pore volume to the intrinsic volume of the silica. Silica particles can be regarded as microsponges in which the pores represent up to 85% of the total volume. By this the matting efficiency of the silica particle is in two ways, firstly, because a much higher number of particles suitable for the application can be made from the same weight and, secondly, because parts of the fluid paint are adsorbed by the porous particles. Therefore the volume concentration of the particles in the paint increases. Compared to nonporous finely divided minerals, the matting efficiency of synthetic silica matting agents can be expected to be three to four times greater. The advantages the paint manufacturer can expect is a reduction of the specific density of the paint and a lowering of the concentration of solids.

Silica particles are *transparent* because they have a refractive index of 1.46 which is very similar to that of most common resin systems. This is the reason why silica

particles can be used to prepare matt, highly transparent coatings which even on dark substrates do not cause hazing.

The manufacturer of silica matting agents can modify the surface of the silica with an *organic coating* to improve the properties of the wet system and the dried coating film. A wax such as a low-melting polyethylene, its derivatives, or mineral waxes are used to modify the surface of the silica to prevent hard settling of the particles in the wet paint during storage. The wax coating causes flocculation of the particles, and if a sediment is formed, it is usually soft and can easily be redispersed. Inorganic surface modifications such as, for example, fluorides can influence the rheological properties and the curing rates of reactive paint systems.

Further important properties of the matting agents are the *average particle size* and the *particle-size distribution*. The appearance of the film surface is determined by the last 5% at the coarse ends of the particle-size distribution. Strict control is necessary during manufacturing to ensure reproducible results for the final user of the paint. Associated with the influence on the surface roughness is the influence on the matting efficiency. Coarse particles lead to rougher surface and consequently result in more efficient light scattering. Matting-agent manufacturers offer a range of particle sizes so that the user can obtain the optimum coating.

Apart from these general properties, the matting agents offered on the market can have significantly different other properties, such as overgrind resistance, ease of incorporation, and chemical resistance.

### Manufacturing Process

The so-called sol-gel process and the precipitation process established the economic importance of synthetic silica production. Apart from these processes, synthetic silica, used mainly as a thickening agent, is also produced by the pyrolysis of silicon tetrachloride in a hot flame (pyrogenic silica) and by thermal decomposition of quartz in a plasma.

The sol-gel method produces a three-dimensional structure through the polymerization of sodium silicate and sulphuric acid.<sup>[5-7]</sup> The hydrogel formed first has to be washed to remove the sodium sulphate. Appropriate process control leads to stabilization of the porous structure of the gel. After the silica has been dried, the desired particle-size distribution is achieved by a jet-milling step with integrated or subsequent classification. In the jet mill the input material is accelerated in gas jets and targeted to other slow-moving particles. The achievable velocities allow the processing of much smaller particles than when mechanical mills are used. Another advantage is that the grinding takes place mainly through particle contact, and therefore much less abrasion wear is found in the mill. There is no discoloration and much fewer impurities result. If desired, wax or inorganic compounds may be added during the jet milling to coat the particles. The most important quality characteristics of such products are the high purity and the constant particle-size distribution.

In the *precipitated silica* process, polymerization is achieved by adding the acid to a stirred vessel filled with a sodium silicate solution.<sup>[5-7]</sup> The conditions control the growth and the structure of the precipitated particles. The solids are separated, the

sodium sulphate is removed by washing with water, and the product is finally dried. The desired particle size is achieved by micronization and classification. In contrast to the sol-gel process, the precipitation can be controlled in such a way, that the desired particle size is ensured already after precipitation.

The main difference between the products made by these two processes is the pore-size distribution. The silica made by the sol-gel process is characterized by a narrow pore-size distribution, in the range of 10–60 nm. The products made by the precipitation process have a pore-size distribution exceeding 1000 nm. This is due to the aggregation of several primary particles to the final secondary particle. In most applications products from both processes are interchangeable.

#### **5.2.2.5 Natural Silica and Fillers**

Natural silicas such as, e. g., diatomaceous earth (Celite, John Manville) are mainly used together with fillers to produce matt wall paints. These products differ from synthetic silicas in their broader particle-size distribution, higher density, lower specific surface area, as well as their partially crystalline character. Compared to the synthetic products, they are inferior with respect to dispersion behaviour and transparency in clear lacquers.

Fillers such as, e. g., talc are able to matt a paint by increasing the pigment volume concentration (PVC). The PVC at which the properties and processing of the paint is severely affected, is reached far earlier than with the more effective porous synthetic silicas. That means also that fillers are inferior with respect to matting efficiency and with respect to their influence on other important paint properties such as mechanical and chemical properties, influence on transparency and suspension behaviour.

#### **5.2.2.6 Organic Matting Agents**

Micronized waxes and polymers can be used as matting agents. First of all, polyolefins such as polypropylene and polyethylene are incorporated into paints by hot precipitation or as dispersions. Because of their lower efficiency, waxes are normally combined with silicas.

The matting efficiency of waxes is independent of particle size and they are able to confer better matting properties at higher film weights. This result supports the theory of the “reservoir effect”, in which the particles float to the surface as the critical step.

Apart from their matting ability, waxes can, of course, also positively influence the film-surface characteristics.

Matting agents based on polymers such as, e. g., Pergopak, a urea-formaldehyde condensate, are very often used in combination with silicas and are able to improve special film-surface characteristics. In this way special matt “soft feel” paints can be formulated to give coated plastic surfaces a pleasant, leather-like feel.

## 5.2.3 Application of Matting Agents

### 5.2.3.1 General Parameter That Influence Matting

Apart from the chemical and physical properties of the matting agents itself, there are several other factors related to the application of matting agents in paints that play an important role with respect to the quality of matting. The most important characteristics of matting agents are related to the creation of a microrough surface as a requirement for light scattering.

Because of the mechanism of matting, by which it is assumed that the film needs to be filled with particles or that the particles have to be concentrated on the surface, it is obvious that the matting efficiency depends primarily on the concentration of the matting agent particles. The higher the concentration of the matting agent the more the gloss of the system is reduced. The concentration of the matting agent strongly depends on its density (see Section 5.2.1.5) This concentration effect is demonstrated in Fig. 5.2-5, in which matting curves for two different grades are shown.

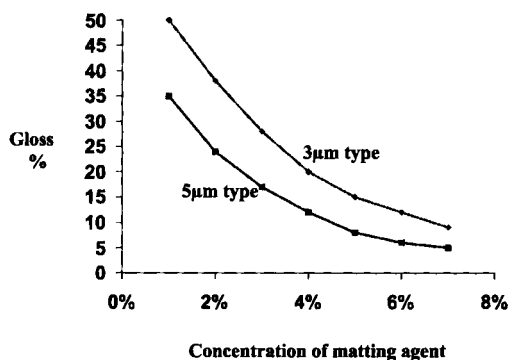
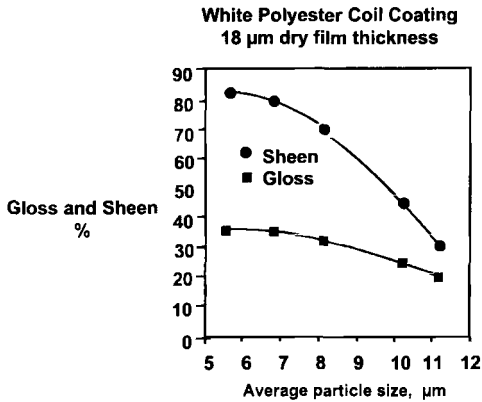


Figure 5.2-5. Influence of average-sized silica matting particles on gloss

The particle size, or better, particle-size distribution, is the second decisive factor for the matting capability of the most important class of matting agents, the precipitated silicas and silica gels. The bigger the particles, the more effective is the matting agent in general. A comparison, however, should only be done at the same dry film thickness. In practice, a matting agent should be selected that fits in well with the paint film thickness because a coarse matting agent can cause unacceptable roughness of the film surface when used in a relatively thin coating film. Coarse matting agents therefore confer the best matting properties at higher film thickness.

The particle size of the matting agents also has a decisive influence on the gloss/sheen relationship. With increasing particle size, the gloss ( $60^\circ$  angle) and sheen ( $85^\circ$  angle) values are more closely matched (Fig. 5.2-6). Coarser products are therefore preferred for coatings for large areas such as cladding and flooring. This



**Figure 5.2-6.** Influence of average-sized silica matting particles (concentration 8%) on gloss and sheen

helps to avoid the impression of different gloss levels when the surface is observed from different angles.

As already mentioned, the pore volume (or density) of silica gels is decisive for the high efficiency of this product class.

When a matting agent is selected, the influence of a high pore volume on the rheology or viscosity should definitely be taken into account. Sometimes, primarily in high-solids systems where the influence of pigments on rheology is more pronounced, it can be advantageous to use products with a lower pore volume and to obtain the desired matting effect through the particle size.

Paint systems can also be matted with the aid of waxes. However, compared to silica matting agents their efficiency is low. Evaluations of the mechanism of matting have shown that for waxes the particle size has no decisive influence on the matting efficiency.

Contrary to silica matting agents, the efficiency of waxes increases with increasing wet film thickness. These results support the theory that the wax particles primarily move to the surface of the wet film to affect the gloss.

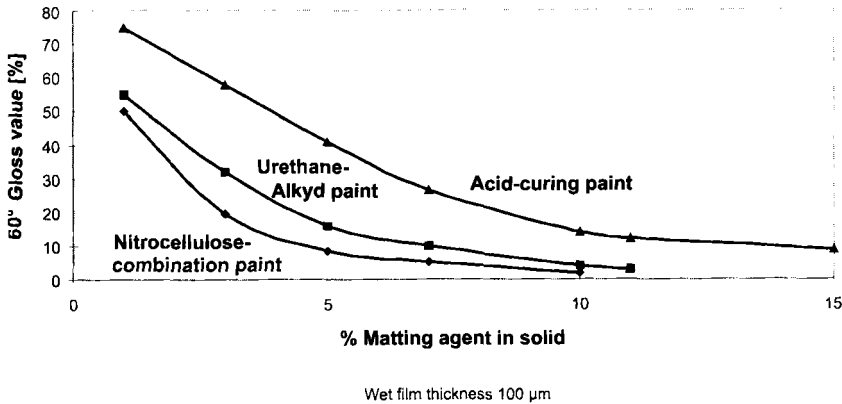
Criteria that are generally important for the properties of paints are also important for the creation of a matt surface, independently from the matting agent. These criteria are formulation, application, and the drying process of the paint.

### Formulation of the Paint System

With respect to the formulation of a paint, the following parameters influence matting:

- type of binder system
- solid content
- solvents
- additives
- dispersion of the matting agent

Matting of paint systems based on chemically different binders varies a lot because of the different curing and wetting properties. Fig. 5.2-7 demonstrates this for for-



**Figure 5.2-7.** Matting effect of SYLOID ED30 in different paint systems

mulations of the same solid content. Nitrocellulose systems are thus far easier to matt than acid-curing systems.

The mechanism by which a matt appearance is conferred on paints that is based on the creation of a microrough surface by the evaporation of solvents to cause shrinkage, explains why a paint with low solids and high solvent content is easier to matt. The chemical composition of the solvent and mainly its volatility also plays an important role in the orientation of the matting agent and the shrinkage process.

Additives, such as levelling agents, influence the wetting behaviour and surface tension of the wet paint and so can strongly influence the gloss of the system.

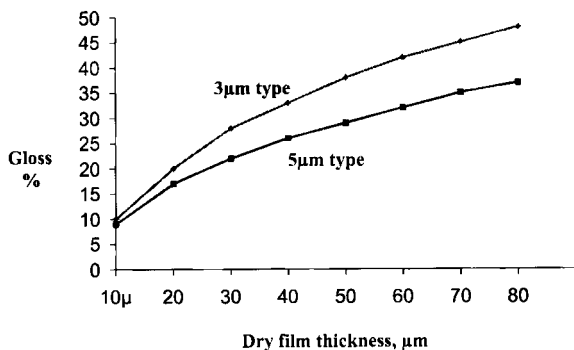
To obtain a regular and, if possible, low gloss, silicas that have an agglomerated powder consistency have to be dispersed by adequate means. For most matting agents based on silica, incorporation by a dissolver with a tip speed of about  $5\text{--}7\text{ m s}^{-1}$  is sufficient.

### Application of the Paint

- application method (spraying, curtain coater, roller coater, brushing)
- film thickness and variation of the film thickness
- substrate

The different application methods for a matt lacquer can lead to different gloss values. Different methods such as curtain coating, spraying, brushing, or roller coating have an influence on the orientation of the matting agent particles and the evenness of the film thickness. The thinner the dried film, the lower the gloss at constant matting agent concentration is (Fig. 5.2-8).

Fig. 5.2-8 also demonstrates that, for a certain film thickness, an optimum matting agent can be chosen. For low film weights, a fine-particle-size product may be optimal because although the coarser grade may matt better, the resulting surface roughness may be not acceptable. However at higher film weights the coarser matting agent is more effective.



**Figure 5.2-8.** Influence of film thickness on gloss (matting agent: silica, concentration: 3%)

With porous substrates, such as wood, a part of the liquid paint may be adsorbed; this leads to an uneven distribution of the matting agent particles on the surface, resulting in an uneven gloss.

### Curing of the Coating

The curing of a coating is a decisive factor for the orientation of the matting agents. Whereas for air-drying lacquers the use of solvents with different volatilities is the key factor, for solvent-free radiation-curing systems only the curing speed is the dominating factor for the efficiency of a matting agent.

The humidity in the atmosphere can influence the evaporation of solvents and so have an indirect influence on the gloss after drying.

In the following sections the matting of the most important coating systems is discussed in detail.

#### 5.2.3.2 Solventborne Systems

These coatings are easy to matt because of their volatile components. The particle size of the matting agents, however, should be tuned to the dry film thickness of the coating to obtain an acceptable surface roughness. When silica gel matting agents are used, the grades with a high pore volume are the most efficient ones. To avoid settling of the matting agents in clear lacquers, wax-treated silicas are preferable.

#### 5.2.3.3 Waterborne Systems

Basically, the matting of waterborne lacquers is unproblematic. Low solid content and a physical drying process in the first step eases the orientation of the matting agent particles. When wax-treated silicas are used, the compatibility with the system should be checked. Too high differences in pH between the matting agent and the coating system should be avoided. When aqueous dispersions are matted, the silica matting agent should be prewetted before incorporation. Otherwise the charac-

teristic strong adsorptivity of the porous silica particles can cause coagulation of the aqueous dispersion. The matting agent can be predispersed in water, co-solvents, and thickener before it is added to the dispersion. An alternative is silica gels that are already prewetted with water. These grades should also be used when binders are not stable against intensive stirring or to avoid the generation of too much foam. The incorporation of matting agents via pastes is another alternative to avoid these problems.

#### 5.2.3.4 High-Solids/Radiation-Curing Systems<sup>[5-6, 5-14-5-19]</sup>

Coatings with as low a content of volatile organic components as possible are becoming more and more important in the coatings market. Their high solid content of up to 100% results in a very small shrinkage during curing. The shrinkage is mainly created by the chemical cross-linking of the polymers. Evaluations have shown that the shrinkage is in the range of 4 to 15% whereas the evaporation of solvents results in a shrinkage of up to 70%.<sup>[5-12]</sup> Therefore a relatively high concentration of matting agent in relation to the wet paint is necessary. Coarse silica matting agents are therefore the most efficient grades in high-solids alkyds or polyurethane systems.

Radiation-curing systems behave somewhat differently. The matting ability strongly depends on the formulation and the related reactivity. Generally, formulations of low reactivity are relatively easy to matt. Highly reactive systems such as electron-beam-curing formulations are very difficult to matt. Individual components of the formulation that influence the curing of the surface have a strong influence on matting. Photosynergists, for example, make matting more difficult. On the other hand, curing techniques such as the use of lamps with different wavelength spectra are able to decelerate curing which is an advantage for matting.

This behaviour of radiation-curing systems also has consequences for the selection of matting agents. Contrary to experience with conventional lacquers in slow-curing UV systems, fine wax-treated silica grades are the most efficient. For fast-curing systems, coarse wax-treated or untreated grades are recommended. An exception are unsaturated polyester lacquers diluted with styrene. The low volatility of styrene leads to a more pronounced shrinkage, which is advantageous for matting.

#### 5.2.3.5 Powder Coatings

Powder coatings differ from liquid paints with respect to their raw-material base and processing. Matting agents based on silica are under-represented in this market segment. Their matting efficiency is not very distinct in these systems and high concentrations strongly influence the melt viscosity. Silicas are, however, used as free-flow agents.

Other possibilities for matting, such as those practiced in liquid-paint systems are basically possible but are associated with the disadvantages already mentioned.

Fillers are not very effective. They influence lacquer properties when used in high concentrations and they have to be combined with other kinds of matting agents.

Waxes are not very effective and can have a negative influence on the flow characteristics of the powder and cause haze in the cured film. On the other hand, waxes are able to improve scratch resistance and anti-blocking characteristics of the dry film.

The best results in powder coatings can be obtained with so-called matt hardeners that produce a matt film with the help of an additional chemical reaction (dual cure).

### 5.2.4 Commercial Products

SYLOID	(GRACE)
Vestowax	(Hüls)
Lanco-Wachs	(Lubrizol)
Ceridust	(Hoechst)
Pergopak	(Ciba)
Acematt	(Degussa)
Gasil	(Crosfield)
Lo-vel	(PPG)
Silcron	(SCM)
Zeomatt	(Zeofinn)

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## **6 Flow-Levelling and Coalescing Agents**

*Johan Bieleman*

Flow and levelling are the designations for the movement of a coating material during and after the application and before the film is formed; it influences, to a large extent, the appearance of the coating.

Coalescing refers to the film formation of emulsion paints.

Various factors influence the flow and levelling as well as the coalescence, in which interfacial properties dominate. The free surface energy of the coating layer is one of the main parameters.

Most coating materials are characterized by relatively low surface tension, and most are applied onto surfaces of higher surface tension than the coating material itself, with the result that the total free energy is reduced.

The film-formation process in dispersion paints is the result of coalescence of the polymeric particles when water evaporates from the emulsion system, thereby permitting contact and fusion of adjacent polymeric emulsion particles. This process is aided with coalescing agents; these are additives that work by temporary plasticization (softening) of the polymeric binder particles. The coalescing agent reduces the minimum film-formation temperature.

## 6.1 Levelling Additives

*János Hajas*

### 6.1.1 Introduction

Coatings are usually used for protection of surfaces or for changing the surface appearance (colour, gloss, uniformity, etc.). Levelling of a coating usually has no influence on the protective properties. Coatings with a worse levelling or flow typically have the same performance properties, gloss retention, or corrosion-protective properties that coatings with the best levelling properties have. The visual appearance of a coating depends very much on the flow and levelling. Coated products such as furniture, refrigerators, or cars are sold more easily when they have superior surface quality. It is for this reason that many types of additives are needed, developed, marketed, and sold world-wide to optimize the flow and levelling behaviour of coatings.

#### 6.1.1.1 Definition and Measurement of Levelling

The terms “flow” and “levelling” mean, for most coating experts, something that deals with the even surface of a coating. This property is mostly judged on the basis of pure visual appearance. Typical surface problems which may have a negative influence on the overall surface property of “good flow and levelling” are, for example:

- orange-peel effect
- structured surface
- crater
- fisheyes
- crawling or air-draught sensitivity
- substrate-wetting problems
- brush marks
- sagging
- seeding
- pinholes, etc.

Levelling and flow are very complex processes, the final result of which may be negatively influenced by several sources. Patton<sup>[6-1]</sup> defined levelling as a purely viscosity-dependent phenomenon; today the origin of most levelling problems is explained by another important technical term, the interfacial tension.

To simplify the complexity of the term “levelling”, we will only discuss the influence of these two factors on surface properties. Other surface problems such as substrate wetting, pinholing, sagging, etc. will be discussed in other chapters of this book.

The old industry norm DIN 55945 defines levelling as *“the more or less pronounced ability of a liquid coating to spontaneously level out its uneven surface*

that originated from its application". Today the term "levelling" also encompasses the abilities of the coating to eliminate surface problems that occurred *after* the application, such as the orange-peel effect or craters, which often can not be seen immediately after application.

### Measurement of Levelling

Levelling can be determined with wet or with dried coating films.

To determine the levelling of the wet coating, the liquid coating can be applied with various levelling gauges on contrast sheets or on other suitable even substrates, followed by an evaluation of the "flowout". This type of levelling measurement is today only used to evaluate architectural coatings.

More important is the evaluation of the levelling of the dry coating, since the application process and application conditions (temperature, air humidity, film thickness, diluent, atomization, etc.) may have a very strong influence on the final result. The visual evaluation of levelling is very important, but will be successively replaced by objective optical measurements.

So called "DOI" measurements have been used for a long time for automotive coatings, mainly in North America. This measurement is based on the principle of mirror-imaging of a high-gloss coating, in which one evaluates how much the mirror image is disturbed by the uneven surface of the coating.

The light scattering of high-gloss coatings can be measured with a goniophotometer. So-called "ALFA" values, which represent light scattering within an angle domain of  $0.6^\circ$  to the main reflection direction of  $45^\circ$ , are used to characterize levelling.<sup>[6-2, 6-3]</sup>

Recent developments in the field of laser technology have created new possibilities for the evaluation of levelling. The Rodenstock company in Germany developed a 3-D infrared laser scanner which gives a true topographic picture of the coating surface as a three-dimensional graphic picture. This method is quite successful in evaluations of relatively small surface areas (from a few  $\text{mm}^2$  to a few  $\text{cm}^2$ ), as well as in evaluations of local surface problems (craters, pinholes). The roughness of a painted surface can also be determined with relatively high accuracy with this technology.<sup>[6-4]</sup>

Laser-beam reflection is also utilized in another type of test equipment, of the German company BYK-Gardner (wave-scan). This equipment analyses the waviness of a high-gloss surface along a line of 10 cm. Dimension-free figures characterize levelling as "short-wave" and "long-wave" waviness. The smaller these figures are, the better is the levelling.<sup>[6-5]</sup> Table 6.1-1 contains a few readings to exemplify the waviness of various paint qualities.

**Table 6.1-1.** The waviness of various paint qualities

Visual evaluation	"Long wave"	"Short wave"
(Car clearcoats)		
Very good levelling	2.1	8.1
Acceptable levelling	8.6	18.3
Poor levelling (orange-peel effect)	14.8	26.9

### 6.1.1.2 Physical Factors Influencing Levelling

#### Surface Tension

A coating film will obtain an even surface through the surface tension of the liquid coating which minimizes the surface area. Theoretically, the higher the surface tension, the better the levelling, because a higher surface tension is accompanied with stronger physical forces that even out the surface. Surface tension (more exactly, the interfacial tension on the interface liquid/air) values of some liquid paint components are listed in Table 6.1-2.

**Table 6.1-2.** Surface tension values of liquid paint components

Components	Surface tension, mN m <sup>-1</sup> (at 23 °C)
<b>Solvents:</b>	
Mineral spirits	25.2–31.4
Xylene	32.2
Water	72.2
Isopropyl alcohol	21.7
<i>n</i> -Butanol	22.3
Propylene glycol <i>n</i> -methyl ether	27.7
Ethylene glycol <i>n</i> -butyl ether	27.4
Butyl acetate	25.5
<b>Resins:</b>	
Alkyd resins	26.5–30.9
Polyester resins (saturated)	24.6–32.8
Melamine resins	34.5–45.9
Acrylic resins	27.4–33.6
Waterborne acrylic dispersions	32.0–36.8
Water-soluble alkyd resins	32.8–37.1

#### Physical Origin of Levelling Problems

Many factors work against the levelling influence of the surface tension:

- rheology: high viscosity or strongly pseudoplastic behaviour, as well as a (high) yield point
- application: structured surface (brush marks, rough atomization, etc.)
- local surface-tension differences caused by solvent evaporation

On the basis of our definition of levelling, we will only discuss the role of rheology and application briefly, but we will discuss the role of surface tension in more detail.

#### Rheology and Levelling

A basic rule is: the lower the viscosity is, the better is the levelling. This physical law is easily understood, since a coating with low viscosity has much less resistance

against the levelling influence of surface tension than a high-viscosity system has. The best levelling can be achieved with liquid coatings that have no or a very low yield point and Newtonian rheology; systems with strongly pseudoplastic behaviour always display worse levelling. The exact shear-rate conditions for levelling are mostly when shear rates are  $1 \text{ s}^{-1}$  and below, where real levelling occurs. For thixotropic systems, the basic rule is that longer thixotropy rebuild times are accompanied by better levelling.

Deflocculating wetting and dispersing additives result in a more or less pronounced Newtonian rheology and a very low yield point, which results in good levelling. When controlled flocculating wetting and dispersing additives are used, a high yield point can result, together with more pseudoplastic flow behaviour, resulting in better sag resistance but with slightly worse levelling.

Despite these large differences in levelling when these categories of wetting and dispersing additives are used, these agents will never be regarded as real levelling additives.

Because not only the levelling, but also sag resistance is important for most paint applications, it is necessary to find a compromise between levelling and sag resistance in most cases.

Viscosity increase during the first “very liquid” phase of film formation is also very important to achieve good levelling. If the liquid paint’s viscosity rises very rapidly, this automatically means a worse levelling compared to what occurs a slower physical drying speed. This behaviour can be adjusted in a very simple way by using suitable solvent combinations (high boiling point, “slow” solvents)

### **Application, Surface Flow, and Levelling**

Many paint applications (brushing, rolling, spraying with rough atomization) create a structured paint surface. The function of the real levelling additives in such cases is to level this application-dependent surface structures. As already mentioned before, deflocculating wetting and dispersing additives produce a more Newtonian than pseudoplastic rheology, and therefore have the side effect of being “levelling additives”.

In other applications (curtain coating, fine atomization) a very even liquid coating surface will be produced, which can be disturbed later by solvent evaporation and local surface tension differences from turbulences in the wet film, to result in poor levelling. These types of levelling problems can be solved when so-called “*surface-flow additives*” are used.

When slowly evaporating solvents are used, both kinds of levelling can be improved, especially the application-related one. To improve “surface flow”, polymeric levelling additives and silicones are much more powerful than solvents. For this reason, polymeric levelling additives and silicone surface additives are today very important ingredients of high quality paint formulations.

### **Surface Tension and Levelling**

As discussed before, surface tension is a technical parameter which influences levelling to a very great extent. Most levelling problems occur when there are local sur-

face-tension differences in the wet coating film. Such local surface-tension differences may arise from solvent evaporation which creates turbulence in the wet film. The liquid coating always moves towards the higher surface tension area, with an uneven surface profile (orange-peel effect) resulting. When the solvent of nitrocellulose lacquers evaporates very fast under favourable conditions (high-volatility solvents, air draught), the paint film can be ruptured (crawling, air-draught sensitivity).

Local surface-tension differences may also result from contaminants with extremely low surface tensions (silicon-containing overspray, oil dust). In such cases, the paint film can also be ruptured, or small concentrated circular discontinuities (craters) or greater circular surface discontinuities (fisheyes) may develop.

A special kind of surface-flow additive, the so-called “anticrater-additives” (silicones, fluorosurfactants) reduce the surface tension strongly and eliminate or significantly reduce local surface-tension differences.

### 6.1.1.3 Improvement of Levelling: Mode of Action of Levelling Additives

Rheology changes or surface-tension changes can, in most cases, improve levelling.

*Polymeric* levelling additives function through their tailor-made incompatibility in the paint film. This incompatibility releases their molecules to the interface. Polymeric levelling additives (for example, polyacrylates) typically do not reduce surface tension of the paint, but create a physically uniform surface, hence reducing local surface-tension differences.

Although *silicones* may reduce surface tension to a great extent, and together with the surface-tension reduction also reduce those physical forces which level the coating, they also, at the same time, eliminate local surface-tension differences resulting from solvent evaporation. Finally, the use of smaller quantities of additives can also lead to an improvement in levelling. When higher dosages of the same additive are used, the levelling can be worse.<sup>[6-6]</sup> Higher dosages of silicones result in greater crater reduction, since anticrater effects always correlate with the surface-tension reduction. Similar effects can be achieved when *fluorinated surfactants*, which reduce surface tension even more strongly than silicones do, are used.

*Solvents* with high boiling points reduce not only the viscosity of the paint, they also effect a slower viscosity increase after application through their slow evaporation speed. In this way, they allow *more time* for levelling. Not only solvents, but also some volatile (mostly cyclic) dimethylpolysiloxanes have the same effect.

## 6.1.2 Commercially Available Levelling Additives

### 6.1.2.1 Polymers

Polyacrylates are the most important polymeric levelling additives, but cellulose acetobutyrate and other speciality polymers are also used. Polymeric levelling addi-

tives have an important advantage over silicones or fluorinated surfactants, since they do not result in recoatability problems and they can be used without any risk of poor intercoat adhesion in primers and primer surfacers.

### **Polyacrylates**

Polyacrylate levelling additives are homopolymeric or copolymeric materials, mostly with a molecular weight between 5000 and 100 000. These polymers are medium- to high viscosity honeylike substances with a glass transition temperature of  $-20^{\circ}\text{C}$  or lower. They are supplied as solvent-free materials or as solutions.

Their levelling performance can be adjusted through variations in their chemical composition (polarity and type of monomers) and their molecular weight. The solubility and compatibility in the coating are also dependent on these factors. Linear acrylic polymers are more incompatible than branched ones.<sup>[6-7]</sup>

Special delivery forms are used for powder coatings (master batches or powder, utilizing adsorbed acrylic polymer on porous silica carrier).<sup>[6-8]</sup>

Mainly *n*-butyl acrylate is used as the monomeric building block. Further comonomers are 2-ethylhexyl acrylate, ethyl acrylate, acrylic acid, or 2-hydroxyethyl acrylate. Acrylic polymers can be modified for waterborne applications with polar groups (mostly carboxylic groups or polyethylene glycol).<sup>[6-7]</sup> These products are mainly used in water-soluble or hybrid coating systems (automotive coatings, primer surfacers, one-coat systems), but they can also be applied in high-solids-type polar solventborne coatings.

Acrylic levelling additives are often used in solvent-free systems such as unsaturated polyester resins or UV-curing systems. Polyacrylates provide epoxy resins not only with improved levelling, but also with good deaeration.

Commercial product examples: Acronal 4F, BYK-355, BYK-361, Modaflow, Resiflow W-50, SER-AD FX 100 SF.

### **Cellulose Acetobutyrate**

It is mainly cellulose acetobutyrate types with high levels of butyric acid and medium molecular weights that are utilized as levelling agents. For unsaturated polyester resins and for UV-curable varnishes, low-viscosity-type styrene-soluble low-molecular-weight modifications can also be recommended.

Commercial product example: CAB 551-0,2.

### **Other Polymers**

Many other polymeric materials are utilized, mostly not as all-round products, but as speciality products, such as aromatic and aliphatic hydrocarbon resins, polymerized drying oils, high-molecular-weight butanol-etherified melamine resins, modified polybutadienes, polyvinyl ether, polyvinyl butyrals, and modified polyalkylene glycols.

These materials are typically not available as commercially sold paint additives, but as chemical intermediates or resins. They often belong to “top-secret” problem solution tools of experienced paint chemists.

### 6.1.2.2 Silicones

Silicones (dimethylpolysiloxanes and modified dimethylpolysiloxanes) have been used in coating formulations since the early 1950s. Unmodified low-molecular-weight, volatile silicones are used as levelling and surface-flow additives. Modified silicones are typically used as surface-flow control agents, but they also improve substrate wetting, anticrater-performance, foam stabilization or defoaming, slip and mar resistance, and many other paint properties.

Many important properties of silicones such as compatibility, surface-tension reduction, heat stability, slip, and mobility in the paint film can be adjusted through chemical modification of the dimethylpolysiloxane chain. Most importantly, modifications can be done on the backbone or on side chains.

When modifying the polysiloxane backbone, dimethylpolysiloxane units are replaced by methyl(alkyl)polysiloxanes or methyl(aryl)polysiloxanes. As side chains, polyethers such as polyethylene glycol or polypropylene glycol, or their combinations, as well as polyester, but also functional side chains carrying chemically reactive end groups (OH, acrylic) can be used.

Commercial product examples: BYK-300, BYK-310, BYK-320, BYK-333, BYK-370, Tego-Glide 444, Baysilonöl PL, Paint Additive 56.

### 6.1.2.3 Fluorosurfactants

Fluorosurfactants are anionic, cationic, or non-ionic surface-active materials with perfluorinated alkyl groups in their molecules. They provide a much stronger surface tension reduction, compared to their non-fluorinated counterparts.

Commercial product examples: Fluorad FC-129, FC-170C, FC-430, FC-431.

### 6.1.2.4 Solvents

Typical solvents are hydrocarbons (alkylbenzenes, paraffinic, isoparaffinic, or cycloparaffinic hydrocarbons), esters (lactates, esters of glycol ethers), ketones (cyclohexanone, terpene hydrocarbons), alcohols and glycols (cyclohexanol, propylene glycol), glycol ethers (ethers of ethylene glycol and propylene glycol), as well as some speciality combinations with an evaporation index of approximately 50 or higher (based on volatility of dimethyl ether = 1).

Table 6.1-3 displays important solvents, utilized as levelling agents, together with their boiling points and evaporation index values. To improve levelling with solvents, evaporation index values and viscosities of the binder in the selected solvent are important.

Apart from these solvents, there are also speciality solvent blends with optimized evaporation curves available on the market.

Commercial product example: Byketol-OK

**Table 6.1-3.** Solvents as levelling agents

Solvent	Boiling point (°C)	Evaporation index (Diethyl ether = 1)
Terpentine	154–185	45
Diisobutyl ketone	163–173	48
Ethyl lactate (Lactonal)	ca. 155	79
Orange terpene	150–190	75–80
Dekalin	189–192	100
Shellsol T	184–212	107
Ethylene glycol butyl ether	ca. 171	119
Solvesso 150	187–207	120
Pine oil	180–230	120–150
Diacetone alcohol	ca. 168	125–147
Shellsol AB	186–215	148
Methoxybutanol	159–163	160
Ethylene glycol butyl ether acetate	186–194	190
Tetralin	ca. 207	200
Crystal Oil 60	180–210	295
Isophoron	ca. 215	330
<i>N</i> -Methylpyrrolidone	202–205	360
Dipropylene glycol methyl ether	ca. 188	400
Cyclohexanol	ca. 161	400
Butyl lactate	ca. 183	443
Glycolic acid butyl ester	ca. 182	460
2-Ethylhexanol	ca. 184	600
1,2-Propylene glycol	ca. 187	600
Shellsol K	195–245	620
Isopar M	204–247	680
Methylcyclohexanol	155–175	800
Solvesso 200	219–282	> 1000
Propylene carbonate	241–242	> 1000
Diethylene glycol ethyl ether	ca. 202	1200
Diethylene glycol butyl ether	ca. 230	> 1200
Benzyl alcohol	ca. 205	1770
Tripropylene glycol methyl ether	ca. 242	> 2000
Diethylene glycol butyl ether acetate	235–250	> 3000
Hexylene glycol	195–199	4800
Texanol	244–247	> 5000

### 6.1.2.5 Other Additives

Other chemicals such as crotonic acid, benzoic acid, various kinds of monoglycerides, and glycidyl esters of branched C<sub>9</sub>–C<sub>12</sub> carboxylic acids are used as levelling additives for limited applications. Since these chemicals only work in speciality formulations, they are of limited importance.

### 6.1.3 Properties of Levelling Additives

Table 6.1-4 overviews the most important levelling additives and their applications.

**Table 6.1-4.** Commercially available levelling additives – typical product properties

	Reduction of surface tension	Application areas	Important remarks
<b>Polymers</b>	Little or no	Solventborne, waterborne and solvent-free systems	Levelling Anti-crater effects Anti-popping effects Good intercoat adhesion Negative: Tackiness at higher dosages Turbidity in clear film when too incompatible
	Little or no	Powder coatings	Levelling Anti-crater effects Negative: Tackiness at higher dosages
<b>Silicones</b>	Little to high	Solventborne, waterborne and solvent-free systems	Levelling, surface flow Substrate wetting Slip Anti-crater effect Negative: Foam stabilization intercoat adhesion (Poly-ether-modified types)
<b>Fluorosurfactants</b>	High to extremely high	Solventborne, waterborne and solvent-free systems	Levelling, surface flow Substrate wetting Anti-crater effects Negative: Very strong foam stabilization Surface problems and craters when overdosed Poor intercoat adhesion possible
<b>Solvents</b>	No or very little	Solventborne and waterborne systems	Levelling Negative: Slower drying speed Lower viscosity and reduced sag resistance possible

## 6.1.4 Application of Levelling Additives

### 6.1.4.1 Polymers

#### Polyacrylates

Both homopolymeric and copolymeric polyacrylates are used for solventborne systems. Commercially available products with a molecular weight of approximately 10 000 and with a surface tension of 24–25 mN m<sup>-1</sup> are very effective levelling additives. With increased molecular weight, incompatibility in resins increases, in clear varnishes turbidity may occur. Defoaming/deaeration behaviour may occur at the same time.

Typical dosages of polyacrylic levelling additives are between 0.1 and 1%. In baking enamels for spray applications (automotive coatings, coatings for household appliances) they are today very essential parts of many coating formulations. Their dosage in these applications is typically between 0.1 and 0.5%. In some special application areas (coil-coating systems, polyester–melamine resin combinations) polyacrylate levelling additives are also used in dosages of 1% and more.

High-molecular-weight polyacrylates from very nonpolar monomers are very incompatible in most coatings resins, and they are used as defoamers and anti-popping additives. These nonpolar acrylates don't improve levelling, and may even result in worse levelling at higher dosages. Their use is recommended in combination with medium polarity, medium-molecular-weight acrylic levelling additives and with polyether- or polyester-modified methyl(alkyl)polysiloxanes.<sup>[6-9]</sup> Dosages of polyacrylates, used as antipopping additives, are typically below 0.1% in clear coats, and a little higher in pigmented coatings (0.1–0.5%).

Polyacrylates with medium molecular weights and with polar structures (carboxylic functional or non-ionic modified structures) are frequently used in waterborne baking systems to control levelling. They are also successfully used in highly polar solventborne high-solid systems.

In powder coatings, the same acrylates that are used in solventborne or solvent-free coatings, are typically applied. Because of the special production technology for powder coatings, liquid polyacrylates can only be incorporated through a masterbatch in a solid powder coating resin, or adsorbed on a solid, porous carrier (mostly porous precipitated silica) as an approximately 60% active-substance preparation. Acrylic levelling additives not only improve levelling, they are also effective against cratering.<sup>[6-8]</sup> Their dosage is typically between 0.3 and 1% additive-active substance on the total powder coating formula weight.

#### Cellulose Acetobutyrate

Cellulose acetobutyrate (CAB) is used not only as a binder, but also as a real additive in many coating systems. Wood coatings based on acid curing resins, polyurethanes, unsaturated polyesters, even UV-curing resins are often modified with CAB in order to improve film forming and levelling. When CAB

is very incompatible in coatings, it can also be used as an effective matting agent.

Baking systems based on alkyd resins, polyesters, or acrylic resins, are also often formulated with CAB as levelling additive. In metallic and pearlescent coating formulations, CAB also improves the orientation of nonleafing-type aluminum and mica pigments.

### Other Polymers

Low reactivity etherified melamine resins are frequently used as levelling additives in baking systems based on acrylic resins, as well as in epoxy-phenolic baking formulations for can coatings and insulation varnishes.

Hydrocarbon resins, modified polybutadienes, and special polymeric oils are used in air-drying alkyd resin systems. Polyvinyl ether and polyvinyl butyral are used in baking systems based on acrylic resins, as well as in epoxy systems and in silicone-modified binders.

All these polymers work through their tailor-made incompatibility, resulting in interfacial activity in the coating.

#### 6.1.4.2 Silicones

##### Unmodified Silicones

Low molecular weight, low viscosity silicone oils have been used in the coating industry since the early 1950s. They are used today in nitrocellulose lacquers and in other low-cost wood coatings as levelling agents, but their importance has diminished greatly during the last decades. Low-molecular-weight silicones are volatile, and their effect is similar to that of high-boiling-point solvents. They also improve slip properties, but this effect reduces significantly after a few hours or days.

##### Modified Silicones

Table 6.1-5 gives an overview of important silicone modifications and their applications.

**Table 6.1-5.** Silicone modifications and their applications

Chemical modification	Application as levelling additive in:	Side effects
Polyether (EO)	Solventborne systems/waterborne systems	Slip improvement Anti-crater effects
Polyether(EO/PO)	Solventborne systems	Slip improvement Anti-crater effects
Polyester	Solventborne systems	Slip improvement Heat stability

**Table 6.1-5.** (continued)

Chemical modification	Application as levelling additive in:	Side effects
Polyester with –OH end groups	Solventborne systems (can coatings)	Permanent slip
Polyester with acrylic end group	Peroxide curing systems, UV coatings	Permanent slip
Polyester/polyether (OH functional groups)	Solventborne and waterborne (can coatings)	Slip improvement Permanent slip
Methylalkyl	Solventborne systems	Slip improvement Elimination of ghosting phenomenon Defoaming
Arylalkyl	Solventborne systems	Defoaming Heat stability

### 6.1.4.3 Fluorosurfactants

Fluorosurfactants are used in solventborne, solvent-free, and waterborne systems, mainly as anti-crater- and substrate-wetting additives. Since they have an enormous surface activity, very small dosages (0.01–0.2%) are enough to improve poor substrate wetting or to eliminate craters. At the same time, problems such as foam stabilization or decreased intercoat adhesion may also occur.

Fluorosurfactants must be perfectly soluble in the binder through the entire “liquid phase” of film forming, otherwise cratering may occur because of the very low surface tension of locally concentrated fluorosurfactant molecules.

Table 6.1-6 gives an overview of applications of the most important fluorosurfactants. When fluorosurfactants are compared to silicones, the main difference is that fluorosurfactants provide a stronger anti-crater effect and very good substrate wetting, but they do not significantly improve levelling. Fluorinated surfactants may even cause worse levelling, since they increase short-wave waviness at higher dosages (see Fig. 6.1-1). When used to improve levelling, typical dosages are merely 0.01–0.05%.

**Table 6.1-6.** Application of fluorosurfactants

Chemical structure	Application in:	Achieved effects
Ammonium perfluorodecylsulfonate	Waterborne: colloidal dispersions	Anti-crater effect Substrate wetting Levelling
<i>N</i> -substituted perfluorooctylsulfonamide, anionic	Waterborne: latex systems (anionic)	Substrate wetting Anti-crater effect Levelling

**Table 6.1-6.** (continued)

Chemical structure	Application in:	Achieved effects
<i>N</i> -substituted perfluorooctylsulfonamide, cationic	Waterborne: cationic binders	Substrate wetting Anti-crater effect Levelling
<i>N</i> -substituted perfluorooctylsulfonamide, non-ionic	Waterborne: latex systems, colloidal dispersions	Substrate wetting Anti-crater effect
	Solvent-free: (one-component PU)	Substrate wetting Anti-crater effect Levelling
Perfluorinated polymeric ester	Waterborne: water-soluble systems	Substrate wetting Anti-crater effect Levelling
	Solvent-free two-pack systems	Substrate wetting Levelling Anti-crater effect
	Solventborne systems	Substrate wetting Levelling Anti-crater-effect

#### 6.1.4.4 Solvents

Compared to additives discussed in previous chapters, solvents are used in much higher dosages. Typical usage levels are 2–5% calculated on the total formula weight. When selecting solvents for levelling improvements, the evaporation index values together with the drying process, and in the case of higher dosages also the solubility of the binder in the selected solvent, are considered.

For air-drying systems, solvents with an evaporation index up to 150–200 can be used at the recommended dosage levels without drying problems occurring. Some drying problems may occur, but only when the drying speed is very high, or when high film thicknesses are used. Typical solvents for this application are turpentine, ethyl lactate, ethylene glycol butyl ether, methoxybutanol, diacetone alcohol. If lower dosages (below 1%) are used, even solvents with higher evaporation index values are acceptable.

For forced drying conditions up to 80 °C, solvents with evaporation index values up to 400–500 (e. g., diisobutyl ketone, dipropylene glycol monomethyl ether, isophorone, *N*-methylpyrrolidone, Shellsol A) can be used in dosages of 2–5% without difficulties.

In baking systems – depending on the baking temperature – solvents with extremely high boiling points, with an evaporation index of 500 and higher (methylcyclohexanol, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, diethylene glycol monobutyl ether acetate, Shellsol K, Solvesso 200) can also be recommended.

Special combinations of solvents with lower, medium, and high evaporation index values are often used. Empiricism plays a very important role in such formulations.

#### 6.1.4.5 Other Additives

Crotonic acid is used in zinc oxide pigmented alkyd resin paints and in oil paints as a levelling additive. Similar effects can be achieved with benzoic acid.

Castor oil and various kinds of monoglycerides are used as reactive levelling additives in some special baking systems and in solvent-free polyurethanes.

Glycidyl esters of branched C<sub>9</sub>–C<sub>12</sub> carboxylic acids (“Cardura”) are used in solvent-free epoxy systems and in baking systems. Their dosage is typically between 1–3%. They only improve levelling, other effects such as anti-cratering or slip improvement can not be achieved.

### 6.1.5 Practical Experiences with Levelling

#### Small Dosages Can Be Better Than High Ones

With increasing dosages of levelling additives, the levelling does not improve continuously. Polyacrylate levelling additives give a typical “saturation-type” curve: at higher dosages the levelling improves but the degree of improvement gets less and less. These additives can not be used at very high dosages, since surface tackiness increases at levels around 1% and more.

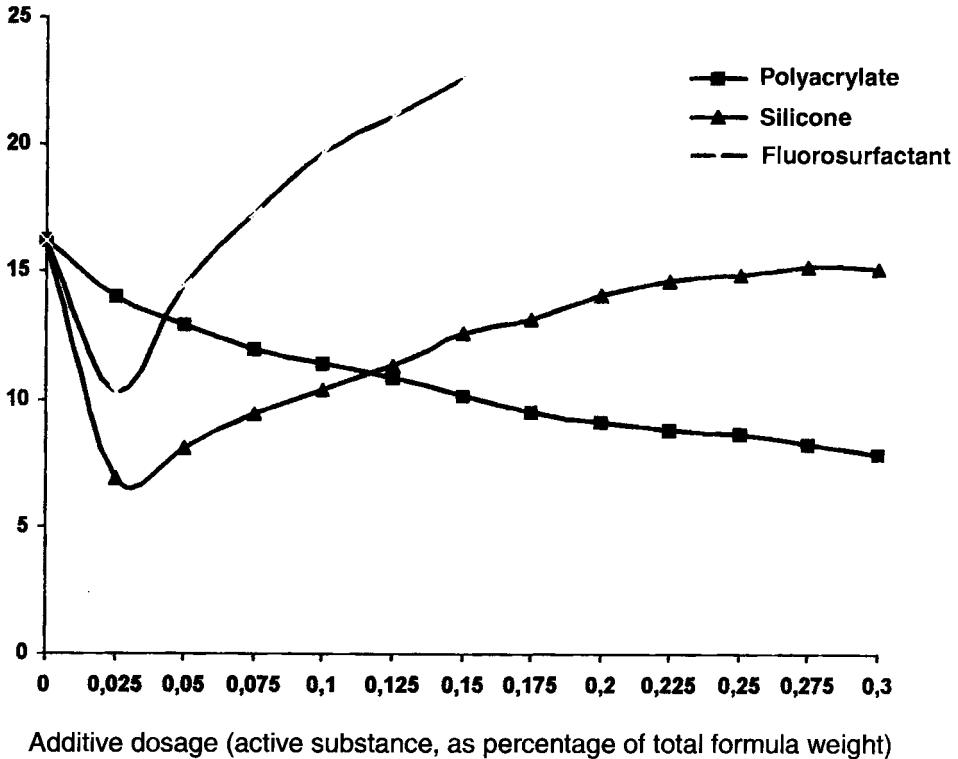
Silicones and fluorosurfactants give optimal levelling in spray applications only in a relatively narrow concentration range of around 0.05% additive dosage on the total formula weight, sometimes below. Fig. 6.1-1 shows the influence of a fluorosurfactant (perfluorinated polymeric ester), of a polyether-modified silicone and of a copolymeric acrylic levelling additive on the waviness (short-wave) of a baking type acrylic-melamine system.<sup>[6-6]</sup> Latest investigations show that polyester- or polyether-modified methyl(alkyl)polysiloxanes with little reduction of surface tension give optimal levelling in a wider concentration range of 0.1–0.2%.

Solvents used to improve levelling don't visibly improve levelling within the concentration range shown in Fig. 6.1-1. At higher dosages of 2–5%, they result in a curve similar to that of polyacrylates.

Acrylic levelling additives have the same effect in powder coatings.<sup>[6-8]</sup>

#### The Art of Application

Under ideal application conditions, even a coating material with poor levelling properties may result in an acceptable surface quality and vice versa: A coating material with excellent levelling properties may show poor results when conditions are not optimal.



**Figure 6.1-1.** Waviness of a baking topcoat with various levelling additives, as a function of additive dosage

Experienced coating applicators can tell long stories about proper adjustment of spray guns, about factors such as air draught, temperature, air humidity, distance between spray gun and substrate, etc. Empiricism plays a very important role in improving levelling. Even when working with automatic spray equipment or robotics, human experience with proper adjustment can not be replaced with theories.

### 6.1.6 Toxicology and Waste Disposal

One handles levelling additives that are based on polymers in basically the same way that one would comparable coating resins. The most dangerous components of polymeric levelling additives are solvents. Since these data are always available from material safety data sheets, we only refer to possible risks when using toxic solvents.

Very critical in this regard are aromatic solvents, terpene hydrocarbons, and isophorone. On the other hand, esters of lactic acid (ethyl lactate, butyl lactate) are classified as physiologically harmless materials.

Waste disposal (incineration) of fluorine-containing products must be done following special regulations. Other combustible solvents, polymers, and solutions of polymers can be easily disposed in normal incinerators, by following their individual operation instructions.

## 6.2 Coalescing Agents

*Klaus Dören*

### 6.2.1 Introduction

#### Definition of Terms

A coalescing agent (CA) is an additive for water-thinnable paints and varnishes that contain polymer dispersions as the binder. Coalescing agents, also known as film-forming agents or aids, or coalescents, have the function of enabling or optimizing the film formation of polymer dispersions under given conditions of application. Since CA's, as is explained below, act as plasticizers but at the same time are required to be volatile, the term "temporary plasticizer" describes their function very well. The much-used designation "solvents" (such as in "solvent-free" emulsion paints), although correct in part in terms of the chemical structure of these additives, is inaccurate as a description of the purpose for which they are used. Like solvents in coating materials, however, CA's are responsible for the emissions which occur when emulsion paints are dried. The emissions arising from these products, which in principle are classed as environment-friendly, are in fact relatively low, since only a few percent of CA's are present; however, this does not isolate them from the general trend towards emissions avoidance. As a result, some interior emulsion paints are even now being produced without coalescing agents. In other paints and varnishes based on dispersions, where the technical requirements are more stringent, it is not yet possible to do without the positive effects of CA's.

Before presenting the product group, it is appropriate to describe first the film-formation process of polymer dispersions and then the part played by CA's in that process. This will be followed by a presentation of the products themselves and their influence on the performance properties of emulsion paints. Considerations relating to ecology and toxicology form the conclusion.

#### Abbreviations

ADE	adipic diesters
BZ1	white spirit, free of aromatics
BZ2	white spirit, containing aromatics
DEB	diethylene glycol butyl ether (butyl diglycol)
DMP	dimethyl phthalate
DPB	dipropylene glycol butyl ether
EB	ethylene glycol butyl ether (butyl glycol)
EPH	ethylene glycol phenyl ether
HPE	hydroxypropyl ethylhexanoate

NMP *N*-methylpyrrolidone  
 PB propylene glycol butyl ether  
 PPH propylene glycol phenyl ether  
 TPiB 3-hydroxy-2,2,4-trimethylpentyl isobutyrate

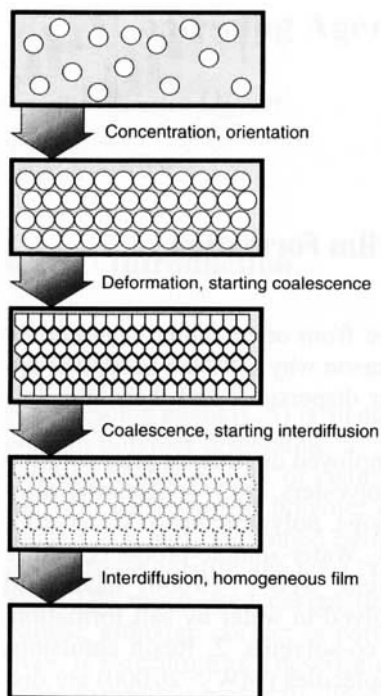
## 6.2.2 Polymer Dispersions: Structure/Film Formation

Polymer dispersions differ greatly in their structure from other binders commonly used in the coatings sector. Since this is the very reason why CA's are used, it is appropriate to consider first the structure of polymer dispersions and their film formation.

Typical binders are generally resins, which are employed directly, or after solution in solvents (in the case of alkyd resins, acrylates, polyesters, etc.), or else after dilution with reactive diluents (in the case of epoxy resins, polyurethanes). Water-dilutable resins<sup>[6-10]</sup> can be divided into two groups: 1. Water-soluble products, whose relatively short-chain molecules (molecular weight, MW < 20 000) have acid groups incorporated into them and so can be dissolved in water by salt formation, possibly with the assistance of small amounts of co-solvents. 2. Resin emulsions (e. g., alkyd resins, epoxy resins), in which resin molecules (MW > 20 000) are distributed in the form of very small droplets in water, stabilized by external emulsifiers. In both these systems, purely physical drying is followed by extension of the initially fairly short-chain molecules by chemical reactions (e. g., oxidative drying in the case of alkyd resins, cross-linking in the case of two-component products). It is only after such chain extension that these resins are able to meet the requirements placed on film-forming binders.

Polymer dispersions consist, much like resin emulsions, of particles finely distributed in water. The layer of emulsifier present on the surface of these particles causes them to repel each other, and so protect them against coagulation and provide them with stability. The particles already include long-chain polymers (MW up to 10<sup>6</sup>) which (in general) are unable to undergo chain extension reactions. The spherical polymer particles have diameters of about 30–500 nm, in special cases up to several micrometres. On drying, these particles form a continuous polymer film by purely physical means.

The film formation of polymer dispersions<sup>[6-11]</sup> can be divided into three component steps (Fig. 6.2-1): concentration, compaction, and coalescence.<sup>[6-12]</sup> First of all, there is a reduction in volume through evaporation and through absorption of the water by appropriate substrates. This decrease in volume forces the spherical polymer particles to move closer together. As the process of concentration continues, the repulsion forces of the emulsifier shells are overcome until there is direct contact between the particles. This process of concentration extends beyond the closest spherical packing, and the polymer particles are forced to deform until ultimately there is a homogeneous, coherent film (coalescence). This process can be followed using a scanning electron microscope.<sup>[6-13]</sup> After the stabilizing system



**Figure 6.2-1.** Film-forming process of polymer dispersions

has collapsed, film formation is irreversible: the polymer particles can no longer be redispersed by adding water. This is the basis for the water resistance of dispersion films, which is a fundamental prerequisite for their use in paints. The final component step occurs after the actual drying phase and can last days or even weeks: By diffusion of molecular chains beyond the original particle boundaries (interdiffusion), the polymer particles are truly fused together;<sup>[6-14]</sup> interfaces disappear and, as a result, high mechanical film strengths are developed.

Film formation is brought about above all by the forces, known as capillary forces<sup>[6-15]</sup>, which occur towards the end of the concentration process. These forces become greater as the films of water between the polymer particles grow thinner. It is these forces which press the spherical particles against one another and deform them so that they fill the entire volume. An additional effect is the attempt of the polymer to minimize the surface tension by reducing the surface area. To understand the process of film formation, it is particularly important to consider the forces which stand in the way of coalescence.<sup>[6-16]</sup> In addition to the forces of repulsion already mentioned, there is the deformation resistance of the particles. This resistance is associated with the polymer hardness, i.e., with the glass-transition temperature,  $T_g$ , of the polymer, and with the actual temperature during film formation. Hard particles can be deformed little, if at all, and are unable to take part in coalescence. The  $T_g$  is determined by the choice of the polymer-forming monomers and by their proportions. It is usual to combine different

“hard” and “soft” monomers. For every polymer dispersion there is a typical limiting temperature above which the particles are so soft that the capillary forces overcome their deformation resistance and are able to bring about coalescence. This temperature is termed the minimum film-forming temperature, MFT, and can be determined with a MFT bar in accordance with DIN 53787. This MFT is closely associated with the  $T_g$  of the dispersed polymer.<sup>[6-17]</sup> In addition to the  $T_g$ , there are other dispersion properties and polymer properties which influence film formation, such as particle size, particle size distribution, molecular weight, degree of cross-linking, emulsifiers, etc.<sup>[6-18]</sup> A detailed examination of these factors is outside the scope of this description. The key facts critical for subsequent consideration are as follows: during the drying of a polymer dispersion, the polymer particles coalesce under the pressure of the capillary forces and by purely physical means, through deformation, form a homogeneous, water-resistant film which is no longer redispersible. This process, however, only takes place above the MFT of the polymer dispersion.

### 6.2.3 Coalescing Agents: Mode of Action

The MFT places a restriction on the use of a dispersion<sup>[6-19]</sup>: On the one hand, it must not be above the processing temperature, and on the other hand it determines, by way of the  $T_g$ , the ultimate hardness of the film, i. e., of the coating. This restriction can be circumvented by forced drying. Normally, however, and especially when coatings are applied manually, application takes place at room temperature – in extreme cases, even at substrate temperatures of 5 °C. Optimum coalescence by the binder must therefore be guaranteed even under such conditions. Dispersions which are able to form films at such low temperatures give rise to coatings which are not hard enough for many applications. CA's combat these two restrictions. When such an additive is employed in a dispersion, it diffuses into the polymer particles and reduces their hardness. It thus acts as a plasticizer, and allows the polymer particles to form films even below the actual MFT/ $T_g$ . Since coalescing agents are, as already mentioned above, temporary plasticizers, they evaporate during or after application and the polymer acquires its original hardness again. To this extent, dispersions can be used to produce hard coatings, resistant to mechanical loading, even at conventional ambient temperatures.

There are three critical aspects to the effectiveness of a CA: its distribution in the dispersion, its ability to soften the polymer, and the rate at which it departs again from the drying coating film.<sup>[6-20, 6-21]</sup>

Naturally, a coalescent does not generally diffuse completely into the polymer particles, but is partitioned in the dispersion between polymer and water. This partitioning is extremely significant with regard to the effectiveness of the CA. It is described by means of a three-phase model<sup>[6-22]</sup> (Fig. 6.2-2), the phases comprising particle core, particle shell, and an aqueous phase (serum). The distribution equilibrium depends on the polarity of the polymer and on the water-miscibility of the

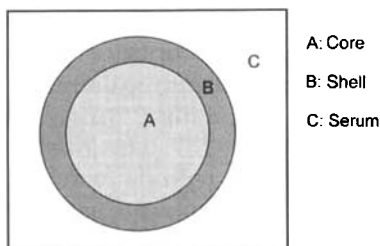


Figure 6.2-2. Three-phase model

film-forming aid. It must be borne in mind that the particle surfaces are generally more polar than the rest of the polymer, since it is here that the hydrophilic components (emulsifiers, initiator end groups, acid groups, etc.) are present in greater concentration. As far as the water-miscibility is concerned, it should be noted that the serum consists not only of water but contains emulsifiers and salts. This means that every combination of dispersion and coalescing agent will establish an individual distribution equilibrium, which is difficult to predict. Since coalescence takes place at the areas of contact between the particles, a CA which is present in the particle shell will be particularly effective. Hydrophilic film-forming aids are located in part in the aqueous phase and are naturally less able to affect coalescence. In addition, that fraction of the CA which is present in the serum will be drawn down with it into absorbent substrates. On nonabsorbent substrates, by contrast, a hydrophilic film-forming agent will be able in turn to migrate more heavily into the polymer from the shrinking aqueous phase, so that its proportion in the polymer is greater than might be assumed from the original distribution. There is also a close connection between the distribution equilibrium and the rate of evaporation of the CA (see Section 6.2-4). Thus, a coalescent which accumulates in the particle core will, owing to its strong interaction with the polymer, be slower to evaporate from the film.

The key task of the film-forming aid is to lower, effectively, the MFT of the dispersion. The literature<sup>[6-20, 6-23]</sup> describes how the glass-transition temperatures of polymer and CA and their proportions by volume can be used to determine the  $T_g$  of the modified polymer. The CA-lowered  $T_g$  of the polymer gives the reduced MFT of the dispersion, which allows film formation at lower temperatures. The activity of a good coalescent, however, is not restricted to lowering the MFT but extends to optimizing the process known as interdiffusion (see Section 6.2.2). This effect is promoted by the swelling of the polymer, i. e., by the increase in its free volume.<sup>[6-24]</sup> As mentioned, interdiffusion causes the high strength of polymer films and also has a positive influence on other performance properties (see Section 6.2-5).

The third factor governing the mode of action of a CA is the evaporation behaviour.<sup>[6-25]</sup> In this context there are two basic requirements. 1. The film-forming aid should depart rapidly from the polymer again so that the applied coating becomes hard as quickly as possible, i. e., exhibits minimal dirt pickup and blocking resistance and high mechanical strength. 2. The CA must still be present in the polymer during the last component step of the film-forming process, in other words during

the actual coalescence of the particles. Otherwise, the MFT is not reduced to a sufficient extent, and a crack-free film is not obtained. This implies that a CA must evaporate more slowly than water. In practice, the attempt to meet these two requirements simultaneously is frequently the cause of problems. This results, for example, from the fact that the evaporation of coalescing agents, unlike that of water, is uninfluenced by the atmospheric humidity (see Section 6.2-4). Looking at the effectiveness at which various CA's lower the MFT of a dispersion (Fig. 6.2-3), and the rate at which dispersion films acquire their hardness (Fig. 6.2-4) leads to the following observation: CA's which are highly efficient in lowering the MFT generally remain in the film for a long time, and vice versa. An example of this is the behaviour of 3-hydroxy-2,2,4-trimethylpentyl isobutyrate (TPiB) on the one hand and butyl glycol (EB, ethylene glycol butyl ether) on the other. Admittedly, a few more rapidly evaporating coalescing agents do make a positive contribution in that during the early phase of film formation they promote mutual wetting and the deformation of the polymer particles. Highly effective substances which stay in the polymer for a long time, and are generally less hydrophilic, have apparently no effect on drying. More polar film-forming aids are able, through interaction with the water (hydrogen bonds), to slow down evaporation. Here again, it is almost impossible to make exact predictions.

Since there is a correlation between the evaporation behaviour of CA's and the drying of emulsion paints, it is appropriate here to deal briefly with the drying of dispersions and emulsion (more properly, dispersion) paints. A variety of hypotheses have been developed in the literature. For instance, it is reported that the

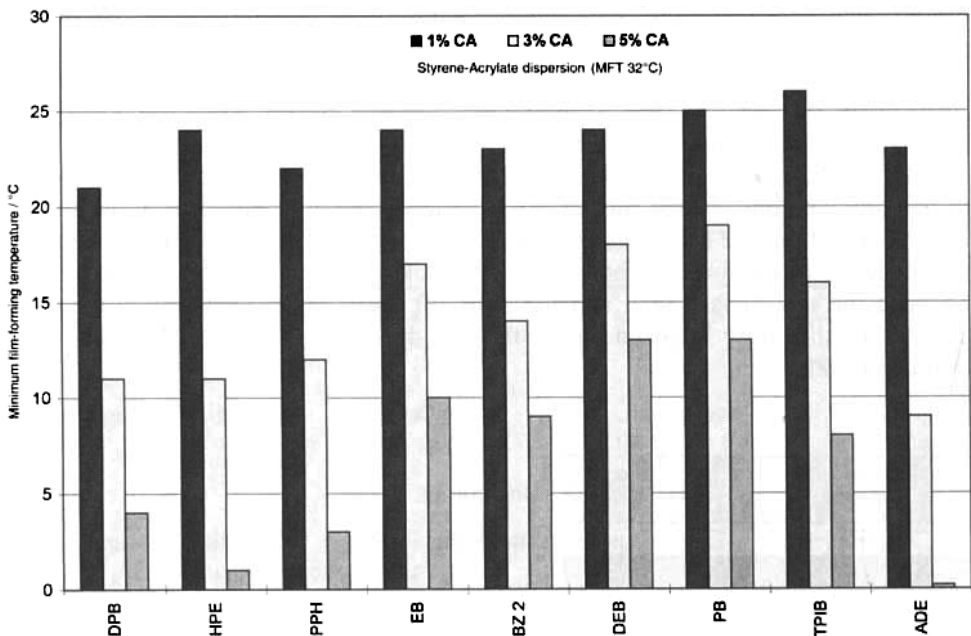
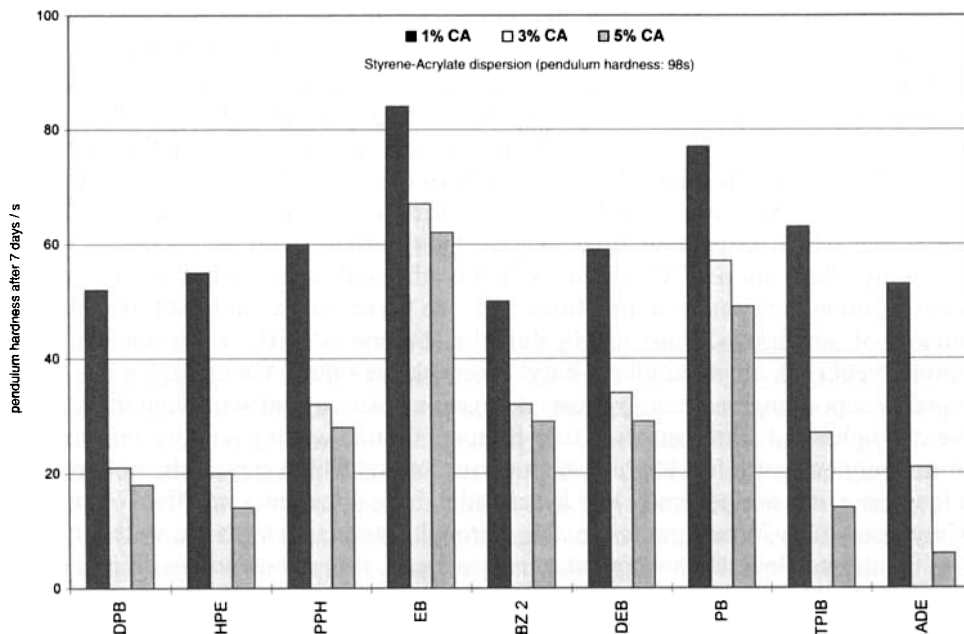
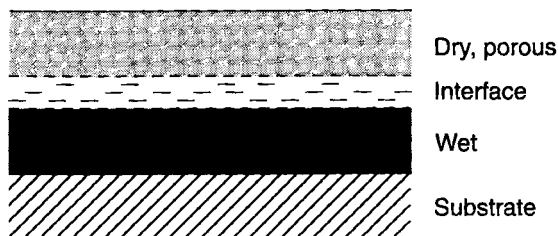


Figure 6.2-3. Effectiveness of coalescing agents: MFT reduction



**Figure 6.2-4.** Evaporation of coalescing agents: development of pendulum hardness

water first of all evaporates at a constant rate which is dependent on external conditions such as temperature, atmospheric humidity, and air movement. As drying progresses, evaporation slows down until finally it becomes a diffusion-controlled process.<sup>[6-26]</sup> Alternatively, a layer model<sup>[6-27]</sup> (Fig. 6.2-5) is discussed: drying starts from the surface, and a so-called interlayer passes from top to bottom through the paint onto the substrate. Above it, the paint is already dry; below it, it is still wet. In terms of the rate of evaporation, this model is similar in principle to the previous one. When the interlayer reaches the substrate, the initially constant evaporation rate drops off and approaches zero. This model is able to explain the tendency of emulsion paints to exhibit cracking, brought about by the tension between the dry surface skin and the still soft lower layer. However, it does not explain the difficulty imposed on the through-drying of the system by the formation of the skin.



**Figure 6.2-5.** Drying of emulsion paints: layer model

Finally, coalescing agents can be put into three groups on the basis of their effectiveness<sup>[6-28]</sup>:

1. Agents which influence not so much film formation as the evaporation of water, i. e., the drying of the emulsion paint.
2. Film-forming aids which promote the mutual wetting and the deformation of the polymer particles and hence also their coalescence.
3. "True" coalescing agents, which support the firm fusion of the polymer particles by making it easier for interdiffusion to take place.

This differing behaviour should be seen not as good or bad but as opening up possibilities in practice to direct the performance properties of dispersion products. These effects will be discussed later on.

## 6.2.4 Coalescing Agents: Product Overview

In terms of chemical structure, a rough distinction can be made between two types of CA's: pure hydrocarbons, and more or less polar products which contain alcohol, ether, ester, or keto functions, or combinations of these. The second group not only embraces far more products than the first, it is of greater importance as well. In Section 6.2.3 a division on the basis of effectiveness was mentioned. Also of interest is a different classification, which was carried out by Mercurio et al.<sup>[6-22]</sup> and is based on the three-phase model (see Fig. 6.2-2) presented in the same publication. This classification is necessarily a simplification, but does assist the user, and so will also be used here to characterize different coalescing agents (Table 6.2-1).

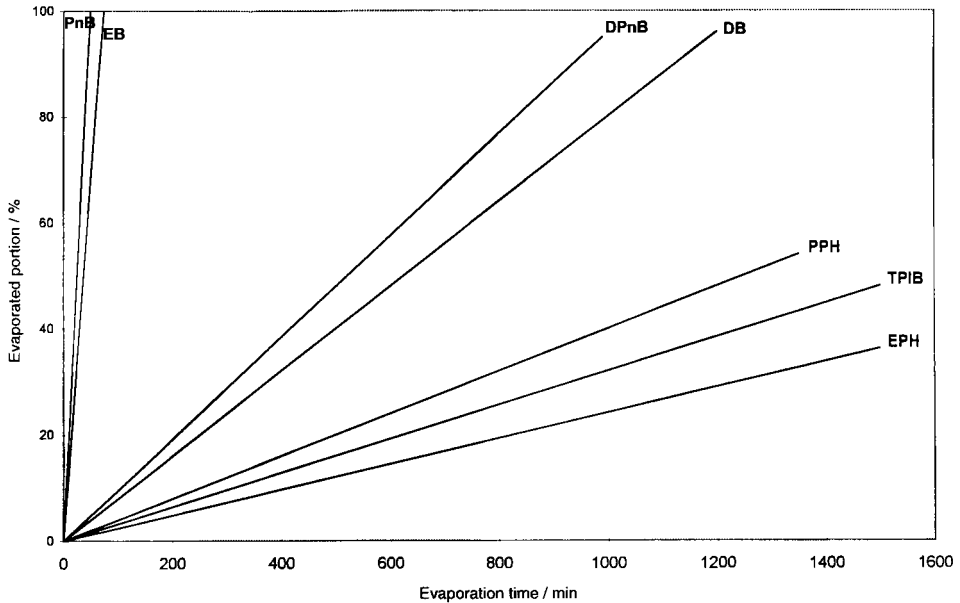
**Table 6.2-1.** Classification of coalescing agents

Location	A	AB	ABC	C
Product	White spirit	Esters Ketones	Ether alcohols	Glycols Hydrophilic ether alcohols
Advantages	Limited coalescence	Excellent coalescence	Good coalescence Control of open time	Increasing of open time Freeze-thaw stability
Disadvantages	Difficult incorporation Loss of gloss	Reduced open time Tendency to block	Stability Diffusion into substrate Tendency to block Early water-resistance	No real CA Diffusion into substrate Early water- resistance

The above-mentioned hydrocarbons are mainly benzines (white spirit), with virtually no use now being made of pure aromatics, such as xylene which was employed formerly. White spirit is nowadays generally low in aromatics and consists, in low-odour, aromatic-free versions, of isoparaffins or cycloaliphatic compounds. These apolar substances diffuse very heavily into the polymer particles, but owing to the marked polar structure of the particle shells,<sup>[6-22]</sup> accumulate to a great extent within the particle core (type A). As a result, although they soften the polymer, they are less effective in influencing the film formation. Incorporating them into dispersions is a problem, and may give rise to cloudy films and, in paints, to a loss of gloss. Their major advantage is, in particular, the favourable price, and it is for this reason that they are frequently used in combination with polar CA's such as ether alcohols. In addition to their odour, other characteristics of the aromatic-free products that are regarded favourably are their defoaming action and their contribution to controlling the open-time.<sup>[6-29]</sup>

The second group of film-forming aids (type AB), which are distributed on core and shell in the polymer particle, includes the products which have become established over many years in conventional emulsion paints. The reason why they have become established is not only their effective lowering of the MFT but also their ease of incorporation in and good compatibility with dispersions (see Section 6.2.5). This group principally consists of esters, such as 3-hydroxy-2,2,4-trimethylpentyl isobutyrate (TPiB), diesters of adipic acid (ADE), dimethyl phthalate (DMP), 2-hydroxypropyl ethylhexanoate (HPE) and benzyl benzoate. The stability of these esters to hydrolysis in paint formulations is good even at high pH, so that no loss in effectiveness need be feared on storage. As described above (see Section 6.2.3), they are ideal promoters of film formation, especially interdiffusion, but remain in the film for a long time. This is less of a problem with emulsion paints, but is a disadvantage in waterborne coating materials in terms of surface hardness/blocking and mechanical strength in the early stages. TPiB, despite its outstanding technical suitability in interior emulsion paints, has fallen out of favour because consumers are no longer willing to accept its characteristic odour. For similar reasons of odour, highly effective ketones such as 2-(1-cyclohexenyl)cyclohexanone, cyclohexanone and isophorone have not acquired any importance as CA's. Dimethyl phthalate has recently become critically regarded within the general discussion surrounding phthalates.

The largest single group is that of the ether alcohols. In addition to the ethylene glycol ether derivatives, which were once used exclusively, an increased share of the market has been taken by propylene glycol derivatives. Owing to their relatively strong hydrophilicity, ether alcohols are distributed on polymer and serum (type ABC). This means that, despite their good action as coalescing agents, they generally have to be added in greater amounts than the above-mentioned esters. Mixtures of the two product groups may give very good results. With ether alcohols it should be noted that they are less universally compatible with dispersions (incorporation) and, owing to their hydrophilicity, are easily drawn down with the serum into porous substrates. Hydrophilicity is again the cause of the disadvantage that ether alcohols may give paint films a certain sensitivity to water in the early stages. On the other hand, their great importance in waterborne coating ma-



**Figure 6.2-6.** Evaporation rate of coalescing agents

materials can be attributed to rapid evaporation (hardness, blocking resistance) and their usefulness in controlling the open-time. Here, the great product diversity in ether alcohols proves to be advantageous in that it allows broad variation in the evaporation rate<sup>[6-30, 6-31]</sup> (Fig. 6.2-6). As examples of rapid evaporation, butyl glycol (EB, ethylene glycol butyl ether), the most widespread ether alcohol in the waterborne coating sector, and propylene glycol butyl ether (PB) should be mentioned. Dipropylene glycol butyl ether (DPB) adopts a position midway between these, while propylene and ethylene glycol phenyl ether (PPH and EPH) have similar and even slower evaporation properties than TPiB. The latter are also used in typical emulsion paints. As expected, EB and PB are much less favourable in terms of MFT reduction than PPH, EPH, or TPiB, whose level is, astonishingly, almost attained by DPB. Under the proviso that a coalescent must evaporate more slowly than water, it is always necessary when establishing the evaporation rate, i.e., when selecting appropriate CA's, to bear in mind the relative atmospheric humidity and the air movement during application. As the two diagrams (Fig. 6.2-7) show, the evaporation behaviour of an 80:20 mixture of water/EB can be entirely different at 50% relative atmospheric humidity than at 70%.<sup>[6-31]</sup> It has been found in practice that successful processing of waterborne coating materials requires good knowledge of the drying behaviour of the solvent/water mixture. In addition to atmospheric humidity and temperature, an important influence is exerted in the case of spray application, for example, by the method of atomization (pneumatic, airless, high-speed rotation) and of drying (air circulation, combined air circulation/IR).<sup>[6-32, 6-33]</sup>

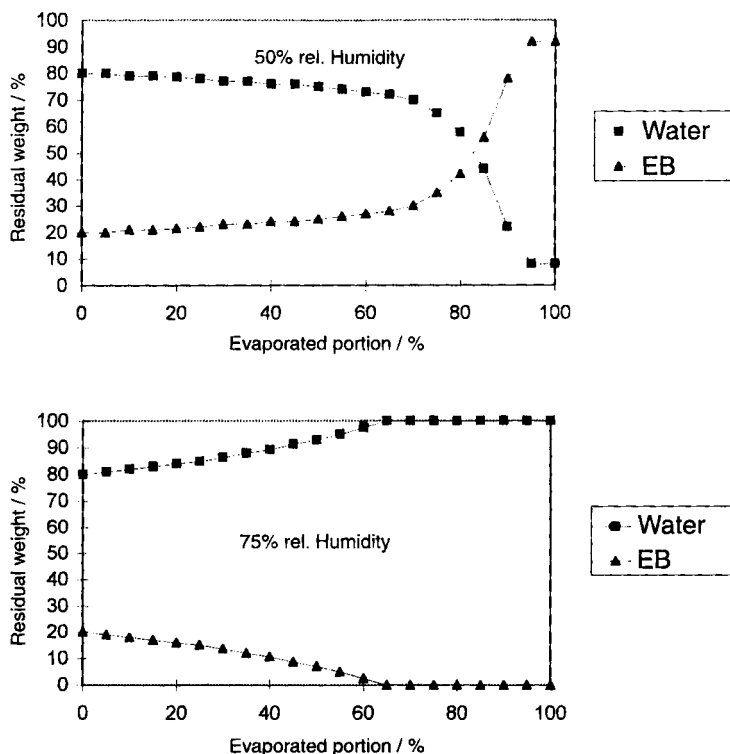


Figure 6.2-7. Butyl glycol/water mixture: evaporation behaviour

The final group of CA's, which includes glycols and hydrophilic ether alcohols, is located largely in the aqueous phase (type C) and therefore cannot be used as sole film-forming aid. Such CA's have a marked influence on the drying of waterborne coating materials, especially on the open-time, on the freeze-thaw stability, and on the action of associative thickeners (see Section 6.2.5). To this extent, these substances are extremely important as paint additives, in dispersion systems albeit only in combination with true coalescing agents. A larger part is played by products of type C, and also of type ABC, as so-called coupling agents, or co-solvents, in waterborne coating materials based on water-dilutable resins (see Section 6.2.2). In such systems they have an important effect on viscosity and stability of the coating materials;<sup>[6-34]</sup> in this context it is the HLB, i.e., the balance between hydrophilic and lipophilic character, that represents the key property.

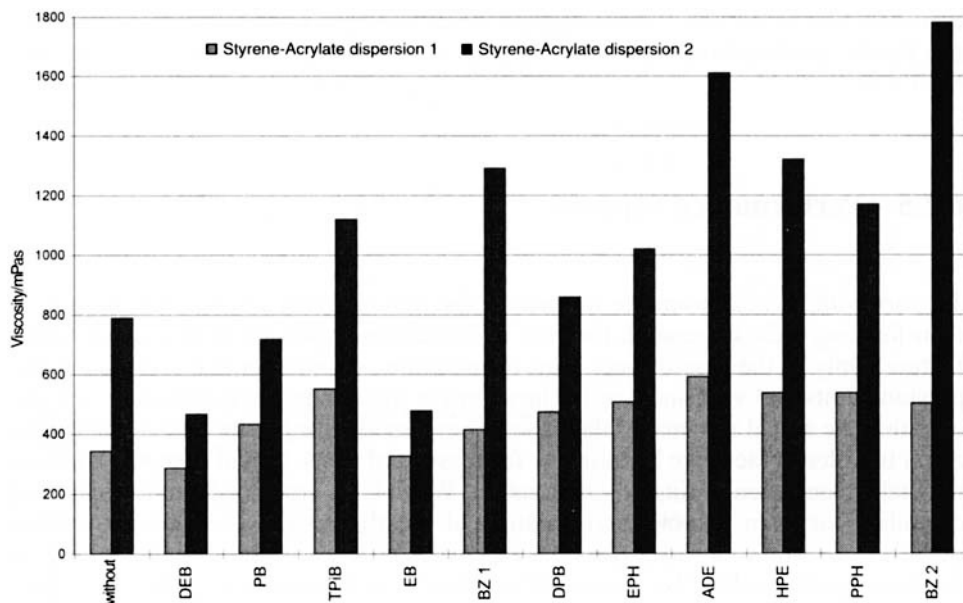
Finally, mention should be made of *N*-methylpyrrolidone (NMP), which is of great importance as a film-forming aid in polyurethane (PU) dispersions. Products produced by the prepolymer ionomer method in particular already contain NMP as a result of this method,<sup>[6-35]</sup> so that their MFT lies at 0 °C. Mention may be made of another interesting aspect of PU dispersions. In terms of their particle morphology, they differ from conventional polymer dispersions in that the hydrophilic segments of the PU molecular chains are swollen by water. This leads to softening and hence

to a reduction in the MFT. To this extent, water acts as a coalescent, and is the reason for the combination, typical of PU dispersions, of high film hardness with low MFT.<sup>[6-36]</sup>

### 6.2.5 Performance Aspects

To start with, it is appropriate to make a few fundamental remarks on the use of film-forming aids. In general, they are added to the dispersion during paint manufacture. Only in the case of very hard formulations of polymer dispersions for dispersion paints and varnishes, or for inexpensive interior paints (Germany), is it the case that the actual raw-materials manufacturer equips the binder with a coalescing agent in order to facilitate handling or for reasons of costs. In that case, the addition may take place even during polymerization. When CA's are added, the formation of coagulant, or even complete coagulation of the dispersion, is a possible consequence as a result of a shock reaction, especially if they are added suddenly. Such a reaction can be avoided by slowly adding the CA with stirring, possibly after dilution with water, by combination with a more hydrophilic product, or, in the case of water-insoluble coalescent, by adding wetting agents such as the ones used for dispersing pigments.<sup>[6-37]</sup> In general, it should be noted that a plasticized dispersion is less stable, and on exposure to shearing, frost, or electrolyte will have a greater tendency to coagulate than in the unmodified state. The reason for this is in particular the – inherently desirable – swelling<sup>[6-24]</sup> and softening of the dispersion particle shell by the CA. The fact that glycols and hydrophilic ether alcohols increase the freeze–thaw stability of dispersion systems does not contradict this. These substances lower only the freezing point of the water, without increasing the stability of the dispersion itself.

A further effect arising from the swelling of the polymer particles is the increase in the dispersion viscosity when film-forming aids are added. In extreme cases, this process may lead to the thickening or even the coagulation of the dispersion. In general, the viscosity should stop increasing one day after the coalescing agent has been added. The effect can be exploited as an inexpensive thickening option, with the “thickener” leaving the film again after drying and so having no adverse effect on water resistance. Fig. 6.2-8 lists the viscosities of two styrene acrylic dispersions as a function of the added coalescent. It is clearly evident that some, more hydrophilic products have a diluent effect, and so cause little or no swelling of the particles, whereas the majority of products bring about a marked increase in viscosity. A particularly strong effect is that shown by white spirit which contains aromatics, thereby confirming its above (see Section 6.2.4) classification as type A (preferential residence in the particle core). Thickening can be regarded as a first indication of the positive effectiveness of a CA, although the effect depends considerably, as shown by Fig. 6.2-8, on the binder itself. After the incorporation of the coalescing agent, the dispersion or paint should be left to age for about 24 hours, to allow the establishment of the equilibrium distribution. Given thorough incorporation and

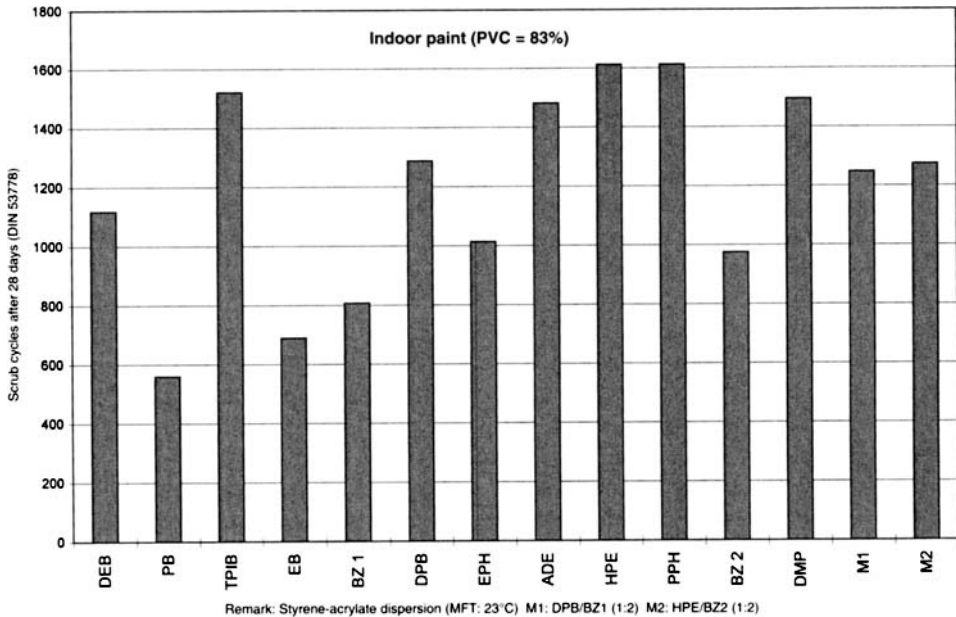


**Figure 6.2-8.** Dispersion viscosity: influence of coalescing agents

good compatibility of the film-forming aid, a dispersion film should subsequently be clear and free from gel specks. Finally, mention should be made of two further prerequisites for the usefulness of CA's. An important part is played by the odour, as already discussed above (see Section 6.2.4). Low odour has now become not merely an important criterion but, especially in the case of interior paints, an absolute must, since long-lasting odour pollution in particular is no longer accepted by today's end users. Furthermore, a coalescent is required to be stable to hydrolysis even at the usually high pH of paints and varnishes. Esters of the glycol ethers may give rise to problems in this respect. Although they are good – in some cases very good – at lowering the MFT of polymer dispersions, hydrolysis converts them into the corresponding, less effective ether alcohols. In such cases it is possible that the MFT will no longer be adequately reduced, and the film will not develop flawlessly (without cracking).

To sum up, finally, the key requirements imposed on a CA: effective lowering of the MFT and rapid evaporation from the film as basic requirements, ease of incorporation, good compatibility (dispersion stability and dispersion viscosity), stability to hydrolysis, low odour, no negative impact on film appearance, and, of course, favourable price.

The text below deals with further performance (i. e., application-related) aspects associated with the use of film-forming aids. Some details have already been discussed in connection with the CA types (see Section 6.2.4). Traditionally, coalescents have played a large part in influencing the pigment-binding power of dispersions. By selecting the right film-forming aid it is possible to optimize the abrasion values of a paint formulation and to achieve both an economic advan-



**Figure 6.2-9.** Pigment binding: influence of coalescing agents

tage and an ecological advantage in terms of reducing the CA content (lower emissions). The effect of different coalescents on the abrasion values of interior paint (PVC: 83%) based on a styrene acrylic dispersion is shown in Fig. 6.2-9. The best results are achieved by the classic CA's of type AB: the paints exceed the level "resistant to washing" significantly. With propylene and ethylene glycol butyl ethers, as with the aromatic-free white spirit, which is difficult to incorporate, the abrasion values are distinctly lower than the limit value set down in DIN 53778, whereas butyl diglycol, ethylene glycol phenyl ether, and aromatic-containing white spirit barely meet the "resistant to washing" criterion. The two mixtures which include white spirit are of interest, since in this case good pigment binding can be combined with favourable price and low odour (compare also mixture 1). The overview makes it clear that the fusion of the polymer particles and, to a lesser extent, the rapid development of hardness (increased abrasion resistance) of the dispersion play the decisive part. This is confirmed by the behaviour of a soft styrene acrylic dispersion (MFT: 4°C), which is usually used without the addition of coalescing agents in solvent- and plasticizer-free interior paints. If the formulation (PVC: 79%) is admixed with increasing amounts of the slow-evaporating coalescent HPE, the abrasion values increase continuously and reach a maximum at about 10% CA, based on dispersion (Fig. 6.2-10). When even higher amounts are added, there is no notable improvement in the abrasion values. Even with an addition of 30%, however, there is no deterioration either, although the polymer film should be very soft with such a high quantity of film-forming aid.



**Figure 6.2-10.** Pigment binding: influence of amount of coalescing agent added

Mention may be made at this point of the use of CA's in pulverulent emulsion paints based on redispersible powders. This product group has recently become the subject of intensified discussion, since it combines ecological advantages (container disposal, absence of preservatives, no transportation of water) with technical and economic advantages (frost stability, storage stability, low packaging price).<sup>[6-38]</sup> Here too, coalescing agents are used in order to optimize the pigment binding power of redispersible powders, which is poorer than that of polymer dispersions. The products involved are solids or substances adsorbed onto mineral fillers. Diols used as CA's, by deactivating the polyvinyl alcohol protective colloids present in the redispersible powders, additionally improve the water resistance of the paints.<sup>[6-39]</sup> From the point of view above all of emissions reduction, here again there is a tendency to use relatively soft polymers in order to do away entirely with the need for film-forming aids.

CA's also have a marked influence on the film mechanics. For each paint formulation, there is an optimum level of added coalescent which reduces the internal tension and hence the tendency of the paint to crack.<sup>[6-40]</sup> The effect is attributed to the softening and to the enlargement of the free volume of the polymer. Propylene glycol, a hydrophilic and relatively ineffective CA, is frequently used, but exerts its effect predominantly in the early phase of film drying. Coalescing agents, however, are only effective below the critical pigment volume concentration (cpvc). Above – even slightly above – the cpvc, an increase in the amount of CA no longer has a favourable effect; in this case, only fillers with a reinforcing action are able to suppress the so-called mud cracking.<sup>[6-41]</sup> This behaviour depends very greatly on the

specific combination of dispersion, fillers and coalescent chosen. The position of the cpvc itself is likewise influenced by the nature and amount of the CA employed. Raising the cpvc improves pigment wetting, which is manifested in turn in an increased number of abrasion cycles.<sup>[6-42, 6-43]</sup>

Closely related to the comments made above on the propensity to crack, is the aspect of film impermeability. Film-forming aids have a drastic effect, for example, on the water-vapour permeability of dispersion films<sup>[6-37]</sup>, which is important for corrosion prevention in particular. Thus it is observed, with a styrene-butadiene dispersion used as a binder in anti-corrosion coatings, that despite the low MFT of 0 °C, the addition of coalescing agent has a very positive effect on the outcome of the salt spray test. This is surprising because the drying temperature under normal conditions (about 20 °C) lies considerably above the  $T_g$  of the polymer; nevertheless, it represents an impressive confirmation of the effect of CA's on the film-forming process. In the case of a very hard styrene acrylic dispersion ( $T_g = 57$  °C), which is likewise recommended for anti-corrosion applications, rapidly evaporating glycol ethers are combined with a true plasticizer in order to achieve rapid development of hardness and optimum coalescence.<sup>[6-44]</sup> The literature reference<sup>[6-45]</sup> reports on the effect of DEB and TPiB and of mixtures of these on the corrosion-prevention behaviour of acrylic dispersions. Here again it is noted that a higher proportion of film-forming aid improves the coalescence of the polymer particles and also the incorporation of pigments and fillers. Higher proportions of the more hydrophilic DEB bring disadvantages, although it is not clearly stated whether these result from the hydrophilicity or from the poorer film-formation effect of DEB. Combinations of ether alcohols and white spirit, in turn, prove to be effective, the latter providing good film-forming properties, hydrophobicity (early water resistance) and a defoaming effect (prevention of microfoam). Further information on the behaviour of CA's in anti-corrosion formulations is given elsewhere.<sup>[6-46]</sup>

Coalescing agents acquire an important function in establishing the surface tension of waterborne coating materials. Normally, dispersion systems possess poorer wetting properties than solvent-containing products. Although wetting agents and surfactants are a remedy for this, they increase the sensitivity to water since they remain in the coating film. A favourable action is exhibited here by ether alcohols, albeit only at levels of 4–5% or more, based on dispersion.<sup>[6-37, 6-47]</sup>

The ability to process waterborne coating materials is determined not only by the right drying behaviour but also by the rheology. Polyurethane thickeners may give dispersion coating materials a flow behaviour which, by reducing the low-shear viscosity (levelling) and raising the high-shear viscosity (brushing resistance) comes close to that of solvent-containing products. This effect is based on the interaction between thickener and formulation components, and thus depends greatly on the composition of the paint. A precise forecast of the actual behaviour is difficult owing to the complexity of the systems.<sup>[6-48]</sup> As far as the behaviour of the polymer dispersion is concerned, important factors are, in addition to the particle structure (size, size distribution, surface nature) and the nature of the emulsifier, the nature of the CA's as well.<sup>[6-49]</sup> These differ in their effect: hydrophobic products increase the viscosity, as a result of the particle swelling discussed earlier, while more hydrophilic products reduce the viscosity. The origin of the latter effect is the influence

that a film-forming aid has on the micelle structure of an associative thickener. Hydrophilic coalescing agents, such as butyl glycol or propylene glycol, for example, reduce the surface tension (see above) and so increase the solubilizing ability of the aqueous phase. As a result, the number of thickener micelles is lowered and so, consequently, is the viscosity of the system. In this context, in general, the low-shear viscosity is influenced much more than the high-shear viscosity.<sup>[6-50]</sup> Here it is possible to deal with the gloss of emulsion paints and varnishes. Gloss is also influenced by coalescing agents, since binders used in such paints generally have a high  $MFT/T_g$  and thus require a large amount of CA. Optimum coalescence, i. e., the addition of a sufficient amount of CA, is a prerequisite for good gloss. If, however, a coalescent destabilizes a dispersion (see above), there may be flocculation during film formation, possibly leading to surface defects and loss of gloss. Water-soluble film-forming aids have a favourable effect on gloss, especially propylene glycols, which, by prolonging the open-time, enhance levelling and gloss of dispersion coating materials.

The effect of CA's on the drying of emulsion paints and varnishes will not be discussed any further here, since important aspects have already been discussed in Sections 6.2.3 and 6.2.4.

### 6.2.6 Ecology/Toxicology

Coalescing agents are employed in emulsion paints – in other words, products which, owing to the absence of solvents, are regarded as eco-friendly but of course are readily miscible with water. This carries with it a risk which is already inherent in the old argument that replacing solvent-containing paints and varnishes by aqueous systems just shifts the environmental problems from the air into the water. Typical CA's and polymer dispersions are classed as fundamentally hazardous to water, and are hence not permitted to enter waterways. In general, the polar substances are classified in German water hazard classes (WGK) 1 (slightly hazardous to water) or 2 (hazardous to water). Only white spirit, which is virtually immiscible with water and so can be separated mechanically, are assigned to WGK 0.

The main argument for the introduction of water-thinnable coating materials was first and foremost the much-reduced flammability. Waterborne coating materials generally have this advantage. For instance, even butyl glycol, with a flashpoint of 63 °C, is not flammable when combined with water. A further aim was to lessen the solvent-induced impact on the health of the manufacturers and users of paints. This has been achieved quantitatively by the switch to water-thinnable products and qualitatively by the selection of less objectionable materials. Nevertheless, coalescing agents are not entirely unobjectionable substances, but are chemicals whose handling should be governed by the same rational attitude to workplace safety as in the case of conventional solvents.<sup>[6-51]</sup> A few CA's are classed as irritant or hazardous to health, and in some cases there are relevant MAK (Germany: maximum concen-

tration at work place) levels. Because of the relatively small amounts employed, the impact of the latter is much less than for solvent-containing products. The specific discussion centered on butyl glycol a number of years ago, because it was suspected of being teratogenic, has not led to this suspicion being confirmed: the product is classed in foetal risk group C, i. e., there is no hazard, provided that the MAK value is observed.<sup>[6-52]</sup> A discussion of individual coalescing agents would go beyond the scope of this work. Reference is therefore made to the information given in the manufacturers' safety data sheets.

Where formerly the direct exposure of paint manufacturers and users was centre stage, now there is, as already mentioned, a general desire to avoid emissions from coating materials. Because of the production of emulsion paints and dispersion plasters in Germany, emissions are approximately 10 000 tonnes per annum.<sup>[6-53]</sup> This relates in particular to the conventional CA's of type AB, which continue to evaporate long after application. Now, already, products are available for the interior sector which manage completely without the addition of film-forming aids. Even in the case of exterior paints and waterborne coating materials for diverse fields of use, a reduction is desirable; omitting it completely, however, gives rise to more problems, since in this case the technical requirements are naturally higher. The trend towards further reduction of emissions is being forced by statutory regulations and by the programmes of the paint manufacturers. For instance, there has for many years been the KELCH Ordinance in Switzerland,<sup>[6-54]</sup> which nevertheless still leaves a relatively large scope for the use of conventional, relatively non-volatile CA's. The EC-drafted ECO label<sup>[6-55]</sup> limits the VOC content in matt emulsion paints to a maximum of 30 g L<sup>-1</sup> (based on "paint minus water"). The Verband der deutschen Lackindustrie (German coatings industry association) in 1996 issued guidelines which made a distinction, for emulsion paints, between "solvent-free" and "solvent-free, plasticizer-free".<sup>[6-56, 6-57]</sup> In this context, CA's with a boiling point of less than 250 °C are dubbed solvents, those with a boiling point above 250 °C are plasticizers. In both classes the limit is 1 g L<sup>-1</sup> (based on the paint), which thus goes well beyond the requirements of the ECO label. The intention of this is to enable the consumer to differentiate products according to their emissions potential and, by means of his or her purchasing decision, to make an informed contribution to reducing emissions.

### 6.2.7 Manufacturers/Tradenames (Selection)

BASF: Lusolvan, Palatinol, Solvenon

Cölner Benzin Raffinerie: Cobersol

DOW: Dalpad, Dowanol

Eastman: Texanol

Exxon: Isopar, Solvesso

Servo: SER-AD FX

Shell: Kristallöl, Shellsol

Other companies likewise offer products for use as film-forming aids, without tradenames, under the products' chemical names.

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## 7 Catalytically Active Additives

*Johan Bieleman*

Catalytically active additives are substances that are used to accelerate a chemical reaction. These accelerators or catalysts form a versatile group of additives and belong to the oldest group of additives.

Paints and other coating systems form a solid layer during the film-forming process where different physical and chemical processes are important.

Physical drying occurs during the evaporation of solvents or by penetration of the liquid coating into a porous substrate.

Oxidative drying is the process by which evaporation of solvents is followed by oxidation of the unsaturated binder under the influence of air/oxygen. This oxidative drying process is accelerated by the addition of catalysts, referred to as driers.

Drying may also proceed through chemical reactions, such as condensation or polyaddition, or by heat (baking enamels) or without (two-component coatings). These chemical reactions may also be accelerated by catalysts.

In this chapter, the group of catalytically active additives is divided into driers and catalysts.

Driers are catalysts as well, but usually they are considered as a separate group.

Photoinitiators may also be regarded as catalysts; these additives are discussed in Section 8.6, where their application in ultraviolet-cured systems is focussed on.

## 7.1 Driers

*Johan Bieleman*

### 7.1.1 Introduction

Driers, also referred to as siccatives when in solution, are organometallic compounds, soluble in organic solvents and binders. Chemically, driers belong to the class of soaps; they are added to air-drying coating systems to accelerate or promote, after application, the transformation from the liquid film into the solid stage within an appropriate time. The transformation occurs by oxidative cross linking, a process which is catalysed by the metallic cation of the drier.<sup>[7-1]</sup>

Metallic soaps are offered in liquid or solid form.

### 7.1.2 Historical Overview of the Application of Driers

The first use of drying promoters is not recorded in the literature on early coatings.

The information available today makes it clear that improved drying properties in vegetable oil coatings became associated with some of the natural earth colours used as pigments. This recognition progressed to the point where small quantities of these materials were added not for colouring purposes but for improved drying. It is reported that such deliberate use was practised during the early Egyptian civilization, or at least as early as 2000 BC. The useful materials were various compounds of lead, iron, and manganese, which were sufficiently reactive to form soaps with the fatty acids in the vegetable oils. Cobalt, which is the most active of our modern driers, was not recognized, probably because the natural cobalt compounds are quite unreactive with fatty acids.<sup>[7-2]</sup>

Already in the year 1388, J. Alcherius used copper sulphate for the production of artists' varnishes. In the beginning of the 16th century, the brothers Van Eyk in Flanders used zinc vitriol to improve the drying of varnishes.

Actual consideration or study of drying materials for oils does not appear to have taken place prior to 1840, when zinc oxide began to replace white lead as the prime white pigment. The stimulus was undoubtedly provided by the poorer drying properties obtained when the reactive lead pigment was omitted. Somewhere along the experimental trail, it must have become evident to an early scientist of the day that solubility of the metal compound was important for its activity – therefore the early efforts to prepare driers concentrated on attempting to dissolve the natural materials in the oils. By the latter part of the 19th century, substantial progress had been

made in the preparation of fused resins and linoleates of lead and manganese. The utility of cobalt as a drying catalyst was discovered close to the turn of the 19th century, but the factors that led to its ultimate discovery do not seem to have been recorded.

The early driers provided a means by which a material could be added to a coating for the specific purpose of improving its drying, but the compounds did not have uniform compositions and therefore could not give predictable results. Even if all of the metal reacted with the acid to give an expected metal concentration, which seldom happened, the anions in use were subject to oxidation. This made it less soluble in the vehicle and therefore less active.

A major advance in drier technology occurred in the 1920s with the preparation of the metal naphthenates. Naphthenic acid does not have a precise composition, but is a mixture of acids of the same general nature. However, if the acid mixture is varied, the number of acid equivalents also change from batch to batch. The next main technological advance was the preparation of solvent solutions of these metal naphthenates, which not only gave materials that were easy to handle, but allowed the metal content to be standardized. Naphthenates soon became the standards of the industry.

The next step in the history of drier development came with the introduction of octanoates. Because these driers are produced from 2-ethylhexanoic acid, the chemical composition can be controlled to ensure the uniformity. Other synthetic acids such as isononanoic acid, heptanoic acid, and Versatic (Shell) acid became available and are used to produce driers. These synthetic acids have higher acid values than naphthenic acids, they are more uniform, paler in colour, and do not have the characteristic odour of commercial naphthenic acids. It is also possible to produce driers with a much higher metal content than is possible with the naphthenates.

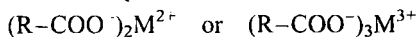
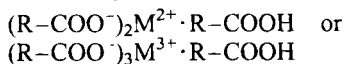
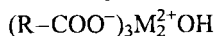
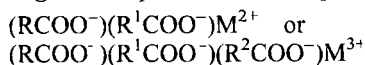
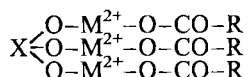
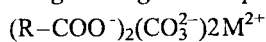
More recently, so-called overbased driers with extremely high metal content became available. These driers are made of combinations of monocarboxylic acids, such as 2-ethylhexanoic acid and carbon dioxide or polyfunctional acids.

Traditional driers are not soluble or emulsifiable in water and show only limited stability in aqueous systems due to rapid hydrolysis. The interest in air-drying paints with low solvent content has led to the development of a new class of highly efficient driers for high-solids paints.

### 7.1.3 Composition

There are many variations of metal soaps that are used as driers. Fig. 7.1-1 contains examples of various possible formulations.<sup>[7-1]</sup>

The neutral soaps that are used as driers are dicarboxylates, present in stoichiometric acid and base ratios; most of the drier metals are present in the oxidation state 2+. Acid driers contain acid in addition to this, to aid processing and to reduce the viscosity of the soap solution in hydrocarbon solvents.

*Neutral soaps**Acidic soaps**Basic soaps**Organic complex or mixed soaps**Inorganic/organic complex- or mixed soaps*

where:

X = P- or B-

R-COO<sup>-</sup> = Carboxylic acid ion

M = metal ion

**Figure 7.1-1.** Metal soaps

The basic driers are those in which the valence of the metal is only partly compensated by carbonic acid. Three types of basic driers may be considered:<sup>[7-3]</sup>

- hydroxides
- oxides
- others

The most important drier metals in practice are cobalt, zirconium, manganese, and calcium. Some other less used drier metals are zinc, copper, barium, vanadium, cerium, and iron, as well as driers based on potassium, strontium, aluminium, bismuth, and lithium. Lead, earlier one of the most important drier metals lost a lot of importance.

The anion in the metal soap determines largely whether the drier will meet its basic requirements, which are:

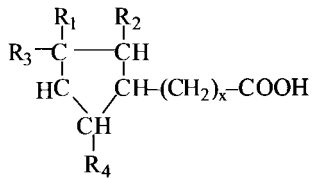
- good solubility and high stability in various kinds of binders; this excludes the use of acids with short aliphatic chains
- good storage stability of the drier
- the ability to be present in a high metal concentration
- a sufficiently low viscosity, to make the handling of the drier easier
- the drier should have an optimal catalytic effect
- the best price/performance relation

The first driers were based, essentially, on rosin or linseed-oil fatty acids. Unfortunately, because of the presence of unsaturated acid radicals, which are polymerization-sensitive, the solubility of these deteriorate.

Tallates, produced from tall oil, were the successors of the resins and linoleates. The tallates have a similar poor storage stability, and their use is limited to mainly printing inks.

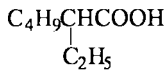
For years, naphthenic acid has been the main commercial drier acid (Fig. 7.1-2). Naphthenic acid is made from naphthenic crude oils. The naphthenic acid content of a crude oil is seldom more than 1 to 2%. The acid basically consists of a cyclopentane nucleus with a side chain terminated by a carboxylic group.

*Naphthenic acid*

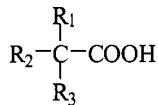


R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are short alkyl chains or hydrogen. X = 1 to 3.

*2-Ethylhexanoic acid*



*Neodecanoic acid*



R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are alkyl chains. There are 8 carbon atoms in all the chains combined.

**Figure 7.1-2.** Typical drier anions

Modern petroleum refinery techniques produce less naphthenic acid than older methods. Moreover, the properties of the synthetic acid alternatives are usually preferred, for both technical and commercial reasons.

Driers based on synthetic acids (in practice referred to as “synthetic driers”) usually have the following advantages over the naphthenates based on naphthenic acid: they are paler, have little odour, and the composition is constant, with a higher metal content. Suitable synthetic acids for drier production are mainly acids with a chain length of C8 to C10.

Primary synthetic acids are obtained by the oxo-process, in which selected branched-chain olefins are reacted with carbon monoxide to yield aldehydes, which are subsequently oxidized to the corresponding acids. The secondary acid 2-ethylhexanoic acid (commonly referred to as octanoic acid) is prepared by the aldol condensation of butyraldehyde followed by oxidation. The salts of this acid are commonly called “octanoates”.

The drier soaps are generally dissolved in hydrocarbon solvents such as white spirit, or in aromatic-free, aliphatic solvents. The latter solvents have the least odour and are increasingly preferred, also for environmental reasons.

To improve storage stability and compatibility with binders and reactive pigments, most driers additionally contain some specific stabilizers, such as polyols or phosphate acid derivatives.

## 7.1.4 Manufacturing

The following three processes are mainly used for the manufacture of driers:<sup>[7-4]</sup>

- precipitation, also known as double decomposition
- fusion
- direct metal reaction (DMR)

The choice of the process and variation depends on the metal used, the desired form of the product, the required purity, the availability of raw material, costs, as well as on the metal content. The fusion process provides the widest possibilities for selection of raw materials, notably the acids used, and is the most popular production process for driers.

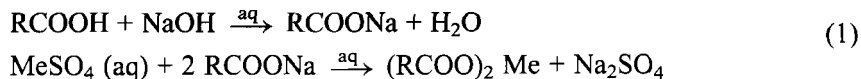
### 7.1.4.1 Precipitation

This is the oldest manufacturing process for driers and was already used for the first naphthenate driers.

During the precipitation process or double-decomposition process the sodium salt of the acid is reacted with the appropriate metal salt in an aqueous medium. The metallic soap precipitates and is filtered, washed, dried, and ground.

A modification of the process is to use, as solvent medium, a combination of water and the hydrocarbon solvent for the drier. The metal drier soap will then dissolve in the white spirit and separate from the water layer. After it has been washed, the drier is filtered and adjusted to the correct concentration.

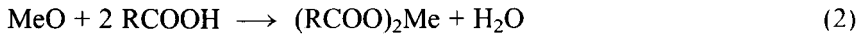
The precipitation process is used for the production of aluminium-, calcium-, magnesium-, zinc-, cadmium-, strontium-, and barium soaps, as well as for cobalt soaps.



### 7.1.4.2 Fusion

In the fusion process, metal oxides, -hydroxides, or -carbonates and other salts react directly with the selected organic acids at 150–200 °C. The reaction is carried out to completion by removal of the reaction water. The molten soap is treated with fil-

ter aids and filtered while still hot. It is packaged directly or dissolved in suitable solvents.



In a process modification, a liquid acid reacts with an aqueous slurry of the oxide, carbonate, or hydroxide. Organic solvent is added and the reaction water is removed by azeotropic distillation. The soap solution is then concentrated or completely stripped of solvent, to give a solid.

In a combination of the precipitation and the fusion processes, the metal oxide or hydroxide reacts with an aqueous solution of ammonium- or alkylamine carboxylates. The reactants are heated to a temperature at which the amine complex is dissociated and metal soap is formed. The volatile amine can be removed and recycled.

### 7.1.4.3 Direct Metal Reaction

For the direct-metal-reaction (DMR) process, the finely divided metal powder is added to the reactor vessel in a molten state or dissolved in hydrocarbons. The oxidation of the metal is carried out over a catalyst, in the presence of air and the organic acids. The metal reacts directly with the acids, to produce the metal soap as well as hydrogen.

Suitable catalysts are water, aliphatic alcohol, or low-molecular organic acids.

The DMR process results in no aqueous effluent. However, hydrogen is produced and needs to be removed carefully! Not all metals are sufficiently reactive to be suitable for the DMR process.



### 7.1.5 Autooxidation Drying and the Function of Driers

Coatings that dry by oxidation, such as air-drying alkyd paints, dry by solvent evaporation followed by chemical reactions. This brings about the transition from the liquid to the solid state. The chemical reactions result in oxidative cross linking and polymerization which have a significant influence on film formation. The cross linking reaction is accelerated by the addition of driers.

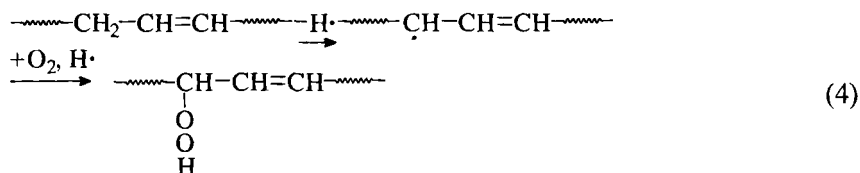
Oxidative cross linking may also be described as an autooxidation process which proceeds through four basic steps:<sup>[7-5]</sup>

- Step 1: Induction period
- Step 2: Peroxide formation
- Step 3: Peroxide decomposition into free radicals
- Step 4: Polymerization

The induction step is measured from the time the coating is applied, and ends when the film begins to absorb oxygen from the air. The absorbed oxygen forms peroxides across the conjugated double bonds in the binder (step 2). When the peroxides begin to decompose, active cross linking sites are formed. As cross linking proceeds during the polymerization, the viscosity increases rapidly.

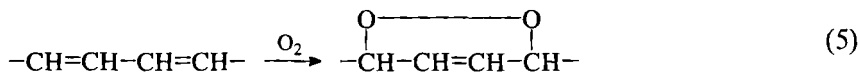
Steps 2 and 4 proceed most effectively with resins containing conjugated double bonds, however, nonconjugated but polyunsaturated resins are also reactive to some extent. In such a case, the multiple double bonds may cause the activation of the various methylene groups, to rearrange the position of the nonconjugated double bonds, to form conjugated double bonds, depending on the original position of the double bonds.

In the case of mono-unsaturated esters, hydroperoxides form from the activation of the methylene group adjacent to the double bond.<sup>[7-6]</sup>

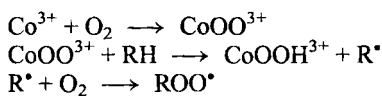


The precise mechanism responsible for the activation of the methylene group is still a matter of controversy.

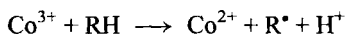
In the case of conjugated structures, such as linseed oil or tung oil (containing eleostearic esters), oxygen adds directly to the conjugated system, to form a 1,4 cyclic peroxide.



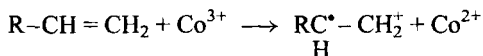
Oxygen absorption



Hydrogen extraction



Direct activation of the double bond



Acid decomposition

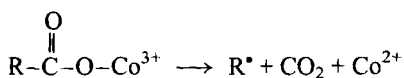


Figure 7.1-3. Cobalt-catalysed reactions

Fig. 7.1-3 shows various possible mechanisms by which the drier functions in the induction and peroxide-formation steps.<sup>[7-5]</sup> Steps 1 and 2 (induction and peroxide formation) are accelerated dramatically by the presence of driers.

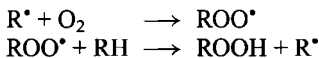
The multivalent metals in the drier system act as oxygen carriers because of their susceptibility to redox reactions. Driers also induce the formation of peroxides; it is assumed that the multivalent metals are associated with the double bonds, so increasing the oxidation susceptibility. The addition of cobalt drier reduces, by a factor of ten, the energy required to activate an unsaturated resin to absorb oxygen.

The penetration of activated oxygen into the film favours peroxide formation. To prove that peroxide formation has taken place, one analyses the iodine value or one follows the reaction by infrared studies, to determine the decrease in double bonds.<sup>[7-7]</sup> As soon as hydroperoxides or cyclic peroxides have formed, their dissociation into free radicals takes place, and some of the reactions shown in Fig. 7.1-4 can occur.

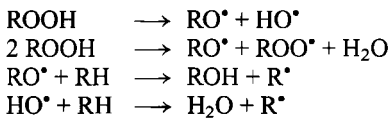
**Initiation:**



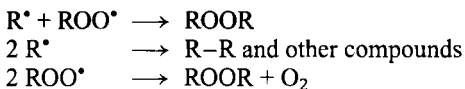
**Propagation:**



**Branching:**

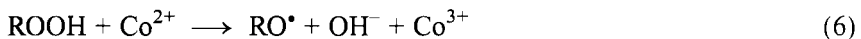


**Termination:**

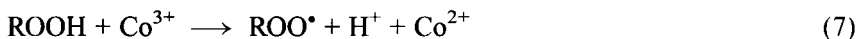


**Figure 7.1-4.** Reactions during autooxidation and polymerization

The effect of a multivalent metal, such as cobalt, on the decomposition of the formed peroxides can be illustrated as follows:



The lower-valency cobalt is regenerated:



This cycle is repeated until all the peroxide has decomposed. Then the polymerization reactions can take place.

### 7.1.6 Drier Metals

Essentially, the metals can be divided into two groups: active driers and auxiliary driers. This difference is really arbitrary, since a considerable amount of overlap exists between them. Active driers promote oxygen uptake, peroxide formation, and peroxide decomposition at ambient temperatures. At elevated temperatures, several other metals, such as bismuth, are also catalytically active, but they are ineffective at ambient temperature. Auxiliary driers are not catalytically active themselves at ambient temperatures, but they appear to enhance the activity of the active drier metals (Table 7.1-1).

**Table 7.1-1.** Drier metals

Active driers	Auxiliary driers
Cobalt	Barium
Manganese	Zirconium
Iron	Calcium
Cerium	Bismuth
Vanadium	Zinc
Lead	Potassium
	Strontium
	Lithium

It has been assumed<sup>[7-7]</sup> that the auxiliary driers increase the solubility and stability of the active drier metal and – as their main contribution – change the redox potential, as the result of complex formation with the primary drier.

#### 7.1.6.1 Active Driers

##### Cobalt

Cobalt is, without any doubt, the most important and most widely used drier metal of all. No other metal is known to be as effective at room temperature. Cobalt is primarily an oxidation catalyst and as such acts as a surface drier.

Used alone, cobalt may have a tendency to cause surface wrinkling and poor through-drying. For uniform drying, cobalt is used in combination with other metals such as manganese, zirconium, lead, calcium, and combination driers based on these metals.

Cobalt has an intense red-violet colour, which colours a clear varnish slightly if used at higher application concentrations. However, if the cobalt drier is mixed with turpentine oils, dipentenes or similar solvents that have a propensity to take up oxygen, a strong green colour develops. This colour usually disappears from the dried coating, but will be more persistent if calcium is used with cobalt.

Cobalt is a transition metal which has two different possible valence states and which is known for its ability to form coordination complexes. If cobalt is added as a drier to an undiluted resin, profound changes in viscosity may occur. This can be avoided by diluting the resin first. Such great viscosity increases only generally take place in higher molecular mass resins and very high viscosity copolymers, and also occur similarly in calcium and zinc driers.

The wrinkling caused by cobalt is turned to advantage in the production of alkyd-based baking wrinkling enamels.

### **Manganese**

Manganese is an active drier as well, though less effective than cobalt.

As an accelerator of polymerization in baking finishes, manganese is normally more effective than cobalt. Cobalt and manganese essentially improve the surface drying of a paint film; the low-temperature drying performance of manganese is better than that of cobalt. Coatings with manganese do not suffer from wrinkling under high-humidity conditions, as films with cobalt alone do. It is generally better to formulate white paints with no manganese or very low manganese content, because a pink or pink-yellow colour develops if high manganese contents are used.

Manganese also has the advantage that it does not cause baked films to become brittle, which happens if cobalt is used alone. Additionally, in systems prone to skinning, such as urethane oil-based coatings, manganese can be used with good results. However, manganese is seldom used alone: cobalt is usually the primary drier with manganese as a useful modifier.

The effect of manganese driers can be modified by organic drier promoters, such as 1,10-phenanthroline and its derivatives.

### **Vanadium**

Vanadium differs from the other metals in that it is most stable in its higher valence state. A considerable disadvantage is its tendency to stain the film; this limits the application of vanadium in paints considerably. Vanadium also seems to tend to be particularly prone to loss-of-drying-ability problems.

### **Iron**

Iron is not effective in oxidative drying coatings. It is sometimes used in dark baking enamels. Normally, it only becomes catalytically effective at baking temperatures above 130 °C. Iron driers have a very dark colour.

### **Cerium/Rare Earths**

Cerium- and rare-earth driers promote the polymerization and through-drying processes. These types of driers are particularly recommended for baking enamels, white varnishes, and overprint varnishes, where colour retention is vital. It is also especially useful for alkyd- and epoxy resins or combinations of both resins with amine resins.

## **Lead**

Lead functions as a drier by promoting the polymerization of drying films to hard, insoluble films. However, its activity as sole drier is very low; this is why lead is often ranked as an auxiliary drier instead of a primary drier.

In contrast to cobalt and other surface driers, lead causes the film to dry through its entire thickness and is therefore known as a through-drier. Lead also improves flexibility and durability of the film.

A strong limitation in the use of lead driers is toxicity: lead is a cumulative poison. Apart from the toxicity issue, lead driers have other disadvantages too, such as limited solubility in certain alkyd resins and low compatibility with aluminium pigments. Lead driers may also cause sulphur staining, because they react with sulphur to form lead sulphide, a black compound.

During storage of the coating material, reaction of the lead drier with long-chain fatty acids, formed by hydrolysis of the alkyd resin, may render the lead salt insoluble (see also Section 7.1.8)

Lead driers are seldom used alone, more often they are used in combination with cobalt or manganese. Calcium is often also added, to avoid precipitation of the lead and hazing.

Because of increasing environmental awareness, the current application possibilities of lead driers in coating materials are limited.

### **7.1.6.2 Auxiliary Driers**

#### **Barium**

This drier is used as a substitute for lead in lead-free coating materials. Barium improves the through-drying of a coating and has good pigment-wetting characteristics.

Unlike lead, barium is not considered as a cumulative poison, although it has quite a high acute toxicity which may preclude its use in certain systems.

Barium driers must be handled with care during paint production.

The presence of barium, as well as other heavy metals, in toys, pens, etc., is, however, not desirable and limits for barium in toys and writing implements are regulated by legislation in most countries.

#### **Calcium**

Calcium itself has only limited effectiveness as a drier, but it is very useful in combination with active driers. It is very effective when used together with cobalt and zirconium, to promote drying under adverse weather conditions such as low temperatures and high humidity. When calcium is used as an auxiliary drier, loss of drying ability becomes less of a problem when paints are stored for a long time. Calcium driers help to improve hardness and gloss, and also reduce skin-formation and silking. In addition, calcium driers are also useful as pigment wetting and dispersing agents. Volume-wise, calcium is one of the most used driers.

**Bismuth**

Bismuth is used as a substitute for lead. It strongly activates cobalt and improves through-drying properties and drying under adverse weather conditions (as calcium does). Bismuth is used in baking finishes to improve the hardness.

**Zinc**

The primary function of zinc is to keep the film “open”, thus permitting hardening throughout and preventing surface wrinkling, particularly in very reactive binder systems and cobalt-containing coatings. It inhibits wrinkling.

Zinc is a very effective wetting agent and pigment-dispersing agent.

Because of its pale colour, relatively large amounts of zinc can be added without discolouring the film.

Zinc also helps to stabilize other driers and to promote hardness, gloss, and colour retention.

**Potassium**

Potassium functions best in conjunction with cobalt. Potassium strongly activates cobalt in aqueous coatings and in high-solids coatings

**Strontium**

Strontium also substitutes lead in lead-free systems. It functions well under adverse weather conditions and promotes through-drying. Paints containing strontium have the advantage over those containing other lead-replacing candidates, such as zirconium, of having the best storage stability and the lowest gelling tendency.

However, outdoor performance may be affected negatively when strontium is used in the place of zirconium.

**Lithium**

Lithium works best in combination with cobalt. It is also sometimes used as a lead substitute in high-solid coatings based on a low-molecular binder. Lithium promotes through-drying and reduces the wrinkling tendency in high-solids coatings.

**Zirconium**

Zirconium driers are the most widely accepted replacements for lead. Zirconium improves through-drying mainly by the formation of coordination bonds with hydroxyl- and carboxylic groups, available from the resin or formed during the drying process. Apart from coordination, zirconium is also assumed to form complexes with cobalt, which influences the catalytic effect of the primary drier.

Zirconium is usually applied in combination with cobalt and calcium. The results reached with this combination are nearly the same as with cobalt/lead/calcium combinations. Compared to other auxiliary driers, zirconium has the best colour, lowest yellowing tendency, and best durability.

### Drier Dosages

Drier systems for decorative paints based on long-oil alkyd resins, cured under ambient conditions, are nowadays very often formulated, using a cobalt/zirconium/calcium combination. The exact dosage and ratio depends on the composition of the coating material and the desired properties and application conditions. Examples of typical and maximum additional quantities in medium- and long-oil alkyd paints are shown in Table 7.1-2.

**Table 7.1-2.** Typical application concentrations of drier metals (metal content based on binder solid content)

Drier metal	Typical concentration	Normal max. concentration
Co	0.06	0.2
Mn	0.02	0.1
Pb	0.5	1.0
Ce	0.2	0.6
Zr	0.3	0.4
Ca	0.2	0.4
Ba	0.2	0.4
V	0.03	0.05
Bi	0.3	0.5
Zn	0.2	0.4
Sr	0.4	0.6
K	0.03	0.08
Li	0.03	0.05

### 7.1.7 Combination Driers

Because of the synergistic effects previously described, it has become common practice in the coating industry to use combinations of metals. These combinations involve one or more active driers with at least one or more auxiliary driers. These combination driers are being offered in various cases by drier manufacturers as ready-to-use or as precomplexed driers.

Ready-to-use mixed driers have the advantage of constant quality, optimal metal ratio and composition, and low solvent content, with a more rationalized production process as result.

In addition to these advantages, the drying performance of precomplexed driers (complexing of various metal types happens during the manufacturing process of the drier) is generally better. These advantages are especially important when the driers are used in high-solids systems, in waterborne air-drying coatings, or in paints applied under adverse weather conditions. Table 7.1-3 contains recommended starting formulations for different binder systems.

**Table 7.1-3.** Recommended formulations for combination driers for different types of binders (% metal based on vehicle solids)

Resin type	Active drier	Auxiliary drier
Drying oils	0.03 Co or Mn	0.2 Zr, 0.1 Ca
Medium-oil alkyd resins	0.04 Co	0.2 Zr, 0.1 Ca
Long-oil alkyd resins	0.05 Co	0.3 Zr, 0.2 Ca
Epoxide ester	0.03 Co	0.1 Ce
Polyurethanes	0.02 Co or Mn	0.1 Zr, 0.05 Ca
Oil-containing systems	0.03 Co or Mn	0.2 Zr, 0.1 Ca
Polyester	0.01 Co	

### 7.1.8 Loss of Drying Ability

The drying time of air-drying coatings usually tend to increase on storage, probably because the drier is inactivated. To function as a polymerization catalyst, the drier should be in contact with the binder and should be mobile to compensate for the relatively low amount of drier relative to double bonds in the binder. Obviously, reactions or interactions in a coating formulation affecting the mobility of the drier molecule will affect the speed of drying as well. In a paint, driers catalyse polymerization.

Oxidative-drying coating materials normally tend to have longer drying time after long storage periods. The possible reason of this is the loss of drier activity.

As a coating material is made up of several ingredients, and since a number of chemical or physical reactions may occur between these ingredients and, for example, the drier, it is difficult to list all the possible reasons for a reduction in the mobility of the driers. However, loss in drying ability is caused mainly by:

- *Chemisorption of the drier onto the pigment surface:* as opposed to physical adsorption, which is a reversible process, chemisorption leads to permanent immobilization of the drier. Chemisorption occurs onto pigments with acidic groups on the surface, and mainly occurs with pigments with a large surface area such as most oxidized carbon blacks and various organic pigments. The solvent composition also affects the chemisorption process; strongest adsorption occurs with poor drier solvents, such as very polar or very nonpolar solvents. Systems with aromatic free mineral solvents are more prone to chemisorption than systems diluted with aromatic white spirit.
- *Salt formation:* The reaction product of the drier ion and the long-chain aliphatic acids – their formation is caused by hydrolysis of the binder or other ingredients – is usually not soluble in the coating material and it deposits after crystallization. This results in loss of the drier.

- *Formation of insoluble complexes:* This phenomenon is typically noticed in low-odour paints, diluted with pure aliphatic solvents. Complexes of different types of driers, made up of relatively short-chain aliphatic acids, such as octanoates, have only limited solubility in these solvents and tend to crystallize out. Overbasic driers are more sensitive to this effect than neutral driers. Driers consisting of longer acids such as C9–C11 are more soluble and are less prone to crystallization in these coating systems.
- *Hydrolysis of the drier:* This is the main reason for drying-ability loss in water-borne coating systems. In the presence of water, the drier is rapidly hydrated. Moreover, water is a good ligand for cobalt and therefore complexes cobalt easily. The formed hydrates are unstable and lead to hydrolysis of the metal soap and subsequently to insolubility of the basic metal soap.<sup>[7-8]</sup>

Loss-of-dry ability may be avoided by the following means:

- The first approach is to choose a drier system that is totally compatible with the coating system. The drier should be soluble in the binder and not result in any haze formation upon storage or during the drying stage. For pigmented systems, it is recommended that a compatibility test should be carried out in the medium, without the addition of pigment or extenders.
- The second approach is to include a sacrificial drier in the grinding paste during the manufacture of the coating. An auxiliary drier such as calcium may be used for this, especially when the drying-ability loss is due to chemisorption of the primary drier onto the pigment.<sup>[7-9]</sup> However, this approach has its limitations and cannot always be used, because if the auxiliary drier is overdosed, the viscosity and hardness (softening effect) as well as durability or colour resistance may be affected negatively.
- The third approach is to use a “feeder drier” such as cobalt hydroxynaphthenate. This feeder drier is available as a paste and is insoluble in mineral spirits. It functions by reacting with the acid which is formed during storage by hydrolysis of the binder; it becomes more soluble in the binder, and thus compensates for the lost cobalt drier.

### 7.1.9 Lead-Free Drier Systems

Lead driers were the main auxiliaries for decades. However, lead is a cumulative poison, and therefore its application in coating materials is nowadays less attractive. In many countries, strict labelling prescriptions for coatings containing lead have to be followed.

Nowadays the application of lead driers in coatings is limited.

Nontoxic lead-free systems, with similar application properties, are being used instead of lead-based drier combinations.<sup>[7-10]</sup>

Lead driers have occupied such an important position because of the unique properties of lead driers, as described in Section 7.1.6. Replacing lead driers successfully means that the specific catalytic properties of a lead drier have to be considered carefully.

Lead is a strong polymerization drier which promotes the oxygen absorption onto the resin molecule; furthermore, lead has, to some degree, a catalytic effect on the formation of radicals. This means that lead has properties typically found in primary as well as in auxiliary driers.

Replacing lead driers means that the complete drier composition must be adjusted; this has been confirmed experimentally, both in the laboratory as well as in practice.

### 7.1.9.1 Lead-Containing Drier Systems

Lead is typically used as a drier in combination with cobalt and calcium. A characteristic composition for a lead-based drier combination is (percentages indicated are the metal proportions of the total resin solids of the coating formula):

0.05% cobalt  
0.5% lead  
0.1% calcium

The main contribution of the lead drier in this combination is to promote the through-drying of the coating layer.

Various replacements for lead-based drier combinations have been proposed. However, in practice, the combination of cobalt, zirconium, and calcium has found wide acceptance. The drying properties of this combination, at ambient temperature and humidity conditions, are quite similar to that of the lead-based combination drier.

However, lead cannot simply be replaced with zirconium, the ratios of cobalt and calcium also have to be adjusted.

### 7.1.9.2 Substitution of a Lead Drier

When replacing a Co–Pb–Ca combination drier with a Co–Zr–Ca combination drier, the following test procedure is recommended:

1. The lead drier is replaced with 60% of a zirconium drier (i.e., 0.5% Pb is replaced by 0.3% Zr).
2. The cobalt content should be increased by 20%.
3. The calcium content should be increased by 50–100%.
4. Replace the lead-based loss-of-drying-ability inhibitor with a lead-free alternative.

If the results are unsatisfactory, further deviations regarding the advised replacement ratios can be evaluated.

All the different combinations of lead-based driers in use have to be evaluated individually.

During the test procedure, the emphasis is on the drying performance, however, the side effects such as the effect on hardness, gloss (lead being a better wetting agent than zirconium, may give higher gloss ratings), yellowing, opacity, etc., have to be considered. Depending on the climate in which the paint will be used, special attention should be given to the drying performance under adverse weather conditions: zirconium-based driers usually perform somewhat poorer than lead-based combinations. The nature of the calcium drier used for the cobalt–zirconium–calcium combination is extremely important: neutral calcium driers perform better than over-based calcium driers if the paint is applied under adverse conditions! A further improvement can be made with organically modified precomplexed drier combinations. Some examples of recommended driers based on lead-free precomplexed driers are mentioned in Table 7.1-4.

**Table 7.1-4.** Lead-free combination driers – recommendations

Drier composition	Metal content %	Dosage <sup>a)</sup>	Exterior varnish	Interior varnish	Remarks
Co–Zr–Ca, basic	10.2	3–7	Limited Suitability	Suitable	Universal drier, lead- and barium- free
Co–Zr–Ca,	8.8	6–9	Suitable	Suitable	Optimal low temperature drying; also for high- solids
Co–Zr	15	0.8–1.2	Unsuitable	Suitable	economical price
Co–Ba–Zn	11.6	3–6	Suitable	Suitable	Barium- containing, toxic
Co–Li	3.0	3–5	Suitable	Suitable	For high- solids, not for white coatings

<sup>a)</sup> Weight proportion of combination drier, based on resin solids

### 7.1.10 Waterborne Coatings

Waterborne, oxidatively drying coatings like waterborne alkyd paints, meet the requirements for environmentally friendlier paints, with lower solvent emissions and as alternatives for solventborne alkyd paints. The binder in waterborne, oxidatively

drying alkyd paints is in most cases an alkyd emulsion or a colloiddally dispersed alkyd resin. Drying takes place physically by evaporation of the water, solvents, and neutralizing agents, followed by oxidative polymerization of the resin.

Waterborne and solventborne alkyd paints have essentially the same drying mechanism. However, waterborne paints have considerable disadvantages such as initial drying speed, drier incompatibility, surface defects, poor hardness and through-drying, and poor drying stability during storage. These differences are related to the different properties of the resins as well as the solvents used.

Water is a strong ligand for metal ions such as cobalt. The oxidation potential of the complex that forms,  $[\text{Co}(\text{OH}_2)_6]^{2+}$ , is lower than that of the free cobalt ion. This makes cobalt less effective as a redox catalyst. Moreover, the complex is quite unstable and tends to hydrolyse, resulting in the precipitation of the cobalt hydroxide.

A practical solution, to compensate for the loss of drier through these reactions, is to use higher concentrations of the primary driers cobalt and manganese in waterborne, as opposed to solventborne, coatings.

### 7.1.10.1 Characteristic Drying Phenomena of Air-Drying Waterborne Coatings

Since the very first attempts to prepare waterborne alkyd paints, it was known that the addition of driers can lead to problems, such as those listed in Table 7.1-5.

**Table 7.1-5.** Typical problems with air-drying of waterborne coatings

---

Poor initial drying
Drying inhibition on storage
Incompatibility between drier and resin
Surface defects
Loss of stability of the colloidal system
Loss of gloss

---

Not all drying shortcomings of waterborne air-drying coatings are directly related to a failure of the drier. A good example of this is the influence of air humidity. The speed of evaporation of the water and co-solvent is naturally largely dependent on the relative air humidity. Experimentally, it could be shown that for optimal application and drying, a relative humidity of between 50 to 80% is necessary.<sup>[7-11]</sup>

During drying of waterborne coatings, a transition from the aqueous to the organic continuous phase takes place. This greatly affects the mobility and the performance of the drier.<sup>[7-12]</sup> Water can slow down the oxygen uptake of the binder, thereby slowing down the autooxidation process.<sup>[7-13]</sup> This is due to the low solubility of oxygen in water.

Apart from the solvent composition, the vehicle system is also responsible for various drying deficiencies in waterborne coatings, such as long total drying time, loss

of drying ability, poor through-drying, and poor hardness. Hydrolysis of the binder – due to the high polarity and alkalinity of the aqueous system – results in the formation of acids and salts the drier metal ion. Precipitation of this salt results in a lower effective drier concentration. The neutralizing agent and pigments may also interact with the other components and driers in waterborne coatings. Nitrogenous neutralizing agents, such as ammonia and amine, form complex metal ions with cobalt or manganese, which have a lower catalytic action.

To optimize the drying process, it is extremely important to adjust the pH to a slightly alkaline range and to ensure that the pH is stabilized during paint storage.

The drying time of paints made with acidic alkyd emulsions can be reduced by mixing the alkyd emulsion first with an appropriate amount of overbased calcium drier. In this case a certain amount of neutralization takes place with the overbased calcium drier.

The different compositions of water-soluble and solvent-soluble oxidatively drying coating materials make accurate adjustments to the drier system essential. The traditional driers, used in solventborne paints, are dissolved in mineral spirits or xylene and are not easily dissolved or emulsified in water. These classical driers can be used in waterborne systems by mixing the drier with the binder system, prior to the neutralization stage of the resin. However, the drier may destabilize the emulsion of the binder, leading to a change in viscosity and stability of the paint. One can improve the compatibility of the driers with such binders by adding suitable surfactants and polar solvents to the drier.

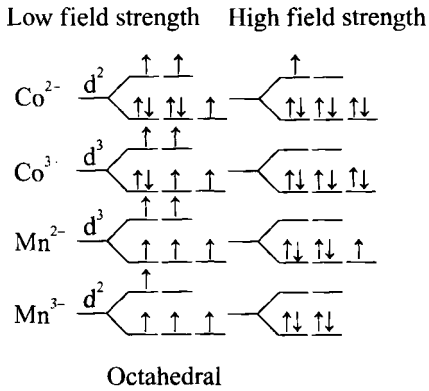
Furthermore, the effectiveness of the drier depends on the stage at which it is added during the manufacturing of the coating material. Best results are normally obtained when the drier is added during the let-down stage of the coating manufacturing process. In this case, only water-emulsifiable driers can be used.

The metals cobalt, manganese, zirconium, calcium, zinc, lithium, and potassium are the ones preferred for use as driers in waterborne coatings. The best drying properties are obtained when metal complexes in which cobalt is the primary drier are used.

#### **7.1.10.2 Coordination Effect on Driers**

In waterborne coatings, ligands are successfully used in conjunction with metal driers to optimize drying properties. Ligands such as *o*-phenanthroline or 2,2-bipyridyl have been known for a long time as drier activators and are used in traditional solvent-based coatings. However, the high costs and specific application fields have limited their use in solventborne coatings. Organic ligands have a strong effect on the performance of primary driers in waterborne coatings. Ligands affect the spin multiplicity of electron distribution in the metal atom. Both stability (thermodynamic) and rate (kinetic) factors are influenced by the ligand. Ligands with low field strengths, such as water, for example, lead to high-electron-spin configurations (Fig. 7.1-5).

The ligand structure can have a great influence on the rate of electron transfer. The relatively low-energy vacant anti-bonding orbitals found in the conjugated phenan-



**Figure 7.1-5.** Electron distribution. For example, the reduction of  $[\text{Co}^{\text{III}}(\text{phen})_3]^{3+}$  takes place more rapidly than that of  $[\text{Co}^{\text{III}}(\text{NH}_3)_6]^{3+}$  or  $[\text{Co}^{\text{III}}(\text{ethylenamine})_3]^{3+}$ .

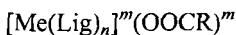
throline facilitate electron transfer. Thus the effectiveness of the drier can be increased by selecting the best ligand for the drier-metal ion. Because both oxidation states of the primary driers cobalt and manganese must be present for them to function effectively, it is complicated to determine which ligand should be chosen for optimal drier properties. When solubility constraints are added to this, the issue becomes even more complicated. The role played by the ligands is mainly that of keeping the active drier in its more active valence state, although its influence on kinetic factors is not fully understood.

Auxiliary driers offer a second metal capable of maintaining multiple oxidation states and can donate ligands to the primary drier metal and keep this in its more active valence, thus increasing the activity of the primary drier.

### 7.1.10.3 Precomplexed Driers

It was already explained that when conventional driers are used in waterborne coatings, poor performance results. Precomplexation of the primary driers with ligands optimize their performance. When ligands that can result in the emulsification of the primary drier in water are used, a second advantage appears: not only is the catalytic effectiveness improved, the compatibility of the drier with the waterborne coating material is also markedly improved. The general structure of this new class of driers is shown in Fig. 7.1-6.

Complexation increases the catalytic effectiveness; furthermore, the ligand prevents or delays the drier metal ion from being complexed with water. As explained



Me = metal

Lig = ligand

$n$  = number of ligands

$m$  = valence of metal ion

**Figure 7.1-6.** Precomplexed driers

before, uncomplexed primary driers are easily hydrated in water, a main cause of the loss of drying ability upon storage of waterborne alkyd paints.

The improved compatibility, derived from the use of ligands that can aid emulsification of the drier in water, leads to the improved storage stability of the liquid coating material and also improved optical film properties.<sup>[7-14]</sup> Table 7.1.6 shows an example of the composition of a typical waterborne air-drying coating.

**Table 7.1.6.** Formulation of a waterborne alkyd gloss paint

– Water	16% (weight)	Disperse in a pearl mill and add:	
– PU thickener	0.6%	– Alkyd resin emulsion (50% in water)	50%
– Dispersing agent	0.2%	– WEB-Co-8 drier	0.3%
– Wetting agent	0.5%	– PU thickener (5% in water)	7%
– Defoaming agent	0.2%	– Water	5.2%
– Titanium dioxide	20%		

Because of precomplexation, the effect of the redox activity of the primary drier can also be halted, and with it the effect that the catalyst has on the decomposition of peroxides, without affecting the catalytic activity regarding the absorption of oxygen; this is very useful in driers formulated in solid-containing coatings.

### 7.1.11 High-Solids Coatings

High-solids coatings meet the requirements for environmentally friendlier coatings, with lower emissions of organic solvents compared to the conventional alkyd varnishes.

The composition of the binder in oxidatively drying high-solids alkyd coating systems is partially similar to that of the binders used in conventional alkyd paints with low solids; the polymerization process is accelerated by driers.<sup>[7-14]</sup> There are, however, a few characteristic differences that are important for the drying performance. Apart from the higher solids content, the molecular mass of the binder is also lower and the reactivity for autooxidation polymerization is much higher.

Therefore, to formulate paints with high-solids contents, low viscosity and acceptable application properties are required. The high solids content result in thicker applied films, making the through-drying properties more critical than in low-solids systems.

#### Drying Characteristics of High-Solids Coatings

A typical composition of a high-solids alkyd paint formulation is presented in Table 7.1-7. According to its definition, high-solids alkyd coatings contain less organic solids than the traditional low-solids alkyd paints do. This explains a shorter flash-off time after paint application (Table 7.1-8). The open-time is nevertheless

much longer, which is explained by the low molecular mass of the high-solids resin with its resulting lower viscosity.

**Table 7.1-7.** High-solids alkyd paint, 88% solids, based on a long-oil alkyd resin

Titanium dioxide	39 (weight-%)
High-solids resin (100% solids)	48
Dispersing agent	0.4
Drier	3.2
Aliphatic mineral solvent	8.8
Odourless anti-skinning agent	0.6
	100

**Table 7.1-8.** Typical drying properties of a high-solids paint compared to that of a traditional alkyd paint (\* BK drying recorder ratings)

	“High-solids” alkyd	Traditional alkyd paint
Flash-off time	0.75 h	1 h
Open time*	2.5 h	1 h
Dust-dry time*	3 h	2.5 h
Tack-free time*	5.5 h	4 h
Dry-through time*	7 h	6 h
Koenig hardness, 100 $\mu$ m layer, wet	22 s	50 s

Both the thicker applied layer, due to the higher solids contents at a comparable application rheology, as well as the higher reactivity of the resin, result in poorer through-drying. As the surface layer is polymerized, the penetration of oxygen to the lower layers is delayed considerably, as is the through-drying. Poor through-drying and hardness are indeed the main shortcomings of high-solids alkyd systems (Table 7.1-9). Both properties are influenced significantly by the selection of the drier.

**Table 7.1-9.** Drying-associated problems in high-solids coatings

Poor initial drying
Poor through-drying
Soft coatings
Wrinkling
Poor appearance
Dark yellowing

The effect of the catalytic properties of the driers are essentially the same for high-solids- as for traditional alkyd coatings. A critical item turns out to be the solubility of the drier in the liquid – nonpolar – coating formulation.

Wrinkling is a typical problem associated with driers. Too high a concentration of a strong primary drier will result in rapid surface drying of the applied film and poor through-drying. Because of the higher polymerization reactivity of the binder, high-solids coatings are more sensitive to this phenomenon than low-solids alkyds are. The right balance needs to be found between the drier effectiveness regarding through-drying and surface drying.

Because cobalt not only catalyses the decomposition of the peroxides into free radicals (fast process), but also catalyses the formation of the peroxides (slow process), it becomes more complicated to adjust the cobalt drier level. When the primary drier cobalt is reduced too much, peroxides are formed slowly, the consequence being a low supply of radicals, leading to slow polymerization, resulting in soft film, and a slow total drying performance.

The surface-drying properties of primary driers, notably cobalt, can be influenced by complexation (Section 7.1.10.2). This retards the surface-drying properties, avoids wrinkling, and enables the formulator to increase the concentration of the primary drier. As properties such as through-drying and hardness are positively influenced, it is assumed that complexation does not greatly influence the catalytic effect of the drier on peroxide formation.

Precomplexed driers of cobalt and alkali metals, as well as cobalt/zirconium/calcium combination driers or cobalt/strontium/calcium drier combinations, are typically used in high-solids coatings.<sup>[7-14]</sup>

### **7.1.12 Analysis Procedures**

As the metal is the active ingredient of the drier, it is mainly the metal concentration that needs to be determined for quality control. The two most common analytical procedures for the determination of the metal concentration of driers are the complexometric method and atomic absorption spectroscopy.<sup>[7-15]</sup>

Other methods used for the determination of the physical characteristics of driers are: specific gravity determination, the colour, the viscosity, and the percentage of non-volatiles.

### **7.1.13 Biological and Toxicological Properties**

Driers for solventborne coatings contain mineral solvents. For ecological reasons, most drier manufacturers have voluntarily adapted the drier compositions, and replaced the traditionally used aromatic mineral solvents with aliphatic solvents.

Table 7.1-10 lists the risk- and safety classifications of different driers, as is valid within the European Union.

Obviously, most of the driers, on the basis of OECD irritant test results, are considered as skin-irritating and/or eye-irritating.

**Table 7.1-10.** Risk- and safety classifications of synthetic driers

Product name	Label	CAS number
Barium 12,5	Xn; R 20/22, 36/38 S 28, 36/37	68876-86-8
Calcium 10	Xi; R 38 S 37	68551-41-7 (basic) 68409-80-3
Cerium 10	Xi; R 38 S 37	24593-34-8
Cobalt 10	Xi; R 43, 38 S 24, 36/37	68409-81-4
Manganese 10	Xi; R 38 S 37	68551-42-8
Strontium 10	Xi; R 38 S 37	2457-02-5
Zinc 12	Xi; R 38 S 37	68551-44-0
Zirconium 6	Xn; R 38, 65 S 37, 62	22464-99-9
Zirconium 12	Xn; R 38, 65 S 37, 62	22464-99-9
Zirconium 18	Xi; R 38 S 37	22464-99-9
Lead 36	T; R 61, 62, 20/22, 33 S 36/37/39, 45, 53	15696-43-2 (neutral) 68603-83-8 (basic)
Lithium 2	Xi; R 38 S 37	27253-30-1
Potassium 10	Xi; R 38 S 37	68604-78-4
Iron 6	Xi; R 38 S 37	68308-20-3
Chromium octanoate	Xn; R 22, 43 S 24, 28, 36/37	20195-23-7
Copper	Xn; R 22 (R 10) S 24/25, 36/37, 46	68308-19-0 or 1338-02-9
Vanadium	Xi; R 38 S 37	68815-09-5
Bismuth octanoate	Xi; R 38 S 37	67874-71-9
Tin octanoate	Xi + N R 36/38, 52/53 S 26/28	301-10-0
Nickel 2-ethylhexanoate	Xi; R 38, 43 S 24, 28, 36/37	7580-31-6

Cobalt driers are potential skin sensitizers (R-classification 43), according to the Kligman–Magnusson (sensitization) test and are correspondingly labelled (see Section 9.4).

Lead-based driers are classified as toxic, according to the 21st modification of the EU guideline 67/548, and are labelled as R-61 and with the skull-and-crossbones symbol; this applies to all preparations containing 0.5% or more lead compounds.

Apart from the 21st and 22nd modifications of the EU guideline 67/548, new regulations on aliphatic and aromatic solvents have been defined (Xn; R-38, 65 and S-37, 62). There is scant information on the biological decomposition of metal driers. As the metal components are not biodegradable, especially in the case of heavy metals, driers should not reach public waters. The synthetic acid part of metal driers is usually easily biologically degradable.

#### **7.1.14 Trade Names**

Nuodex	(CONDEA-Servo)
Octa-Soligen	(Borchers)
Valirex	(van Loocke)
Manosec	(Rhone Poulenc)
Cuprisec	(Durham)

## 7.2 Catalysts

*Rainer Lomölder*

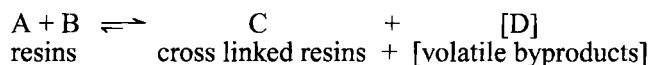
### 7.2.1 Introduction

High-performance coatings are characterized, for example, by excellent chemical resistance, weathering durability and low VOC. To achieve this property profile, low- or medium molecular weight resins are cross linked after application. The performance of such resins are generally better than that of resins that dry only physically. Therefore, a coating formulation for high-performance applications consists of a cross linkable binder resin and a cross linker, all of low or medium molecular weight. The chemical reaction between resin and cross linker leads to the high-level property profile.

Similar to other organic chemistry reactions, cross linking reactions normally proceed rather slowly. The curing speed of a paint may be accelerated significantly by higher temperatures or by the use of a catalyst. The proper choice of the type and the amount of catalyst is one of the most important tools at a formulator's disposal for matching the customer's requirements on the reactivity of a paint.

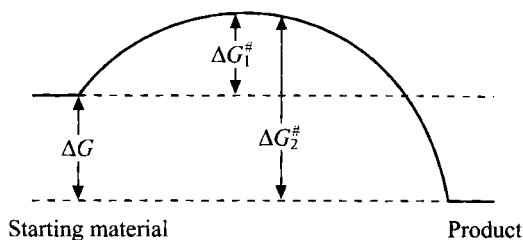
Before the use of catalysts in paints is dealt with in greater detail, some fundamental concepts regarding the kinetics of chemical reactions and the influence of catalysts will be explained.

As with any other chemical reaction, a cross linking reaction proceeds to an equilibrium. For coatings, this equilibrium must lie far on the side of the products, otherwise a highly cross linked coating will not result.



In coating technology, the shift of the reaction equilibrium to products C + D can be achieved in two different ways: Either by the use of components which lead to a high free Gibbs enthalpy ( $\Delta G$ ) of the system, as found in two-component systems, or by the removal of one of the reaction products, such as alcohols in melamine cross linked systems, or the blocking agents of blocked polyisocyanates; both these cross linkers are used in storing paints.

How *fast* an equilibrium is obtained is not only dependent on the free Gibbs enthalpies of the starting materials and the products, but depends basically on the enthalpy of activation ( $\Delta G^\ddagger$ ). This is the enthalpy required to reach the so-called "activated state" of a reaction.  $\Delta G$  is the difference between the free Gibbs enthalpy of the starting materials and that of the products (Fig. 7.2-1), and it determines the direction in which a reaction proceeds. Whether a reaction is favourable or not is de-



**Figure 7.2-1.** Schematic representation of reaction enthalpy ( $\Delta G$ ) and activation enthalpy ( $\Delta G^\ddagger$ )

terminated by the enthalpy of activation ( $\Delta G^\ddagger$ ). It is, for example, possible in organic chemistry that a reaction does not occur, despite a favourable  $\Delta G$ , because the  $\Delta G^\ddagger$  is too high.

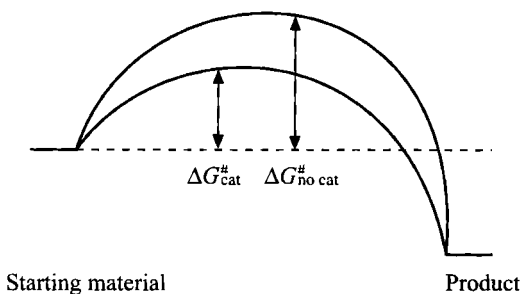
The connection between the enthalpy of activation and the reaction rate constants was developed in the 19th century by Arrhenius and Van't Hoff (Fig. 7.2-2). This equation is also the physico-chemical reason for the well-known phenomenon that reaction times can be reduced significantly by increased temperatures.

$$K = c \cdot e^{-\frac{\Delta G^\ddagger}{RT}}$$

**Figure 7.2-2.** Arrhenius equation

Generally, the accelerating effect of catalysts can be explained by a lowering of the  $\Delta G^\ddagger$  value. This means that at a certain temperature there is a higher probability for unreacted molecules to pass the activated state towards the products, which, for coatings, means the cross linked coating. Of course, similar considerations are valid for the reacted specimens. Reverse reactions in coating technology are usually not very likely, because the reaction partners are no longer present in the coating after cross linking (Fig. 7.2-3).

For the formulation of a coating, this relationship between catalysis and reactivity has another severe consequence: in the case of, for example, 1 component (1K) heat-curing coating systems, the use of a catalyst does not only lead to a lower minimum curing temperature, but may also influence the storage stability of the paint at ambient temperature negatively. Because each type of cross linker needs to be catalysed by a specific type of catalyst, this chapter is not divided accord-



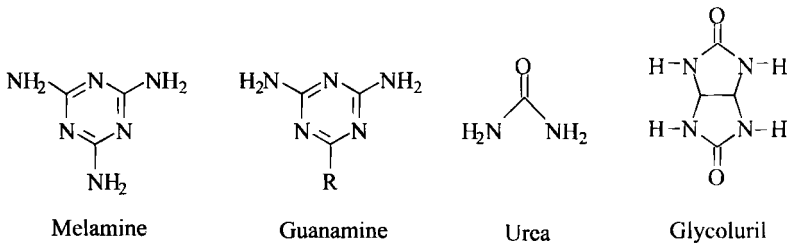
**Figure 7.2-3.** Schematic representation of the enthalpy of activation for a catalysed and an uncatalysed reaction

ing to the different groups of catalysts, but is divided according to the different types of cross linkers or cross linking mechanisms and the specific catalysts used in these technologies.

## 7.2.2 Melamine Cross-Linking Systems

### 7.2.2.1 Introduction

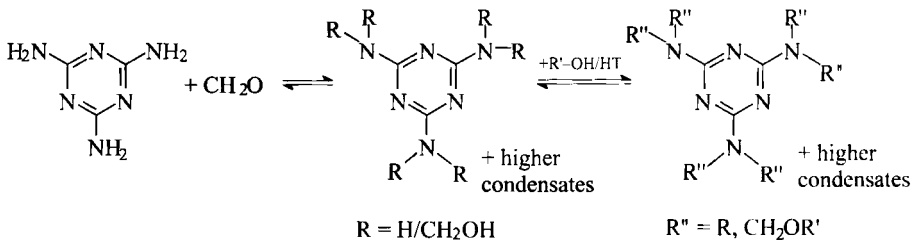
Amino-resin cross linkers are obtained from the raw materials shown in Fig. 7.2-4 by reaction with formaldehyde and subsequent acetalization with alcohols.<sup>[7-17]</sup>



**Figure 7.2-4.** Raw materials for amino resins

Because all members of this group react by the same cross linking mechanism, the most important representative, the subgroup of melamine resins, is employed in this chapter to discuss special aspects with regard to reaction mechanisms and catalysis.

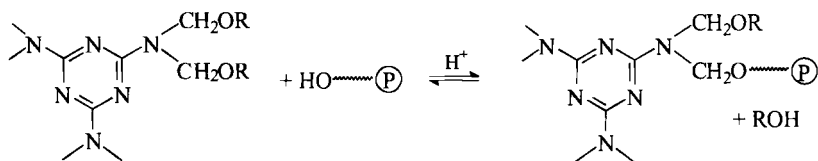
There is a tremendous variety of different melamine resins used in coatings. The starting monomer, melamine, is reacted with formaldehyde to form *N*-methylol-melamine, which is finally converted with alcohols such as butanol, isobutanol, or methanol, in the presence of acid catalysts; the products formed are acetals (ethers) (Fig. 7.2-5).



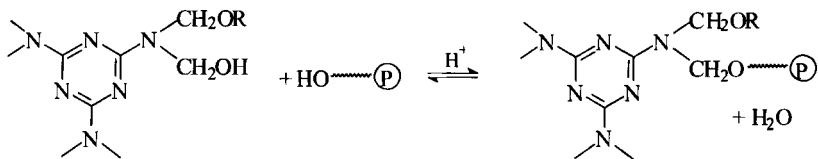
**Figure 7.2-5.** Melamine resin synthesis

In this reaction, the ratio of melamine, formaldehyde, and alcohol determines the amount of unreacted NH- and CH<sub>2</sub>OH- groups. The way in which this species is processed further, i.e., partial self-condensation of these unreacted groups, influences the molecular weight of the final resin.<sup>[7-18]</sup>

Melamine resins are typically used for the cross linking of hydroxy-functionalized resins, and also for carboxyl-group-bearing resins. Due to the different functionalities, the curing reaction between melamine and binder is complex and not completely understood. In principle, the reaction is acid-catalysed, the same catalyst-type used for the synthesis of the melamine resins. This is because the mechanism for resin synthesis and cross linking is the same, i.e., the product is an acetal, obtained either by acetalization or transacetalization (Fig. 7.2-6).



(1) Transacetalation



(2) Acetalation

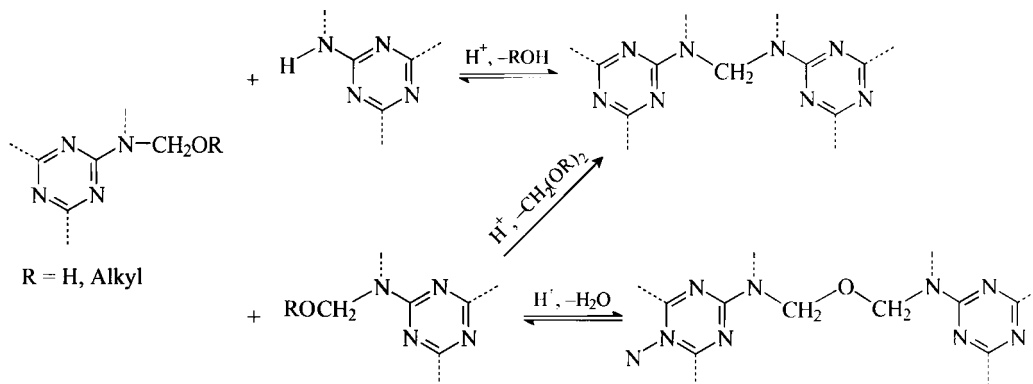
**Figure 7.2-6.** Cross-linking reactions with polyols

The carboxyl groups of the polyol can also act as a nucleophile towards the melamine resins, although this reaction is considerably slower.<sup>[7-19]</sup>

Whether the reaction of carboxylic or hydroxyl groups with melamine resins occurs by an S<sub>N</sub>1 or S<sub>N</sub>2 mechanism is not yet clarified. Different reaction rates were found for primary and secondary hydroxyls, carboxylic acids, and mercaptans; this indicates an S<sub>N</sub>2 mechanism.<sup>[7-20, 7-21]</sup>

Not only the hydroxyl or carboxyl groups of the binder might act as a nucleophile, the H-active species of the melamine resin can also react. Therefore, typically, self-condensation of the melamine resin occurs alongside the cross linking reaction. The extent of this competing reaction depends on the type of melamine resin. Whereas self-condensation only occurs to a small extent in fully methylated melamine resins (HMM: hexamethoxy melamine), this reaction plays a significant role in partially alkylated resins.<sup>[7-18, 7-19, 7-21, 7-22]</sup> (Fig. 7.2-7).

This reaction is also catalysed by acids, for reactive melamine resins only weak acids are required. This is in principle the same reaction that is employed to increase the molecular weight of melamine resins during resin synthesis.



**Figure 7.2-7.** Self-condensation of melamine resins

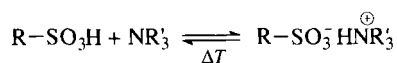
Because of its complexity, and disregarding the huge overlapping area between cross linking of polyols and self-condensation of melamine resins, the cross linking reaction will be discussed in the following chapter on HMM resins, and the self-condensation reaction will be dealt with in the chapter on the more reactive partially alkylated melamine resins.

### 7.2.2.2 Catalysis of HMM-Based Systems – Cross Linking

As mentioned above, cross linking by transacetalization (1) is catalysed by acids. As sources for  $\text{H}^+$  ions, either inorganic acids such as HCl, phosphoric acid, or organic carboxylic acids or sulfonic acids can be chosen. The enthalpy of activation has been reported to be  $12.5 \text{ kcal mol}^{-1}$ , irrespective of the type of acid used.<sup>[7-23]</sup> The relative efficiency of the different catalysts is proportional to the square root of the ratio of the dissociation constants,<sup>[7-21]</sup> i.e., it depends on the strength of the acid. Acceptable curing conditions for HMM resins are usually achieved when strong acids, such as *p*-toluenesulfonic acid (*p*-TSA), dodecylbenzene sulfonic acid (DDBSA), dinonylnaphthalene sulfonic acid (DNNSA), or dinonylnaphthalene disulfonic acid (DNNSA), are used as catalysts, rather than weak carboxylic acids.

Another tool for adjusting the reactivity of an HMM-based paint is to vary the catalyst concentration, because the reaction rate is directly proportional to it.<sup>[7-21]</sup> Typical concentrations for stove systems are approximately 0.5% of the resin solids.

Storing paints based on (HMM) melamine resins, catalysed by free sulfonic acids, have a very limited storage stability. Even at slightly elevated temperatures, the viscosity of such formulations increase significantly, and there is sometimes a strong tendency for craters or hazing to occur. One way of solving this problem of poor balance between high reactivity and limited storage stability, is to use blocked sulfonic acid catalysts. Then a second equilibrium, between the blocked and the unblocked form of the catalyst, which is also influenced by temperature, increases the storage stability of the corresponding paints, because at ambient or slightly elevated



**Figure 7.2-8.** Ionic blocking of sulfonic acids

temperatures the catalyst remains in the blocked form. Increased temperatures liberate more free catalyst, to increase the reaction rate for the cross linking reaction. Two different methods have become established: the neutralization of the sulfonic acids by addition of tertiary amines of the morpholino-, pyridine-, or *tert*-alkylamine types (Fig. 7.2-8), or the use of non-ionic adducts of *p*-TSA (Fig. 7.2-9). In the case of ionically blocked systems, the activation enthalpy is reportedly increased from 12.5 to 21 kcal mol<sup>-1</sup>.<sup>[7-21]</sup>



**Figure 7.2-9.** Non-ionic blocking of sulfonic acids

Again, the concentration of blocked catalyst depends on the reactivity required for the storing paint; the resin typically contains approximately 0.5–1% active sulfonic acid, which means, depending on the molecular weight of the blocking agent, 1–5% of blocked catalyst.

The difference between ionic- and non-ionic blocking is the significantly lower conductivity values of paints using the covalently blocked catalyst, which is advantageous in electrostatic spray applications. With regard to yellowing upon baking, the use of non-ionically blocked catalysts is also often better.

Normally, ionically blocked catalysts are more catalytically active in the lower baking temperature ranges, than the non-ionic types are. However, this higher reactivity is accompanied by lower storage stability. This is in principle because covalent bonding results in much more stable blocking. The difference between the two types is not very significant at temperatures >180 °C, although ionic blocking may be advantageous in borderline conditions. In Figs. 7.2-10 and 7.2-11 the reactivity of an HMM system, expressed as the development of the König hardness after 20-min curing at different temperatures, and the corresponding storage stability at 60 °C, is given. The HMM resin was combined with a branched medium molecular weight saturated polyester polyol (DYNAPOL H 905, acid value approximately 5 mg KOH/g), in a ratio of 80:20, and the white-pigmented system was catalysed with different types of sulfonic acid catalysts, all adjusted to a level of 0.5% *p*-TSA based on the solid resins.

There is a very clear reactivity difference between the *p*-TSA catalysed system and the practically ineffective catalysis by the carboxyl groups of the polyester resin, i. e., the uncatalysed case. Similar activity is seen when the morpholino salt of *p*-TSA is used. The more stable covalent blocking results in significant catalytic activity at temperatures of 140 °C and above. At 160 °C there is no significant difference between the catalysed variants. As expected, the blocked catalysts improve the storage stability significantly (Fig. 7.2-11).

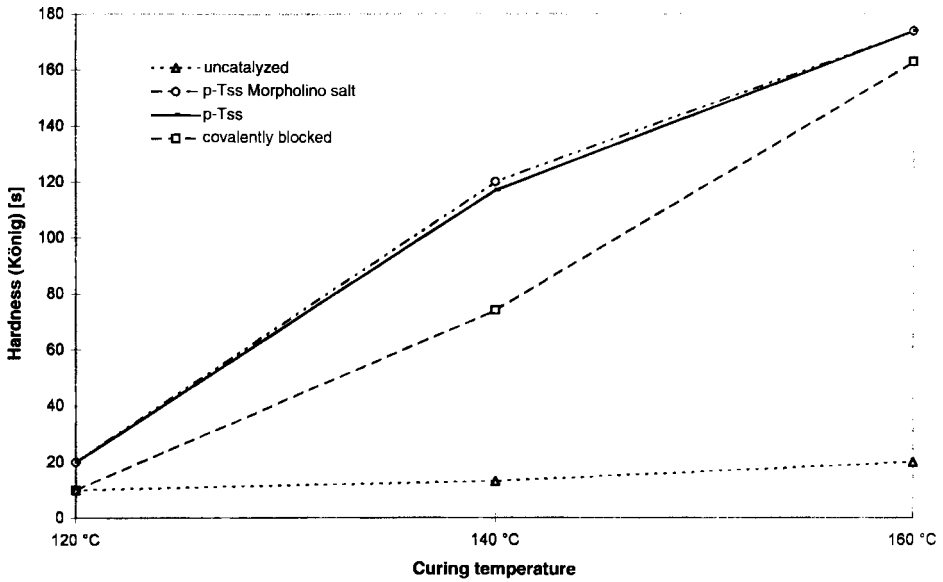


Figure 7.2-10. Influence of catalyst type on hardness (König) of a white-pigmented stove-paint based on DYNAPOL H 905/HMM (80/20). Curing time: 20 min

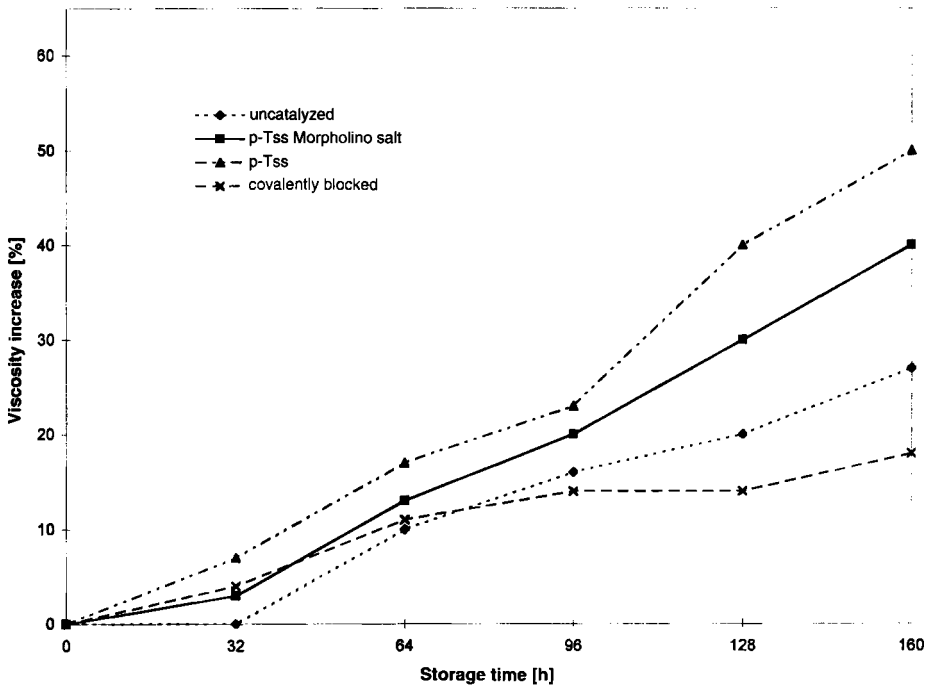


Figure 7.2-11. Viscosity increase of a DYNAPOL H 905/HMM formulation at 60 °C

Please note that the study presented here is only for the purpose of demonstration. Many parameters affecting the reactivity of an HMM-based storing paint, such as molecular weight, acid value, branching, glass-transition temperature, and type of the reactive groups, i. e., monomer composition of the polyester resin, as well as the type of polyol (acrylic, alkyd, epoxy, etc.) were not taken into consideration.

### 7.2.2.3 Catalysis of Reactive Melamine Systems – Self-Condensation

The self-condensation of, e. g., imino-group-containing melamine resins is much faster than the cross linking reaction between acetalized methylol groups and the hydroxy functions of the binder resin. The cured coating therefore consists of a network of cross linked polyols as well as hard segment areas of melamine self-condensation products. Because there is a higher concentration of hard segments in melamine homocondensates than in cross linked HMM, there is often a poor balance between hardness and elasticity. Another problem is that when the melamine and polyol content in the formulation are comparable, the chemical resistance is affected negatively. Formulations based on reactive melamine resins therefore contain a higher amount of melamine.<sup>[7-18, 7-21]</sup>

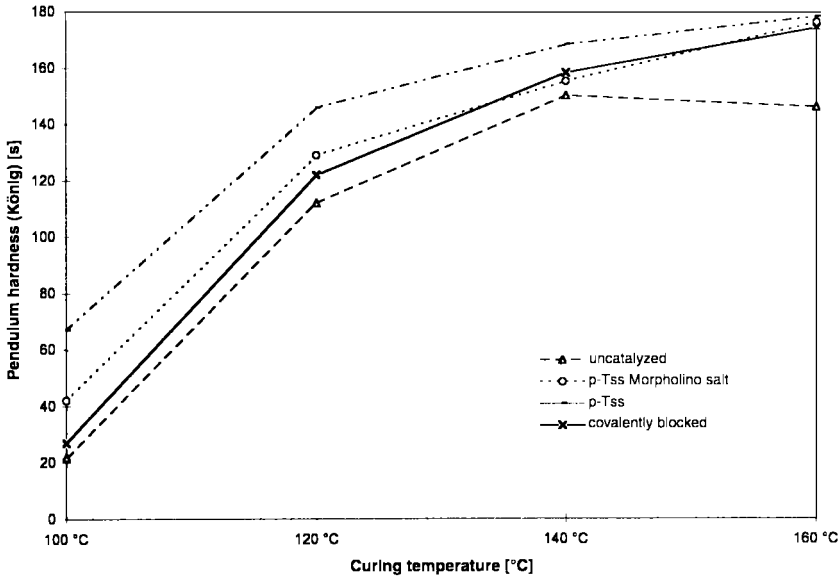
In one-component storing paints based on reactive melamine resins, a level of 10–25 mg KOH/g is sufficient for the catalysis of self-cross linking and partial cross linking of the polyol with the carboxylic groups of the binder.

Higher reactivity can be adjusted by the use of the above-mentioned sulfonic acid catalysts or the corresponding blocked adducts. In the case of free sulfonic acids, special care has to be taken to ensure the storage stability of the formulated paints. An extreme case of such a system is a very highly reactive acid-cured system, e. g., in the field of wood coatings. Such formulations contain up to 5% free sulfonic acids. Due to the high catalyst concentration, curing occurs at ambient or elevated temperature (<100 °C).<sup>[7-24, 7-25]</sup>

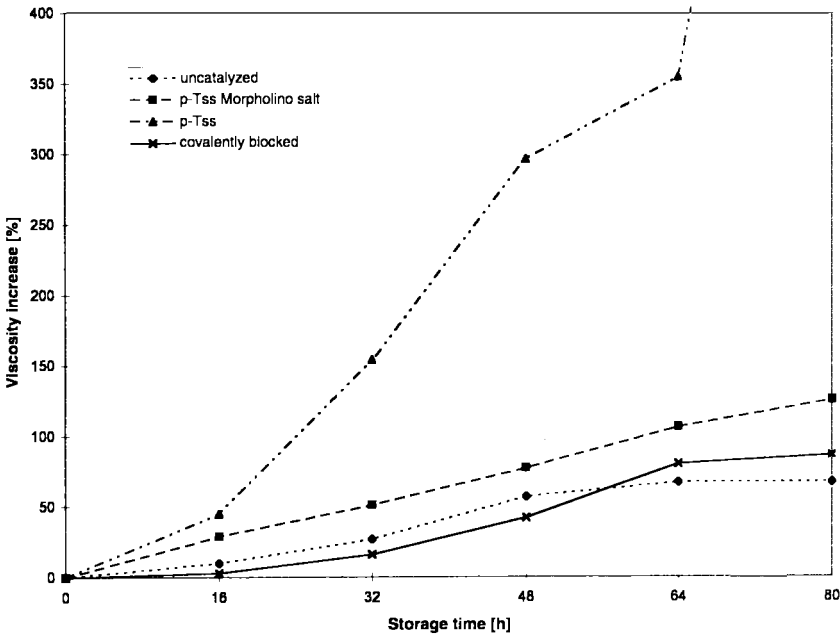
Fig. 7.2-12 demonstrates the effect of various catalysts based on the above-mentioned polyester (DYNAPOL H 905, acid value 5 mg KOH/g) and CYMEL 325, as reactive melamine resin (imino-group-containing). Although the binder has a considerably low acid content, the curing reaction is shown to proceed catalytically – in contrast to the HMM-based system shown in Fig. 7.2-10. The addition of only 0.5% sulfonic acid (PTSA), or corresponding concentrations of blocked catalysts, results in formulations with very high reactivity. But, as a consequence, with the exception of non-ionically blocked catalysts, the storage stability of the paint is poorer (Fig. 7.2-13). Only, in this case, the viscosity plot vs. time is identical to that of the uncatalysed formulation.

### 7.2.2.4 Formulation Advice

With the exception of the non-ionically blocked catalyst, the use of catalysts leads, even at slightly elevated temperatures, to a viscosity increase due to partial reaction of the melamine resin with itself or with the polyol. As mentioned before, this reac-



**Figure 7.2-12.** Influence of catalyst variation on the reactivity of a white-pigmented storing paint based on a polyester resin (DYNAPOL H 905) in combination with a reactive melamine resin (CYMEL 325, 70/30) (0.5% active catalyst per solid resin, curing time: 20 min)



**Figure 7.2-13.** Storage stability (DIN cup 4) at 60 °C of a polyester-based storing paint (see also Fig. 7.2-12)

tion is equilibrium-controlled. The cross linking of the formulated paint may therefore be suppressed by the use of hydroxyl-containing solvents. Primary alcohols are typically preferred.

When formulating the paint, care should be taken that the catalyst and other acid-sensitive materials do not come into contact in a concentrated form. Typical acid-sensitive materials are alkaline wetting agents, epoxy resins, corrosion inhibitors, UV-stabilizers, etc. These materials should be added separately from the catalysts after complete dilution. In the case of pigmented paints, the catalysts should be added after the grinding of the pigments, to avoid poorer wetting of the pigments, adsorption of the catalyst to the pigment, or partial cross linking of the paint because of the higher temperatures during grinding. Non-ionically blocked sulfonic acid catalysts sometimes act like wetting agents, therefore it might be useful to add them before grinding.

Some pigments and extenders, as well as alkaline-modified amorphous silica or pigments such as  $\text{Al}_2\text{O}_3/\text{ZnO}$ -treated titanium dioxide have alkaline properties. They may therefore deactivate the acid catalysts, and should not be used in highly reactive stove-paints.

One would expect acid catalysts to cause poorer corrosion resistance. This negative effect is usually more than compensated for by the higher degree of cross linking in the paint. Differences between different types of catalysts might be related to different wetting of the pigment and the surface. The use of phosphoric-acid-based catalysts can be recommended in the case of aluminium- and magnesium-based substrates because they often improve adhesion significantly.

In waterborne stoving systems, free acid catalysts should be avoided because a shift in pH value is often observed, which affects the stability of the non-ionically stabilized resins negatively. Ionically blocked catalysts are normally used in these applications.

## 7.2.3 Polyurethane Systems

### 7.2.3.1 Introduction

Polyurethanes are one of the most important types of polymer groups in coatings technology due to their outstanding property profile. It is, in principle, much easier to subdivide polyurethanes into different groups, than it is to do for the chemistry of melamine resins. Due to the broad variety of different applications of polyurethanes, some will have to be ignored in this chapter. More detailed information can be obtained from PUR monographs.<sup>[7-27-7-29]</sup>

The way in which polyurethane chemistry can be subdivided with regard to its applications in coatings technology is shown in Fig. 7.2-14.

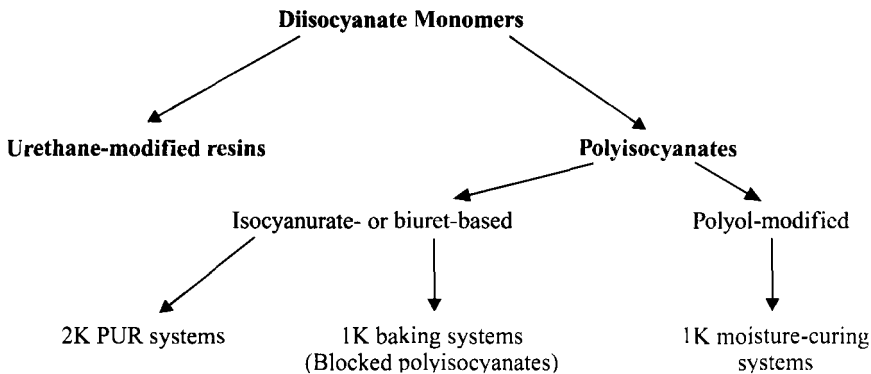
On the one hand, urethane-modified resins are employed to introduce the property profile of urethanes into the binder: typically a good balance of hardness and elasticity, chemical resistance, and good drying properties. Examples of this type of re-

sins are TPU (also solventborne types), urethane-modified alkyd resins, waterborne PUD, and radiation-curable urethane acrylates. *Diisocyanate monomers* are typically employed for this type of application.

The high reactivity of the isocyanate groups with alcohols, water, or amines is used, on the other hand, for cross linking reactions at ambient or even lower temperatures, to form urethane or urea structures. Thermally reversible blocking of the isocyanate moiety leads to storage-stable, heat-curing coating systems. *Polyisocyanates* are typically used for these applications.

These groups of PUR resins or technologies could be subdivided again according to whether they are based on aromatic or aliphatic isocyanates. Because these two groups differ significantly in weathering durability and yellowing resistance, and also in cost, the application of aliphatic diisocyanates (HDI, IPDI, H-MDI) and aromatic diisocyanates (TDI, MDI) are clearly delineated in practice.

In this chapter, the raw materials most relevant to the formulation of coatings, the *(cyclo)aliphatic polyisocyanates* are discussed (Fig. 7.2-14).

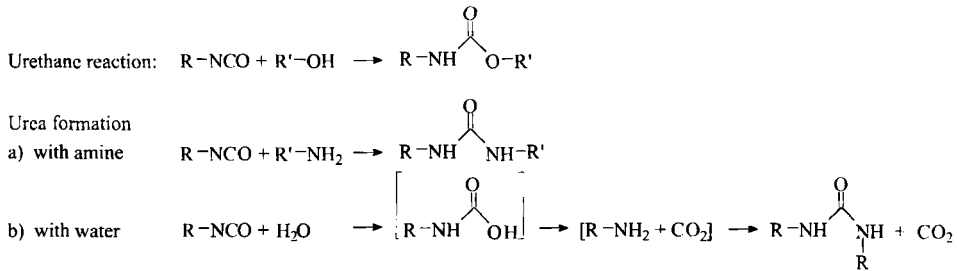


**Figure 7.2-14.** Subdivision of PUR resins

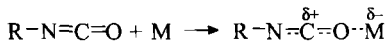
From a chemical point of view, the cross linking reactions in PUR technology can be divided into two basic groups (Fig. 7.2-15): the formation of urethanes by reaction of polyols and polyisocyanates, and the formation of urea structures through the reaction of isocyanates with water or amines.

The reaction between amines and isocyanates is normally so fast, that it is generally not used in coatings. It can be employed if one of the two components is modified or blocked to ensure delayed action.<sup>[7-30, 7-31]</sup> The other two reaction types of isocyanates – with alcohols or water – are commonly used. Because they are often not fast enough, additional catalysis is required. PUR systems are typically catalysed by Lewis-acidic metal catalysts or Lewis bases such as tertiary amines.

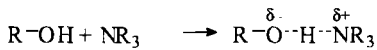
Lewis-acidic catalysts such as the typically used tin catalysts act by bonding to the carbonyl oxygen. Lewis-basic catalysts such as tertiary amines act by increasing the activity of the hydroxyl groups of the polyol (Fig. 7.2-16).<sup>[7-32–7-34]</sup>



**Figure 7.2-15.** Reaction of isocyanates with alcohols, amines, and water



Lewis-acid catalysis



*tert*-amine catalysis

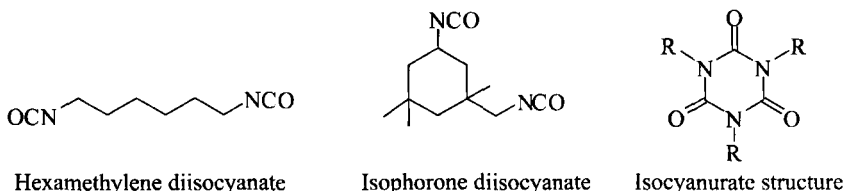
**Figure 7.2-16.** Mechanisms of PUR catalysts

### 7.2.3.2 2K-PUR Systems

2K-PUR systems based on aliphatic or cycloaliphatic polyisocyanates are well established in coatings technology and are well known for their superior quality. Besides the classical applications for 2K-PUR systems such as car refinishing, aircraft-, fleet-, and plastic coatings, they have also been used since 15 years ago for clear coats in automotive OEM<sup>[7-35]</sup> as well as general industrial- and wood coatings for high-performance end use. Aliphatic-2K-PUR technology is also relevant in solvent-free systems for elastomer applications, for bullet-proof windows,<sup>[7-36]</sup> for plastic windows,<sup>[7-37]</sup> in the field of window encapsulation, in interior automotive trim as vinyl substitute,<sup>[7-38]</sup> as well as in optical applications.<sup>[7-39]</sup>

Waterborne 2K-PUR systems have also in the meantime been developed, and used to a certain extent, in industrial applications to reduce VOC.<sup>[7-40]</sup>

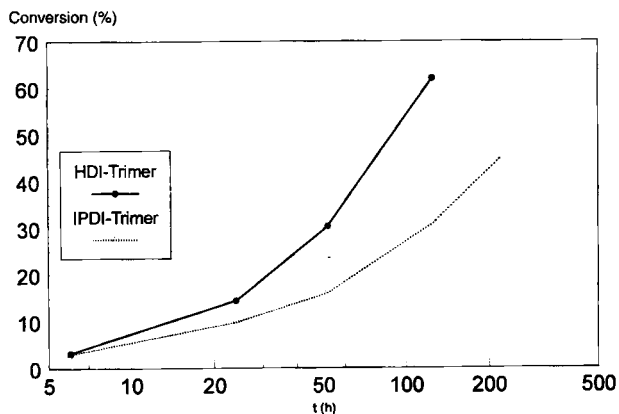
The field of polyisocyanates for light- and weather-stable PUR coatings is dominated by derivatives of two aliphatic isocyanates: the aliphatic HDI and the cycloaliphatic IPDI, both mostly as the isocyanurate derivative (Fig. 7.2-17).



**Figure 7.2-17.** Hexamethylene diisocyanate (HDI), Isophorone diisocyanate (IPDI), and isocyanurate

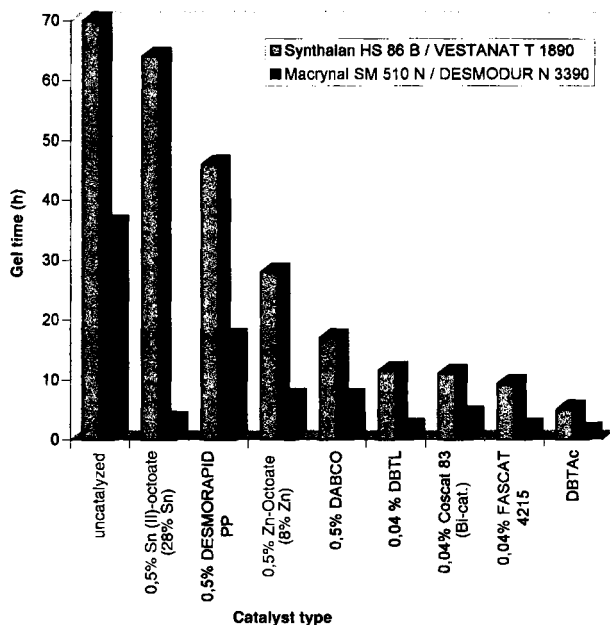
Due to its aliphatic structure, HDI-isocyanurate can be characterized as a soft resin, in contrast to the cycloaliphatic IPDI-isocyanurate, which can be classified as a resin imparting hard segments. The latter is typically used to improve the property profile of HDI-based 2K coatings, for example, to improve the resistance against environmental etch of DEM clear-coats<sup>[7-41, 7-42]</sup> or to improve the drying characteristics of car refinish paints.

Polyisocyanates based on HDI bear primary, nonsubstituted NCO groups; such groups are therefore more reactive towards nucleophilic agents or protic acidic materials such as polyols or water, than the IPDI trimer bearing a secondary, cycloaliphatic, and a sterically hindered NCO group is. In Fig. 7.2-18 the different reactivities in the urethane reaction of the two types of polyisocyanates is demonstrated. The experiment was an uncatalysed urethane reaction between polyisocyanates and 1-octanol at 20 °C. In principle, this difference in reactivity can also be seen in the reaction with water.



**Figure 7.2-18.** A comparison of the reactivities of HDI and IPDI polyisocyanates (urethane reaction with 1-octanol, uncatalysed, 20 °C)

This difference in reactivity has to be considered when formulating 2K-PUR paints with one of these two polyisocyanates. Whereas formulations based on derivatives of HDI can be accelerated even by the use of catalysts with low activity such as zinc octoates or tertiary amines, coatings based on IPDI trimer require more active catalysts such as DBTDL or bismuth salts. In Fig. 7.2-19, the gel times of 2K-PUR formulations based on either the HDI trimer (Desmodur N 3390, Bayer AG), with Macrynal SM 510n as HDI-compatible acrylic resin, or the IPDI trimer (VESTA-NAT T 1890L, Degussa-Hüls AG), with Synthalan HS 86 B (Synthopol Chemie) as a low-T<sub>g</sub> acrylic resin, suitable for combination with the more rigid IPDI derivative, are compared. Especially significant is the difference in gel time of the two systems, formulated with various catalysts, at the same catalyst concentrations. Less active catalysts like tertiary amines and tin compounds were used at a level of 0.5%, highly active ones at 0.04% (percentage value based on the resin). It is clear that less reactive catalysts such as tertiary amines, Zn- and Sn(II) catalysts, even at a level of 0.5%, are too inactive, especially in combination with IPDI trimer. A very attractive alternative to the Sn(IV) catalysts is a bismuth catalyst.<sup>[7-43]</sup>



**Figure 7.2-19.** Catalytic activity of different catalysts in 2K-PUR systems based on HDI or IPDI derivatives

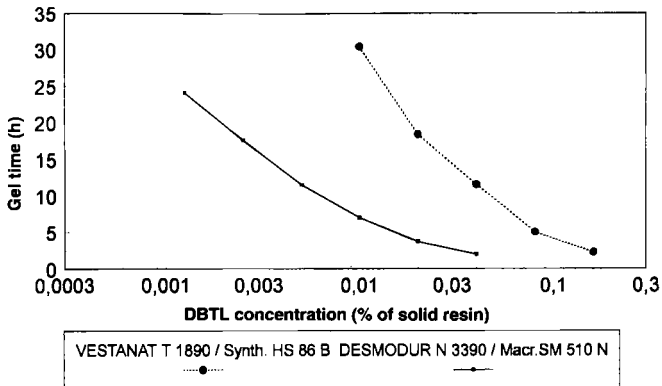
It is very interesting to note that the two different polyisocyanates respond differently to the use of different catalysts: Whereas the IPDI trimer is not enhanced significantly by the use of Sn(II) octoate, the HDI trimer is very sensitive. HDI derivatives seem to be, in general, more sensitive towards Sn catalysts, which generally have to be used in high concentrations, also apparently have very little effect on the formulations based on the IPDI trimer.

Dibutyl tin dilaurate (DBTDL) can be regarded as one of the most effective and most commonly used catalyst types. The amount which has to be used depends on the type of polyisocyanate (see Fig. 7.2-19), the degree of reactivity desired, and the shelf-life required. As a first approximation for an acrylic PUR system, a DBTDL concentration of 0.001–0.01% is required for HDI formulations, and 0.01–0.1% is required for an IPDI-trimer-based system. These concentrations would achieve a gel time of approximately 10 h for clear-coat spray formulations at 20°C.

The less active catalysts such as zinc octoates or tertiary amines are typically at levels of 0.2–0.5% in formulations employing HDI derivatives.

Finding the appropriate catalyst level in order to adjust the desired reactivity level of a 2K-PUR paint may be a very laborious process. As a general rule, doubling the catalyst concentration reduces the gel time by approximately one third, as shown in Fig. 7.2-20. This diagram also shows the differing basic reactivity of the two polyisocyanates, as well as the different sensitivity towards catalysts and towards slight changes in catalyst concentration.

In contrast to the IPDI-trimer-based resin, the HDI one can be characterized as a soft resin. Therefore, 2K-PUR formulations based on HDI trimers often exhibit



**Figure 7.2-20.**  
Influence of catalyst level on the gel time of 2K-PUR formulations

somewhat poor physical drying characteristics. This slow drying performance can only be compensated to a certain extent by a higher catalyst level, i. e., faster drying by faster chemical cure, due to the fact that this higher catalyst level leads, as a consequence, to a serious reduction of the shelf life of the two-component paint (Fig. 7.2-20).

To improve the drying time of a 2K-PUR paint based on the HDI trimer while maintaining the pot life, blends with IPDI trimers are commonly used. In Table 7.2-1 the improvement in the drying time of a 2K clear coat based on the HDI trimer and Macrynal SM 510 N by the use of such blends is demonstrated. It is again evident that, due to the lower reactivity of IPDI derivatives, increasing amounts of IPDI trimer in a blend requires a higher DBTDL concentration to obtain the same shelf life.

**Table 7.2-1.** Mixtures of HDI- and IPDI polyisocyanates to improve the drying performance. Resins: DESMODUR N 3390, VESTANAT T 1890 L, Macrynal SM 510 N; OH:NCO = 1:1; gel time approximately 13 h; spray application; dry film thickness approximately 30  $\mu\text{m}$ .

	Resin vehicle: ratio HDI:IPDI		
	100:0	70:30	50:50
DBTL concentration [as % of resin]	0.0075	0.01	0.015
Dust dry time [min]	270	180	120
Pendulum hardness [König, s], after:			
4 h	n.d.	n.d.	14
24 h	35	45	64
3 d	154	157	154
final hardness	188	188	188

It should be mentioned that such techniques have their limitations, especially when the portion of IPDI trimer in the blend exceeds 50%. This is because in the original formulation the polyol was chosen for straight cross linking with the HDI trimer

and that very high concentrations of IPDI trimer might therefore lead to limited flexibility and brittleness. Blending should always be done very carefully.

For formulations based on the HDI trimer, tertiary amines are often recommended as catalysts. With this category of catalyst, it should be taken into account that the hydrolysis of isocyanates is accelerated significantly.<sup>[7-44]</sup> This does not at first appear to present mechanical or chemical resistance problems with HDI derivatives, but disadvantages may be found at higher dry film thickness and high humidity levels due to pin-holing and other film defects which may be due to the formation of CO<sub>2</sub>.

Tertiary amines are not recommended in 2K formulations that employ IPDI trimers for two reasons. Firstly, they are poor catalysts (see also Fig. 7.2-19) and secondly, the “moisture-curing” of the IPDI trimer could lead to poor mechanical properties of the cured film.

With polyester polyols, Lewis acid catalysts, typically tin or titanium compounds, are commonly used for resin synthesis. Residues of these catalysts may also affect the demand for catalysts in the 2K formulations. This is not a problem as long as this amount and its activity is constant for each polyester batch. Therefore it might be advisable to check different polyester batches for their reactivity. Similar considerations also play a role in lactone-modified acrylic resins.

For various reasons, waterborne 2K-PUR systems are formulated without catalysts. Most of the metal-based catalysts are sensitive to hydrolysis and would react to form inactive species. Furthermore, they would also catalyse the hydrolysis of isocyanates although formulated to accelerate the urethane reaction. As a consequence, a stronger foam-formation tendency, also after application, is possible.

### **Formulation Advice**

In general, catalysts are formulated into the A-component, the polyol part. This is a must in the case of HDI-based formulations; in the case of IPDI trimers it is only a recommendation. Due to the fact that “urethane-grade” solvents with <0.05% water content have to be used for formulating 2K-PUR paints, the deactivation of catalysts by hydrolysis is not likely. When the DBTDL catalyst is used, the use of diluted solutions of the catalyst for formulating the paint, to achieve easy and thorough mixing and exact dosage, is recommended. In pigmented systems with a critical or borderline reactivity, the catalyst should be added after the grinding of the pigments to avoid adsorption of catalyst to the pigments. The reactivity of the finished paint should be checked in all cases. For polyesters or lactone-modified acrylic resins, a laboratory formulation for new polyol batches is recommended, because of the danger of varying residual catalyst concentrations.

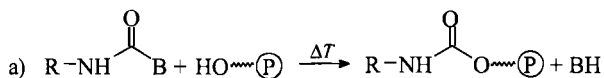
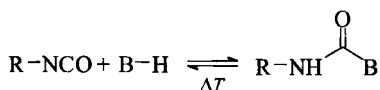
#### **7.2.3.3 Blocked 1K-PUR Systems**

2K-PUR systems can not be used for all application methods, such as dip coating or roller-coating technology for applying the paint to the substrate. To be able to use PUR systems in these application methods, the strategy of thermally reversible

blocking of polyisocyanates was developed. In principle, such blocked 1K-PUR systems are able to achieve the quality and performance level of 2K-PUR systems with the advantage of avoiding 2K equipment. The main field of application is in high-quality storing paints for:

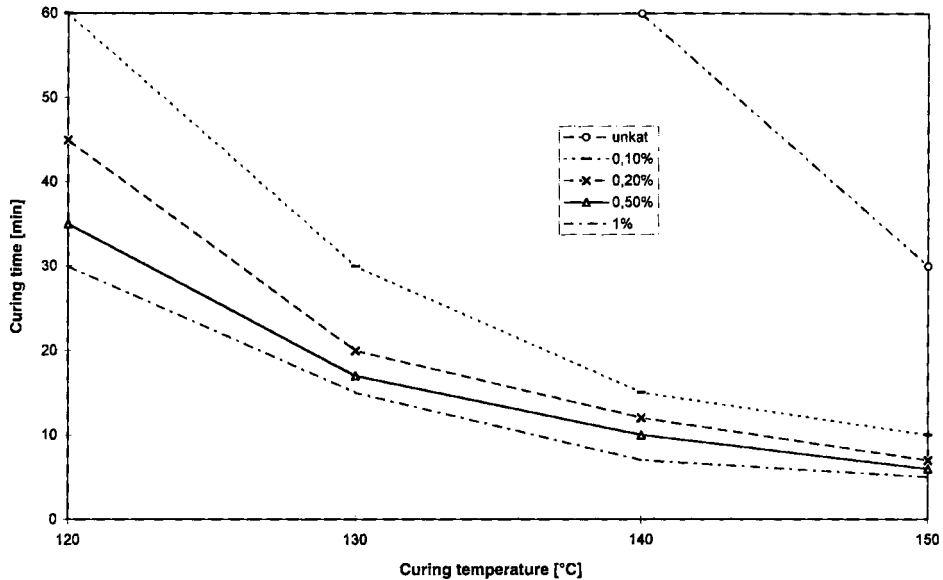
- coil- and can coatings, due to the excellent weathering durability, excellent deformability and sterilization resistance under acidic conditions
- automotive OEM for clear coats that have excellent weatherabilities and resistance to environmental etches, or for stone-chip resistant primers/surfacers
- powder coatings with high weathering durability

The blocking reaction, shown in Fig. 7.2-21, can be performed with a variety of H-acidic components. In fact, only very few blocking agents are used on a significant commercial basis:  $\epsilon$ -caprolactam is used as a universal blocking agent for curing temperatures  $>160^\circ\text{C}$ , such as in coil- and powder coatings; oxime-type blocking agents such MEKO or acetone oxime are used for the lower-temperature curing at  $>130^\circ\text{C}$ , which is important for automotive applications. Other blocking agents for curing at  $<130^\circ\text{C}$ , such as malonates or acetoacetates lead to highly reactive systems, but also to limited storage stability, nevertheless relevant in automotive OEM clearcoat technology.<sup>[7-46, 7-48]</sup> A very interesting strategy for the blocking of isocyanates, with increasing importance in the field of powder coatings, is the internal, blocking-agent-free blocking technology with uretdione structures (see also Section 3.4).<sup>[7-49]</sup>



**Figure 7.2-21.** Blocking of polyisocyanates; a) blocked 1K-PUR systems, cross-linking

The cross linking reaction may occur by one of two possible mechanisms: a) addition of the hydroxyl group to the blocked NCO-group with successive elimination of the blocking agent, or b) deblocking followed by urethanization of the released isocyanate and the hydroxyl. A significant number of recent publications point to the latter mechanism as being the favoured one.<sup>[7-50–7-53]</sup> The equilibrium between blocked polyisocyanates and polyol, blocking agent, and polyisocyanate also needs to be considered in this case: In a row (group?) of homologueous blocking agents the reactivity of a blocked 1K-PUR system, or the unblocking temperature, depends roughly on the boiling point of the blocking agent. On the other hand, the equilibrium can be shifted towards the cross linked species by fast removal of the isocyanate towards the more stable structure, i. e., the urethane. And this is where catalysis plays a crucial role. Lewis acid catalysts, similar to those employed in 2K-PUR systems, are typically used. Significantly higher concentrations of catalysts are generally needed to achieve significant acceleration of the curing reaction. In the case of DBTDL, concentrations of 0.2–0.5% (based on resin) are recommended. In Fig.



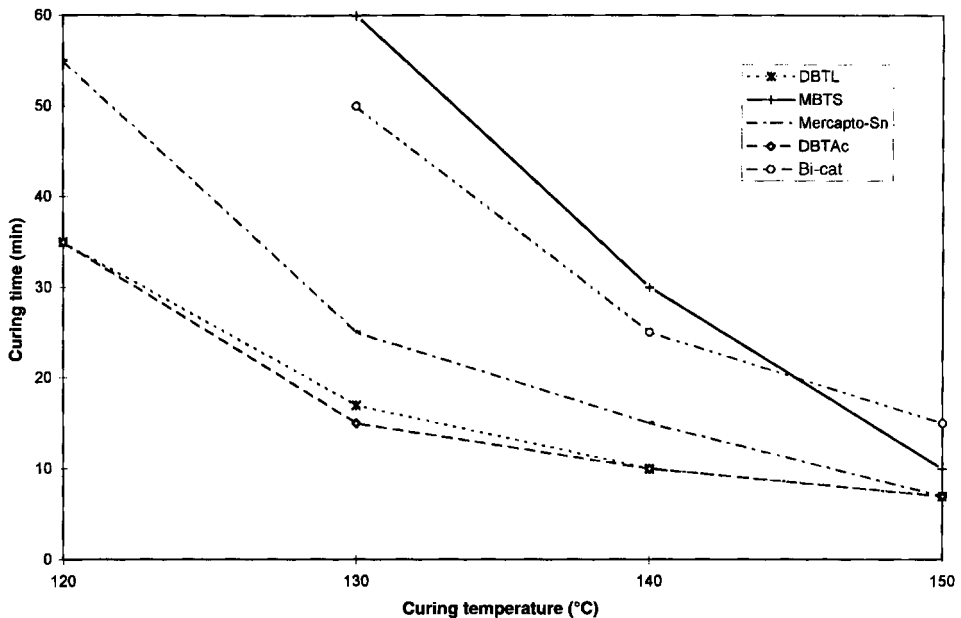
**Figure 7.2-22.** Influence of DBTL concentration on the reactivity of an oxime-blocked 1K-acrylate-PUR system

7.2-22, the effect of different catalyst concentrations on the reactivity of a  $\text{TiO}_2$ -pigmented system is demonstrated. This system is based on an oxime-blocked IPDI trimer (VESTANAT B 1358 A, Degussa-Hüls AG) and an acrylic polyol (Synthalan HS 86 B, Synthopol Chemie, Germany). Even a concentration of 0.1% of DBTDL leads to a dramatic decrease in curing temperature and time. Concentrations higher than 0.5% only lead to a marginal improvement in reactivity.

Recent developments in the field of tin catalysts indicate that further improvements are possible through appropriate catalyst design so that oxime-blocked polyisocyanates might potentially be completely cured at 120 °C.<sup>[7-54]</sup>

The activity of some commercially available catalysts, mostly tin based, is shown in Fig. 7.2-23. Again the basic formulation consists of the oxime-blocked IPDI trimer VESTANAT B 1358 A (Degussa-Hüls AG) and the above-mentioned acrylic polyol. The metal atom concentration in the catalysts were formulated to be equivalent to a 0.5% DBTDL concentration. As already shown in the section on 2K-PUR systems, DBTAc is very similar in activity to DBTDL, while monobutyl tin triisooctate (MBTA) and a bismuth catalyst (Coscat 83) are significantly less active. It is interesting to note that the difference between the less reactive MBTA and the "benchmark" DBTL is dramatically reduced at higher temperatures.

In automotive applications, as in many other important applications, the aqueous 1K stoving systems are gaining more importance in areas beside that of the CED paints. Most of the catalysts mentioned above can't be used, because they are easily hydrolysed into inactive species. It has been reported that mercapto-bearing ligands can shield and stabilize tin atoms against hydrolysis.<sup>[7.55]</sup> But the very efficient



**Figure 7.2-23.** Dependence of the reactivity of a 1K-PUR system on the type of catalyst

shielding can also result in the tin atom losing its activity in urethane catalysis, so that the activity is significantly lower than that of DBTDL. Waterborne oxime-blocked polyurethane systems are unlikely to be cured below 140 °C.

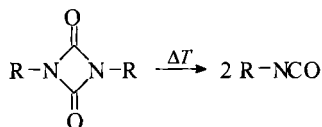
### Formulation Advice

The thermal curing of PUR systems is typically catalysed. Because of the sensitivity towards hydrolysis, the polyols and solvents used should be free of water. To avoid absorption of catalyst on the pigment surfaces and to avoid reactivity loss of the paint, the catalysts should be added after the pigment has been ground. Especially in systems with matting agents such as amorphous silica, water content and adsorption effects can not be avoided. In such cases, special catalyst preparations such as DYNAPOL catalyst C 31 (Degussa-Hüls AG) are recommended.

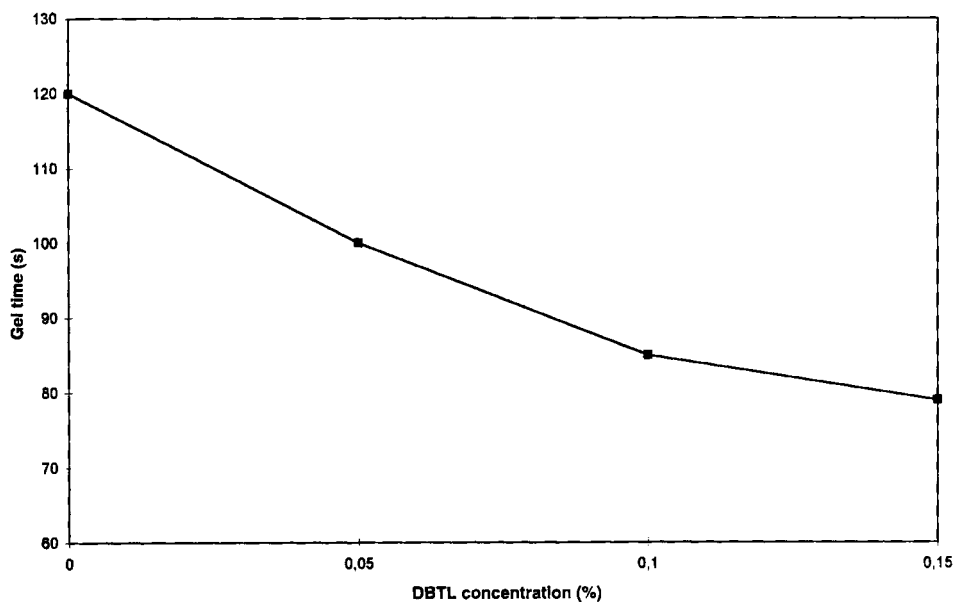
#### 7.2.3.4 PUR Powder Coatings

PUR powder coating hardeners are typically based on caprolactam rather than oximes because oximes tend towards yellowing upon baking at the high film thickness of powder coating applications. Because the catalytic effect is limited, such systems are not necessarily catalysed, although 0.15% of DBTDL is sometimes recommended.

The more innovative PUR powder coating hardeners are made from internally blocked systems based on uretdione structures (Fig. 7.2-24). Here catalysts have a significant influence. In Fig. 7.2-25, the influence of the DBTDL concentration on the reactivity of a powder coat based on IPDI uretdione and a polyester is shown, expressed as the gel time at 200 °C. The amount of tin catalyst used for the preparation of the uretdione-based hardener was not considered. Typically, 0.15% of DBTDL is recommended. The liquid DBTDL catalyst is generally introduced into the powder coating formulation via a masterbatch.



**Figure 7.2-24.** Uretdione as an internally blocked cross linker



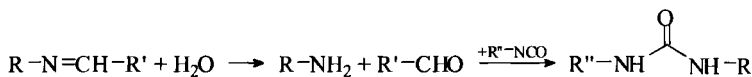
**Figure 7.2-25.** The influence of DBTL on the gel time of an IPDI-uretdione-based powder paint, at 200 °C

### 7.2.3.5 Moisture-Curing 1K-PUR Systems

In the group of ambient-temperature-curing PUR systems, the 1K-moisture-curing prepolymers of the non-yellowing type based on the cycloaliphatic IPDI are niche products compared to the 2K-PUR ones, but they are becoming more interesting for some applications. They are typically used for plastic, concrete, or cork coatings, and are employed for corrosion protection and as roof coatings. This type of resin

is characterized by its good hardness combined with excellent elasticity, very good adhesion on various substrates, very good chemical resistance, and an outstanding curing response at low temperatures, as well as defect-free curing at high humidity.

Non-yellowing types of moisture-curing prepolymers are typically based on isophorone diisocyanate, IPDI. The basic reactivity of this type of resin towards water is considered to be very low. For sufficient reactivity, a catalyst is required. As mentioned in Section 7.2.3.1, the reaction between isocyanates and water is catalysed by tertiary amines. For this, diazabicyclo[2.2.2]octane [triethylenediamine, DABCO crystal (Air Products)] is usually used at a level of 0.2–0.8% (based on solid binder), depending on the reactivity required. Synergistic effects with DBTDL, at a level of 0.1% (Fig. 7.2.26), are also commonly employed. Cyclic amidines such as diazabicyclo[5.4.0]undec-7-ene (PC CAT DBU, Nitroil) are significantly more reactive, so that 0.2% is normally sufficient.



**Figure 7.2-26.** Aldimines as curing agents in moisture-curing systems

The hydrolysis of isocyanates is accompanied by the formation of  $\text{CO}_2$ . At high film thickness, bubbling may occur due to the  $\text{CO}_2$ . To overcome this problem, components to avoid the  $\text{CO}_2$  formation are often used in the formulations; they function through chemical reactions that occur before isocyanates are hydrolysed. Typically, carbon dioxide does not form in the final product of cross linking of such formulations. The substances used, e.g., aldimines, ketimines, or oxazolidines (e.g., VESTAMIN A 139, bisaldimine from Degussa-Hüls AG, Hardener OZ, bisoxazolidine from Bayer AG) are sensitive to hydrolysis. Upon hydrolysis, the blocking agent, a carbonyl group, and the cross linking group, often a diamine, are released. (Fig. 7.2-26).

Due to their electron-rich C–N double bonds, ketimines have the disadvantage of reacting with isocyanate prepolymers, even in the absence of water, so that storage-stable one-component formulations are not possible.<sup>[7-56]</sup> The double-bond system of aldimines is characterized by a lower electron density due to the higher electronegativity of the aldehydes. Therefore, formulations based on aldimines and NCO prepolymers are more stable; depending on the materials chosen clear coats may be stable for several months. Often aldimines are mixed with the prepolymer moiety directly before use. With this strategy, the highly accelerating effect of aldimines can be used while avoiding storage-stability problems of the paint. Typically, only cross linking of approximately 50% of the NCO groups is recommended, because the accelerating affect is sufficient and the danger of non-cross linked amine groups, which would lead to yellowing, is avoided. In Table 7.2-2, the effect of various strategies to catalyse the moisture-curing of NCO prepolymers based on IPDI is shown.

Oxazolidines are much less reactive than aldimines. To achieve an acceptable curing speed it is necessary to use catalysts to hydrolyse the oxazolidine ring. Typi-

**Table 7.2-2.** Catalysis of moisture-curing IPDI prepolymers

	Catalyst (as % of solid resin):				
	Uncatalysed	0.1% DBTL	0.4% DABCO	0.4% DABCO 0.1% DBTL	12.7% VESTAMIN A 139
Dust drying time	4.5 h	3 h	2.5 h	2 h	0.75 h
Tack-free time	3 h	2.25 h	2.25 h	1.1 h	0.5 h
König hardness	65	75	85	96	91

cally, acid catalysts such as carboxylic acids or the corresponding anhydrides at a level of 0.5% (HHP SA, methyl-HHP SA, salicylic acid, 2-ethylhexanoic acid, oleic acid) are used. For suitable reactivity, the urethane reaction of the released hydroxyl group also has to be accelerated by the use of DBTDL.<sup>[7-57]</sup> In contrast to aldimines, the bisoxazolidines (Hardener OZ, Bayer AG) are formulated stoichiometrically, either calculated for a pure urea cross linking (functionality 2) or for the more preferred urea and urethane cross linking (functionality 4).

Humidity should generally be avoided during the preparation of the paint. Therefore, pigments and solvents should be free of water. Recently, different easy-to-apply methods have been developed to scavenge residual water from all constituents of the paint, for example, anhydrous aluminium sulphate (Giulini Chemie, Ludwigshafen, Germany), calcium oxide (BYK Chemie), or monooxazolidines (Angus Chemie).<sup>[7-58, 7-59]</sup>

## 7.2.4 Epoxy Systems

### 7.2.4.1 Introduction

Epoxy resins can be cross linked with a variety of different chemical partners. Due to their low price, the outstanding chemical and corrosion resistance of the cured coatings, epoxy resins are one of the most favoured types of resins in coatings technology.

The versatility of this type of resin is due to the ability of the epoxy groups to react with various nucleophilic reagents such as amines, phenols, or carboxylates. Highly reactive nucleophiles such as amines are suitable for formulating two-component systems with a long shelf life; less reactive components such as phenols or carboxylic acids are used to formulate one-component stove-paints.

The cross linking reaction of epoxy resins occurs by nucleophilic ring-opening of the oxirane ring by polyfunctional reagents with acidic protons (Fig. 7.2-27).<sup>[7-60]</sup> The speed of addition depends on the nucleophilic character of the reagent and is ranked: amines  $\gg$  acids > phenols > alcohols.<sup>[7-60]</sup>

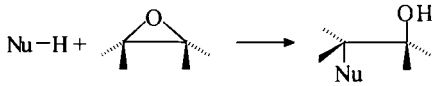
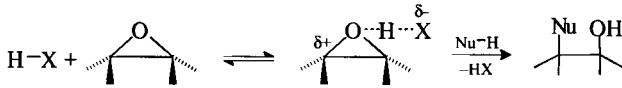


Figure 7.2-27. Ring-opening of oxirane

As in isocyanate or melamine cross linking systems, the ring-opening and addition reaction of epoxy systems are also often catalysed. In principle, both alkaline and acidic catalysts can be used, although the latter is preferable. Acidic catalysts bring about the polarization of the oxirane C-O bond, thus supporting the ring-opening reaction with the nucleophile (Fig. 7.2-28).<sup>[7-60]</sup> Because the secondary hydroxyl group generated by the ring-opening reaction may also act as a nucleophile, the acidic catalysis may lead to a considerable extent of homopolymerization. As a consequence, this, not really defined as cross linking, may lead to somewhat changing property profiles of the cured coating under different conditions. Although not as pronounced, this effect could be compared with melamine cross linked systems.

Figure 7.2-28.  
Acid catalysis

Alkaline catalysts act by activating the nucleophile; this leads to partial deprotonation and enhanced nucleophilicity of the oxirane-opening agent. With alkaline catalysis, homopolymerization of the epoxy resin occurs to a much lesser extent (Fig. 7.2-29).<sup>[7-60]</sup>

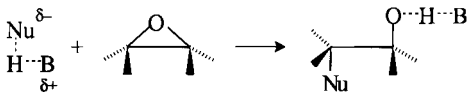


Figure 7.2-29. Alkaline catalysis

The following sections will deal with the catalysis of the most important epoxy-based systems: the two-component epoxy/amine systems, the heat-curing epoxy/carboxyl, and epoxy/phenol/formaldehyde resin systems.

#### 7.2.4.2 Epoxy/Amine Systems

Amines as nucleophiles are highly reactive towards epoxy resins. Because the reaction takes place even at ambient temperature, such systems are, in principle, two-component systems. The reactivity of the amines declines in the order: aliphatic > cycloaliphatic > aromatic amines. Important applications of two-component epoxy systems based on amines and bisphenol A derivatives are: flooring, concrete coating, and maintenance (corrosion protection).

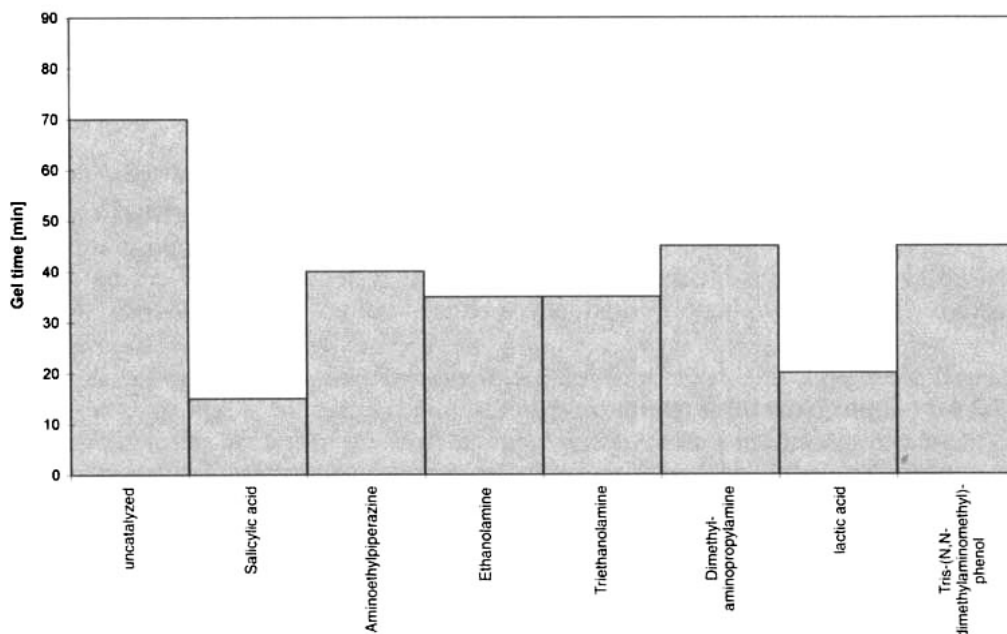
Although the speed of addition of an amine to the oxirane ring is often fast enough, a catalyst may be necessary to achieve an even faster cure. Especially in the case of the less reactive cycloaliphatic diamines, the use of catalysts is state of the art for a

better cure at low temperatures. The reaction of diamines with epoxy groups can be catalysed with carboxylic acids, if no insoluble salts are formed, phenols, or alcohols. There is generally a correlation between the reactivity and the  $pK_a$  value of the catalyst. Acid catalysts such as salicylic acid, lactic acid, or hydroxyl (phenolic)-group-bearing tertiary amines such as tris(dimethylamino)phenol may be employed. The particular effectivity of the latter catalyst is ascribed to the combination of an alkaline group with an acidic phenolic group. The acidic OH group can stabilize the transition state by the formation of hydrogen bonds, i. e., a mixture of the mechanisms shown in Figs. 7.2-28 and 7.2-29 appear to operate.<sup>[7-60]</sup>

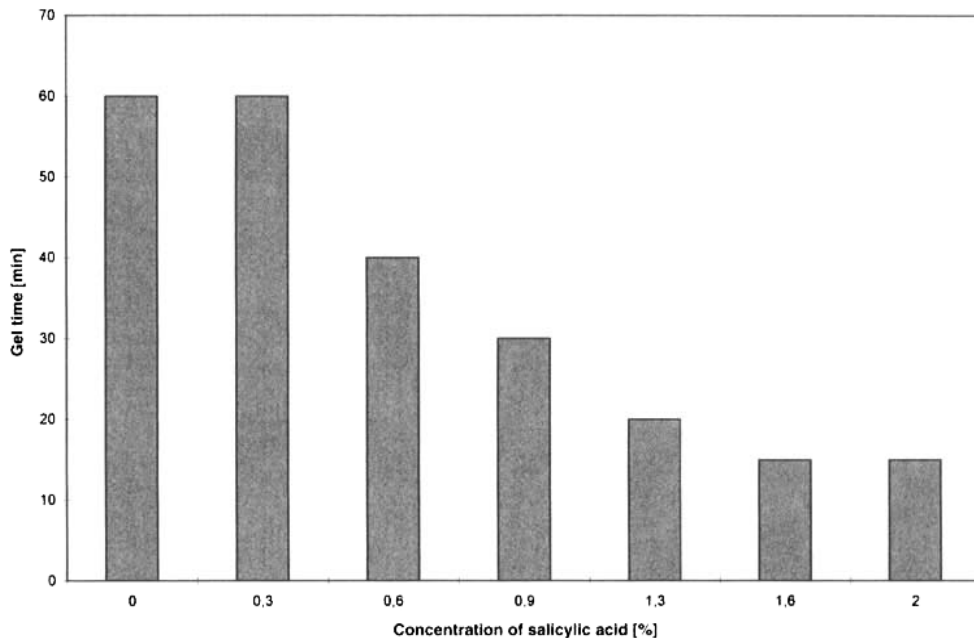
The very common use of benzyl alcohol in epoxy/amine formulations is not only related to the catalytic activity of benzyl alcohol but also to its plasticizing effect, leading to a high degree of mobility of the functional groups and therefore leading to a faster and a more complete cure.

The efficiency of various catalysts in a formulation based on isophorone diamine (IPD) and a bisphenol A resin is shown in Fig. 7.2-30. The same concentrations of catalysts were used. The most common catalysts used in the field of solvent-free two-component epoxy systems are tris(dimethylamino)phenol and salicylic acid. The influence of the catalyst concentration of salicylic acid on the gel time is demonstrated in Fig. 7.2-31. In practice, 2% is typically used.

In general, the catalysts are formulated into the amine component. Salicylic acid is a solid and has to be dissolved before formulation, typically in benzyl alcohol.



**Figure 7.2-30.** Gel time of 2K epoxy/amine formulations with different catalysts. Basis: 50 g VESTAMIN IPD, 44 g benzyl alcohol, 6 g catalyst, 219 Epikote 828. 200 g at bath temperature of 23 °C



**Figure 7.2-31.** Influence of the concentration of salicylic acid on the gel time of 2K epoxy/amine formulations. Basis: 50 g VESTAMIN IPD, 50 – x g benzyl alcohol, x g salicylic acid, 219 Epikote 828. 200 g at bath temperature of 23 °C

Hardeners based on salicylic acid are more viscous. Lactic acid leads to a lower degree of discoloration of the hardener, but problems with solubility at lower temperatures are often reported. Tris(dimethylamino)phenol is less active than salicylic acid, is characterized by a strong odour, and leads to less flexible cured coatings. Due to its low  $pK_a$ , *p*-toluolsulfonic acid (*p*-TSA) has a high catalytic activity, but is often incompatible.

It is in practice possible to obtain epoxy hardener formulations that are optimized with regard to reactivity by the use of catalysts from system suppliers.

#### 7.2.4.3 Epoxy/Carboxy Systems

Apart from an application of limited relevance in the field of solventborne automotive OEM clearcoats,<sup>[7-61]</sup> this cross linking chemistry is of great importance in the field of powder coatings, namely in the “hybrid systems” based on higher molecular weight bisphenol A derivatives, in carboxylated polyesters, and in the TGIC systems. The latter systems are used for non-yellowing, weathering-resistant powder coatings.<sup>[7-62]</sup> A new generation of powder coatings for automotive OEM clearcoats is based on an epoxy group bearing an acrylic resin and an acidic curing agent.<sup>[7-63]</sup>

Carboxylic groups are considerably poor nucleophilic agents and don't react very fast with epoxy groups. Fast cross linking can only be achieved at higher tempera-

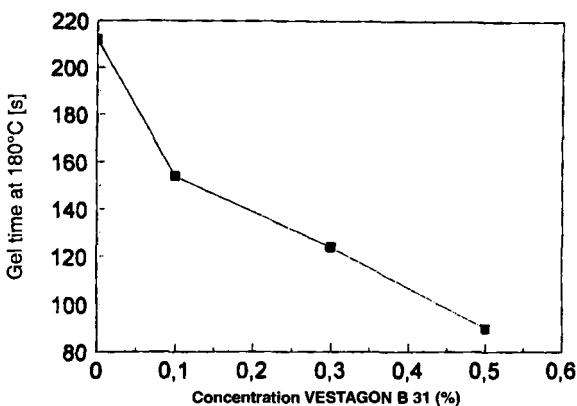
tures or by the use of catalysts. To improve the reactivity of the carboxylic groups, the catalysts have to be alkaline (see also Fig. 7.2-29).<sup>[7-64]</sup>

The reactivity of uncatalysed systems depends directly on the acid strength, i. e. the  $pK_a$ . In model reactions, sulfonic acids react at ambient temperature with epoxy groups, with heat generation; for a very fast and complete conversion with adipic acid,<sup>[7-65]</sup> a temperature of at least 150 °C is required. Under uncatalysed conditions, significant homopolymerization of the epoxy resin always occurs because the carboxyl groups also act as catalysts for the addition of hydroxyl groups to epoxy groups (see also Section 7.2.4.1).

Although inorganic alkaline materials could be used to catalyse this system, organic materials like tertiary amines are much more preferred, due to greater efficiency and compatibility. Amidines and imidazoles also belong to this group of organic alkaline catalysts.

Proper choice of monomers and/or catalysts for the manufacture of the carboxylated resins, for hybrid as well as TGIC systems, is usually enough to ensure sufficient reactivity of the corresponding formulations. Catalysts have to be used for highly reactive systems.

In Fig. 7.2-32 the effect of the concentration of an amidine catalyst on the reactivity of a hybrid system is demonstrated.



**Figure 7.2-32.** Dependence of the gel time of a hybrid powder coating at 180 °C on the amidine concentration

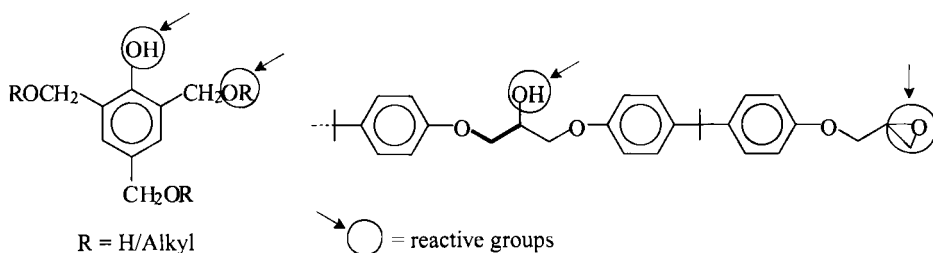
Other tertiary amines such as DABCO, amidines, or other *N*-heterocyclic compounds can be used similarly and in similar concentrations. In all such cases, the concentration of catalyst, the conditions for extruding the system, as well as the cooling conditions have to be determined carefully because of the danger of partial polymerization of such highly reactive systems.

The use of catalysts in hybrid systems may lead to a distinct yellowing upon baking, so that they are generally not used for white colours.

#### 7.2.4.4 Epoxy/Phenol/Formaldehyde Resin Systems

The chemical structure of phenol/formaldehyde resins as well as the kind of functional groups suitable for cross linking is complex and versatile.<sup>[7-68, 7-69]</sup>

In the field of cross linking of coating systems, resolic resins and ether derivatives play an important role. Combining such types of resins with higher molecular weight bisphenol A derivatives are extremely important in the area of interior can coatings.<sup>[7-70-7-72]</sup> In such formulations, there are at least four different types of reactive groups: the secondary OH-groups and the epoxy groups of the epoxy resin, as well as the free methylol groups and the methylol group ethers of the resol. Each one of these resins is also capable of homopolymerization, and the ether derivatives of the resols have two different functional groups that can react with the epoxy resin (Fig. 7.2-33).<sup>[7-73]</sup>



**Figure 7.2-33.** Resol resin/high-molecular-weight bisphenol A epoxy resin (representation of phenol, methylol, secondary OH, and epoxy groups)

According to the nucleophilic strength, the phenolic and the secondary hydroxyl groups of the resols are not very reactive towards epoxy groups, so that typically such systems, when not catalysed, have to be cured at high temperatures,  $>200\text{ }^{\circ}\text{C}$ . When acidic catalysts are used, the tendency for homopolymerization of epoxy (see also Section 7.2.4.1) and resol (see Section 7.2.2) resins is greater, with the consequence of better chemical resistance,<sup>[7-74]</sup> but also of poorer flexibility.<sup>[7-71]</sup> Typically, strong acids such as phosphoric or sulfonic acids are used in a range of 0.3–1% active acid within the solid resin. Phosphoric acid and its derivatives often lead to improved corrosion resistance. Phosphoric acid should be diluted with glycols before use to make it easier to handle and to avoid too high local acidity.

Phenol/formaldehyde resins of the novolak type are widely used in high-molecular-weight epoxy resins in powder-coating systems for heavy-duty applications where non-yellowing properties are not required.<sup>[7-68, 7-70, 7-72]</sup> Because cross linking occurs by reaction of an acidic phenolic group with the epoxide, alkaline catalysts are used to accelerate this reaction.<sup>[7-64]</sup> Tertiary amines or imidazoles are usually employed.<sup>[7-64, 7-70, 7-72, 7-75, 7-76]</sup>

## 7.2.4.5 Commercial Products

	<i>tert.</i> amines	Acids	EP powder coatings
Anchor	ANCAMINE K 54 (DMP 30) – BDMA	Anchor (BF <sub>3</sub> )	AMICURE DBU-E AMICURE (Cyanoguanidine)
Bakelite	RÜTADUR DMP 30 BDMA	RÜTADUR BF3-500 RÜTADUR DDS	
Ciba-Geigy			Accelerator DT 3126
Degussa-Hüls			VESTAGON B31, B55, B68
Prümmer	POLYPOX DB POLYPOX DMP 30	Polylox Salicylic acid	
Witco	Euredur 13		

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## **8 Additives for Special Functions**

*Johan Bieleman*

This group of additives are those that have a specific function in the coating during production, storage, or use. They include anti-skinning agents, which are used in oxidatively drying coatings, and light-protection agents, which are used against light effects. The protective action of corrosion inhibitors and biocides operates in the liquid coating material as well as in the dried coating. Flame-retardants are used as protective agents to inhibit the oxygen access of heavily combustible coatings.

In this chapter we will also deal with photoinitiators for ultraviolet-hardening coatings.

## 8.1 Anti-Skinning Agents

*Johan Bieleman*

### 8.1.1 Introduction

Anti-skinning agents are additives that are added to the coating material to prevent skinning during production or storage of the coating material.

These additives are included in the formulations and are added in small portions during coating material production or when the coating material is used.

Skinning is the result of film formation on the surface of a liquid paint or any other coating material. The mechanism of this undesired skinning is identical to that of film formation after application of the coating material. Skinning may be divided into the following types:

- skinning as a result of physical processes
- skinning as a result of chemical processes
- skinning as a result of physical and chemical processes

Skinning does not only lead to material losses, but also to quality depreciation of the coating material and should therefore be prevented. In this chapter we will explain reasons, consequences, and treatment against skinning.

### 8.1.2 Definitions

Anti-skinning agents: Additives that prevent the undesired skinning on coatings, paints, or printing inks

MEKO: Abbreviation for methyl ethyl ketoxime (2-butanone oxime)

### 8.1.3 Causes of Skinning

Skinning is usually the effect of early film formation on the surface of the liquid coating material.

In practice, skinning is most frequently noticed in oxidatively drying coatings. These coatings contain air-drying oils or macromolecular binders. Example of

these are air-drying alkyd resins, epoxide esters, urethane alkyds, and many other modified oils. Under the influence of oxygen, the liquid-coating-material binder solidifies.

Although skinning is mainly a problem in oxidative drying coatings, it can also arise in other systems such as highly pigmented dispersion paints and in physically drying solvent systems, such as chlorinated rubber coatings and vinyl coatings.

In principle, the skinning mechanism is identical to the film-formation mechanism.

As for determining factors, which result in skinning, one can distinguish between:<sup>[8-1, 8-2]</sup>

- polymerization processes on the surface, in the can, or in other packing materials
- gelling effects as a result of the coating-material surface drying out
- a combination of both effects

In practice, skinning as a result of polymerization processes occurs especially in colourless and pigmented coating materials that are based on oxidatively drying solvents.

### **8.1.4 Consequences of Skinning**

Skinning in the packaged material means quality losses from several points of view. Because of skinning, the coating material can not be used immediately, because the skin has to be removed first, with material losses. Not only has a part of the coating material been lost, but it has been proved that the strength of the driers in the skin is above average compared to that in the remaining coating material, therefore skinning could lead to drying being prolonged.

Parts of the skin could remain in the coating material and be visible as disturbing spots or particles in the drying film. As a result, the coating has to be ground off, associated with a considerable operating-cost increase. Therefore the risks of skinning should be reduced.

### **8.1.5 Avoiding Skinning**

To avoid skinning, several methods can be used. Firstly, adapting the composition of the coating material is an option. For example, a reduction in or a change of driers or film-forming resins could lead to less skinning. But as a consequence of this, general coating-material characteristics such as film formation could be affected negatively.

Secondly, in the case of oxidatively drying coatings, the space above the coating-material surface can be filled with an inert atmosphere, for example nitrogen. This

will result in keeping the liquid coating material surface free from oxygen. This procedure is also associated with considerable economical and practical disadvantages. This method would necessitate the renewal of the inert atmosphere with each opening of the can, and the can needs to be closed in such a way that the inert gas cannot disappear.

Another very simple method is the inverse storage of the can; only when in use should the can be put in its normal position. But this method is risky, and unattractive because of marketing reasons and not very useful.

The most successful method against skinning of coating materials, in practice, is to add anti-skinning agents as additives. These agents can be classified as follows:

- antioxidants
- agents blocking the polymerization catalyst
- solvents
- retention agents

In practice, the agents blocking the polymerization catalyst have proved themselves. Especially oximes, such as methyl ethyl ketoxime, prevailed.

For the selection of anti-skinning agents the following criteria are the most important ones:

- the effectiveness in skinning prevention
- compatibility with other coating-material components
- influence on the drying time
- influence on fading and film characteristics
- influence on odour
- viscosity
- toxicity

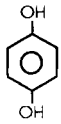
### 8.1.5.1 Antioxidants

Antioxidants are organic compounds that retard autoxidation reactions, and they are added to systems that have a tendency to oxidize.

There are only a few chemical compounds that are known to have an oxidation inhibiting effect. The antioxidants most known are combinations based on phenol and amine. However, these compounds have low volatility and therefore prolong the drying time of the coating. The effective phenol-based compounds retard the drying too much to be suitable for use in oxidatively drying paints and coatings. The drying retardation effect can be reduced by chemical modification of the phenol compound. An example is the ortho-substitution of the ring by an alkyl group. But these modified phenols – also known as sterically hindered phenols – still have a strong antioxidant effect, so that the dosage can be kept to a minimum in order to keep the influence on the drying time within acceptable limits. BHT (2,6-di-*tert*-butylphenol) is one of the antioxidants used most often; it is used in many industrial sectors, including the paint and coating industry.

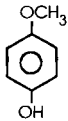
Examples of phenolic antioxidants are:

Hydroquinone



(1)

Hydroquinone methyl ether (MON)



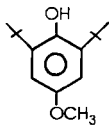
(2)

*p*-Cresol



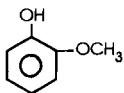
(3)

2,6-Di-*tert*-butyl-4-methoxyphenol (BHT)



(4)

Guaiacol



(5)

*o*-Isopropylphenol



(6)

### Mode of Action

The mode of action of the phenol antioxidants is based on its reaction with the oxygen-containing free radicals, which are formed during the autoxidation process:<sup>[8-31]</sup>



where ROOH is a peroxide and AH is a phenol antioxidant.

The antioxidant competes with the organic substances involved in the autoxidation process.



But the reaction speed<sup>[8-1]</sup> of an effective antioxidant is much higher than that of autoxidation.<sup>[8-2]</sup> During this process the newly formed phenol radical  $\text{A}\cdot$  should not abstract hydrogen atoms from other molecules, that is, it should not participate in chain extension:



It has been shown that hindered phenols can even remove two peroxy radicals. The initially formed radical  $\text{A}\cdot$ , from the reaction represented in Eq. (7), can react with another peroxy-radical:



Phenolic antioxidants, as well as secondary amines, almost only react with oxygen-carrying radicals such as peroxy and alkoxy radicals<sup>[8-3]</sup>.

### Application

Phenolic-based antioxidants are typically added in quantities of 0.05 to 0.2%, as calculated on the total quantity of the coating system. Phenolic antioxidants are used only to a limited extent, predominantly in oxidatively drying printing ink formulations. Because of their strong retardation effect on the drying time (they only escape very slowly from the drying system) these products have found only limited application for this purpose.

In white coatings, phenolic antioxidants tend to cause yellowing. Besides the negative effect on the paint (intensively coloured complexes are formed especially in combination with iron compounds) further disadvantages of the phenolic antioxidants are their relatively high toxicity and the adverse effect on the odour.

For this reason these antioxidants are only of lesser importance as anti-skinning agents.

Amines are rarely used as anti-skinning agents, too, as these products have only a weak anti-skinning effect. And the disadvantages are comparable to those of the phenols (yellowing, retarding of drying time, strong odour). However, amines, as well as ammonia, are excellent ligands for driers, especially for cobalt.

#### 8.1.5.2 Blocking Agents for Polymerization Catalysts

The most widely applied anti-skinning agents belong to this group. Their anti-skinning effect is based on complexation reactions of the polymerization catalyst.<sup>[8-4]</sup>

The most important representatives of this group are the oximes. The molecule structure is characterised by the oxime group:  $\text{>C=NOH}$ .

The following oximes are the most widely used ones in commercial quantities:

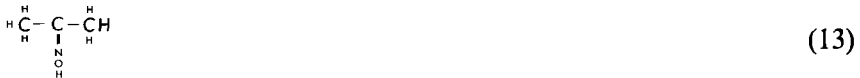
**Methyl ethyl ketoxime**



**Cyclohexanone oxime**



**Acetone oxime**



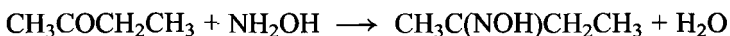
Methyl ethyl ketoxime (MEKO) is by far the most widely used anti-skinning agent in air-drying paints.

Cyclohexanone oxime is a solid material and evaporates very slowly compared to MEKO; it stays largely in the coating layer, retarding the drying time. In practice, the use of cyclohexanone oxime is limited to printing inks, such as air-drying offset inks. In this application, the main benefit is the prevention of skin formation on the rollers, even during the long standstill through the night. A disadvantage of cyclohexanone oxime is, furthermore, the incorporation: the powder form in which cyclohexanone oxime is supplied, is difficult to incorporate in coating systems or in solvents such as aliphatic hydrocarbons.

Acetone oxime is also available as a powder; however, this oxime evaporates faster from the coating layer than cyclohexanone oxime does. It is practically without odour and has found some application in odourless coating systems.

**Production of Methyl Ethyl Ketoxime (2-butanone oxime)**

Chemically, methyl ethyl ketoxime (generally abbreviated as MEKO) is an imine. It is produced by the direct transformation of methyl ethyl ketone with hydroxylamine:



In practice, this reaction is carried out in a weakly acidic medium, for example, in an acetic acid/sodium acetate medium. Strongly acidic media should be strictly avoided, as this may result in exothermic decomposition reactions of the oxime!

### Typical Properties and Applications of Methyl Ethyl Ketoxime

MEKO is a low-viscosity liquid and is supplied as a 100%-material. Typical physical characteristics of MEKO are shown in Table 8.1-1.<sup>[8-5]</sup>

**Table 8.1-1.** Physical characteristics of methyl ethyl ketoxime

Appearance:	colourless, low-viscosity liquid
Density (20 °C):	923 kg m <sup>-3</sup>
Melting point:	-15 °C
Flash point (DIN 55679), °C:	62 °C
Boiling point:	152 °C
Acid number (DIN 53402):	<1
Odour:	mild
Vapour pressure (20 °C):	3.5 mbar
Evaporation rate (for butyl acetate: 1):	10

The popularity of MEKO as an anti-skinning agent is explained by its high effectiveness, the low concentration necessary for use, and its lack of side effects. MEKO does not remain permanently in the dried coating layer, in contrast to products such as antioxidants. MEKO has a high vapour pressure, which explains its fast evaporation after application of the coating. Typically, already within the first minutes after application of the coating, most of the MEKO has been released from the coating. Therefore, the drying time of the coating is not or hardly at all affected when MEKO is used (Table 8.1-2).

**Table 8.1-2.** Drying time of a high-gloss air-drying alkyd paint with and without MEKO. Driers: 0.05% Co/0.3% Zr and 0.1% Ca, calculated as metal on solid resin. Drying times were determined for a wet-film thickness of 60 µm, drying temperature 23 °C, relative humidity 65%

	Without anti-skinning agent	With 0.2% MEKO
Dust-free drying after:	1 h 45 min	2 h
Totally dry after:	4 h 45 min	4 h
Skinning after:	3 d	>250 d

Typical use concentrations of MEKO as anti-skinning agent in conventional alkyd-based coatings are between 0.1 and 0.5%, calculated as MEKO to coating material. The optimal dosage depends on the drying characteristics of the coating material and its tendency to form skins. This is also related to the level of primary drier in the formulation. As a rule: the higher the concentration of cobalt drier, the higher the required dosage of MEKO is.

In high-reactive oxidative-drying high-solids coatings, higher doses, up to 0.7%, are used. The applied film thickness of high-solids coatings is much higher than

that of medium-solids alkyd paints. These higher concentrations prevent the film from drying too fast at the top layer of the applied film. A too fast polymerization at the surface of the film would prevent the penetration of air (oxygen) and may result in the trapping of solvent as well as generated gases in the drying coating film and so result in surface defects. Moreover, an increase in the concentration of MEKO leads to a reduction in the initial polymerization speed on the surface of the applied layer. The result is that the oxygen absorption of the coating film increases and, therefore, the through-drying and hardness of a high-solids coating is improved.

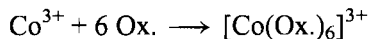
MEKO is added preferably during the let-down stage during the coating manufacture, just before the filling stage. An earlier addition, immediately after the dispersing process, into the still warm coating material can not be recommended, as in that case part of the MEKO will be lost by evaporation.

In practice, in cans with a large air space above the paint, a small quantity of a solution of MEKO, diluted to approximately 25% in aliphatic solvent, is put on the already filled coating material in the can as well. This results in additional anti-skinning action during storage.

Apart from its application as an anti-skinning agent for air-drying coatings, MEKO is widely used as a blocking agent for isocyanates and silanes in the coating industry.

### Mode of Action of MEKO

The mode of action of MEKO as an anti-skinning agent is based on its ability to complex the metal ions of primary driers, mainly cobalt and manganese<sup>[8-6]</sup> (Fig. 8.1-1).



where Ox. = methyl ethyl ketoxime

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**Figure 8.1-1.** Methyl ethyl ketoxime as complexing agent for cobalt driers

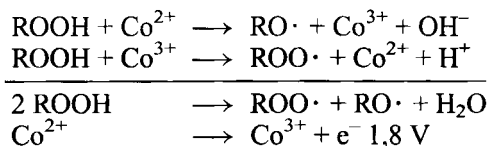
The stoichiometric relationship between cobalt and MEKO is 1 : 6. The formed complexes are quite stable in the liquid coating material. Relative to the free cobalt ion, this complex is inactive as a catalyst for autoxidation polymerization.

The oxime evaporates immediately after the coating is applied, e. g., brushed onto the substrate. Application of the coating results in a strong increase in surface area of the coating material. As soon as the paint is applied, the oxime evaporates, because of the high vapour pressure of MEKO. The complex with cobalt or other primary driers is broken up, restoring the catalytic function of the metal ion.

A primary drier, such as cobalt, accelerates the drying of oxidative drying coatings by functioning as a redox catalyst. During the drying process, oxygen from the air is absorbed onto the unsaturated groups of the resin molecules. In further stages, hydroperoxides are formed. Cobalt, and to a lesser extent other primary driers, catalyse

the formation of free radicals from the hydroperoxides; this leads to further polymerization and the formation of a dry and hardened film (see also Section 7.1.5).

Hydroperoxide decomposition:



The redox function of cobalt is explained by its high EMF for the valency change  $\text{Co}^{2+}/\text{Co}^{3+}$ .

The cobalt ion complexed with MEKO does not have this catalytic ability. Therefore, the complexed cobalt ion is inactive as a catalyst for forming radicals from the peroxides.

### 8.1.5.3 Solvents

Solvents also act as anti-skinning agents in solventborne paints; their effect is based on their dissolving of the component that causes skin formation and which forms during storage of the coating material. The selected solvent should be a good solvent for the generated skin-forming component. This method is mainly used in systems where skin formation is the result of physical processes, such as a local increase in concentration, for example, as a result of the evaporation of other solvents from the coating material.

Organic solvents are used in highly pigmented aqueous coating systems or in pigmented dispersions mainly as water-retention agents (see Section 8.1.5.4). Satisfactory results are only rarely obtained with "additive" dosages, i. e., small additions up to 5%. Solvents that have a sufficiently inhibiting effect on skin formation in additive amounts, are mainly limited to organic solventborne physically drying systems, for example, chlorinated rubber or vinyl coatings. Non-drying oils can also be used as solvents.

For oxidatively drying coatings, terpenes, such as turpentine oil (see Section 6.1.2.4), have been used to a limited extent; terpenes have an inhibiting effect on the polymerization of the binder.

A general disadvantage of using solvents for preventing skinning is, apart from their limited effectivity, that they also affect the rheological properties of the coating material.

### 8.1.5.4 Retention Agents

Retention agents are used to prevent a too rapid drying out of the coating material or pigment dispersion. Aqueous pigment dispersions or emulsion paints usually contain retention agents, which slow down the evaporation of water at the surface

of the coating. The evaporation would lead to an increase in solids concentration and subsequently the formation of a paste or solid surface layer.

A solid layer is formed by coagulation of the polymeric binder in case of emulsion paints. Furthermore, due to the evaporation of solvent and the subsequent increase in solids, pigment flocculation can occur, followed by the formation of a cake or thick skin.

The retention agent – or, for this application, also called moisturizing agent or humectant – prevents the drying out of the aqueous paint in the can, by hydration of the water molecules.

If these retention agents are not used in waterborne systems, the formation of a solid top layer, or caking at the cap and wall may result. For example, in aqueous coating materials or pigment dispersions that are stored in open cans or containers, redispersion of the dried particles becomes difficult, seed-formation results in the coating film, and the nozzles are blocked during spraying or the screen gets blocked in the case of screen printing.<sup>[8-7]</sup>

Typical examples of retention agents are high-boiling solvents such as multivalent alcohols, e. g., mono- or ethylene glycol, 1,2-propylene glycol, and glycol ether. Depending on the volatility, these retention agents remain only temporarily in the coating film after application. Because they are volatile organic solvents, these retention agents obviously cannot be used in NO-VOC- (“no volatile organic compounds”) or in solvent-free paints. As solvent-free retention agents, polyethylene glycol ether is used, as well as sucrose or urea derivatives.<sup>[8-7]</sup>

Some thickeners, such as cellulose ether and polysaccharide, also have water retention properties.

Polyethylene glycol ether is a surface-active agent and is an adduct of ethylene oxide with alcohol or water. Products that contain a long polyethylene glycol chain, for example, 15-ethylene oxide units, usually perform best. The mode of action is based on hydration of the polyethylene glycol chain. The surface activity of these compounds contributes to the effect as an overproportionally high concentration of the substances is in the top layer of the coating material.

The addition of these solvent-free retention agents inhibits the drying-out skin formation sensitivity of the aqueous coating system. However, the effectivity of organic solvents such as ethylene glycol or 1,2-propylene glycol can usually not be attained completely.

### 8.1.6 Practical Hints

All the mentioned anti-skinning agents prevent the formation of a skin or an undesired film at a specific time during the manufacturing process of the coating material and storage. During the drying stage of the coating system, the anti-skinning agent is not supposed to have a negative influence on the drying speed during the film-formation process. These demands appear to be contradictory. It is therefore important to be aware of any possible side effects related to the anti-skinning agents

in the formulation. An undesired effect is that of some anti-skinning agents which, like the antioxidants, delay the film-formation process greatly. Oximes evaporate fast and have no or a minor influence on the drying speed.

Anti-skinning agents with a high vapour density, for example, MEKO, are preferably added during the let-down stage of the coating material manufacturing process.

### 8.1.7 Toxicological Properties of MEKO

As a very widely used chemical compound, methyl ethyl ketoxime (MEKO) has been tested toxicologically according to the requirements of the American EPA (Environmental Protection Agency).

Test results show that with long exposure times additional risks could occur. Changes in red blood corpuscles were noticed. An oncogenic study showed that irreversible damage can not be excluded.

The safety-data sheet of the product shows the most actual information.

The biological decomposition of MEKO can be considered good at >70% (oxybiological activated slime, after 14 and 18 days).

### 8.1.8 Commercial Products

Exkin (CONDEA Servo)

Additol (Vianova)

Antigel (Schwegmann)

## 8.2 Light Stabilizers

*Thomas Bolle*

### 8.2.1 Introduction

Pictures for the eternity! The first traces of human art were created during the late stone age. World famous are the animal paintings in the caves of Lascaux in southern France. Several thousand years later the outstanding grave paintings of the Valley of the Gods were produced in Egypt during the New Empire. They were painted as pictures for the eternity – as symbols and company for the long trip of the pharaoh after his death.

The paints of the artists of prehistoric times were based on natural products, but already contained some of the important components of modern paints. Animal fats were used as binders, ochre was a prehistoric pigment. The day of their discovery was the end of the eternity for the prehistoric works of art. Thousands of visitors brought a lasting disturbance to the many thousands of years' balance of darkness, constant temperature, and protection from negative environmental influences. The caves of southern France and most of the graves in Egypt are closed today to preserve these unique testimonies of past cultures for future generations.

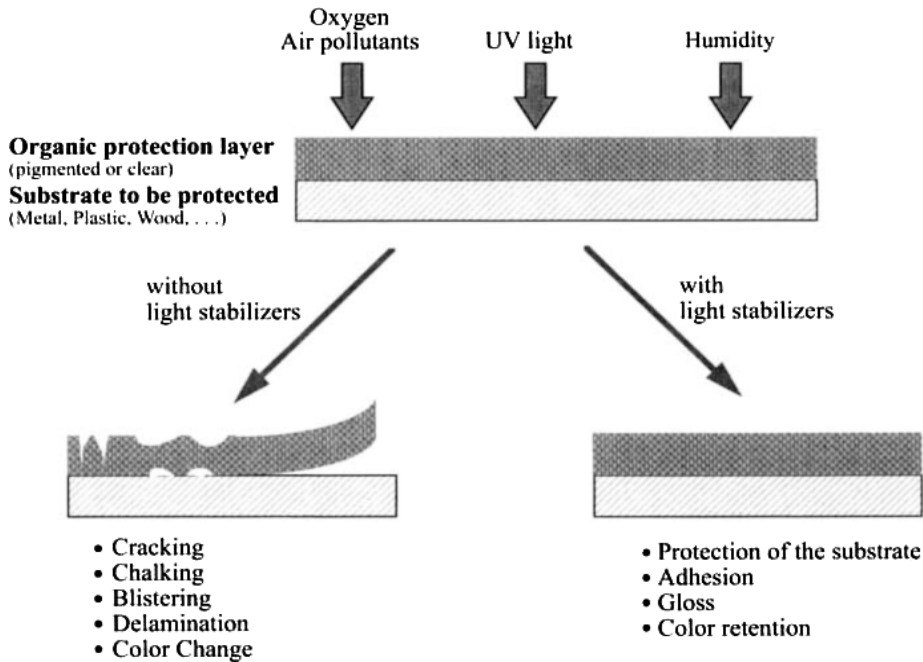
Modern coatings have not only a decorative function, they also need to protect the substrate. During their lifetime, modern paintings have to withstand drastic environmental influences. Modern paints are no longer designed for the eternity but they can reach a considerably long lifetime due to the use of highly specialized raw materials.

#### 8.2.1.1 Environmental Influences on Coatings

The binder is the backbone of a coating. Other compounds included in a coating are organic solvents, water, pigments, fillers, and additives. The binder acts as the carrier of all other coating components, brings about the adhesion to the substrate, and is mainly responsible for the quality of the coating. The functionality and lifetime of a coating after the application are also significantly influenced by the binder.

As already mentioned, a coating has to withstand various environmental influences. Fig. 8.2-1 shows the most important environmental influences and the damages caused by them. The tasks of an intact coating are also shown in Fig. 8.2-1. The loss of quality caused by UV light, oxygen, humidity, and air pollutants can be separated into two groups:

- changes on the surface, such as colour change, loss of gloss, and chalking
- reduction of the protective activity through blistering, cracking, and delamination



**Figure 8.2-1.** Environmental influences on coatings and coating damage

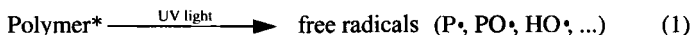
The deterioration in appearance caused by surface changes at the beginning of the lifetime of a coating can be followed by the total loss of the protective function of the coating when further damages occur (e. g., delamination). The consequence of damages of the coating can be the destruction of the substrate.

### 8.2.1.2 Photooxidation of Polymers

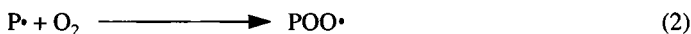
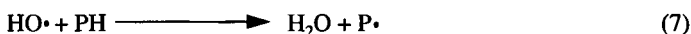
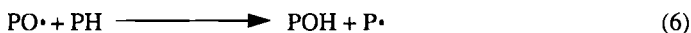
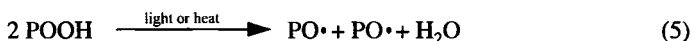
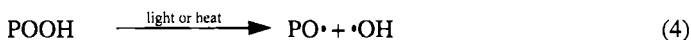
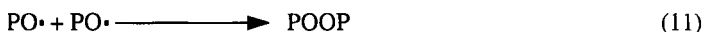
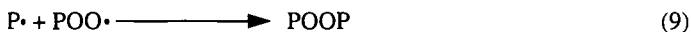
Of the environmental influences described in Section 8.2.1.1, the influence of light will be discussed in more detail.

Light is, by definition, the visible range of the electromagnetic spectrum, between 400–750 nm.<sup>[8-8]</sup> UV light is the adjacent radiation with shorter wavelengths and therefore with more energy. The considerations here will be limited to wavelengths >280 nm because shorter-wavelength radiation is absorbed by the atmosphere. The UV radiation between 280–400 nm is mainly responsible for the polymer degradation, despite UV light only making up 6% of the radiation which reaches the surface of the earth.<sup>[8-9]</sup>

Photochemical reactions can only be initiated when light is absorbed. Fig. 8.2-2 shows the most important steps of the photooxidative degradation of polymers.<sup>[8-10]</sup> The acrylate chains or aliphatic polyesters cannot absorb light. But all technical polymers contain light-absorbing impurities which can act as sensitizers. These sensitizers

**Chain initiation**

(\*: may contain:  $\text{>C=O}$ , Hydroperoxides, remaining catalyst)

**Chain propagation****Chain branching****Chain termination**

**Figure 8.2-2.** Photooxidative degradation of polymers

(e. g., remaining catalysts or solvents) can transfer the absorbed energy to the polymer chain. The consequence is the formation of radicals which can react with oxygen (photooxidation). Apart from photooxidation, purely thermal reactions can occur. Polymers such as polystyrene or aromatic polyesters absorb UV light themselves. They are susceptible against photooxidative degradation even without impurities.

**8.2.1.3 Stabilization Possibilities**

Fig. 8.2-2 also shows the basic possibilities for stabilizing polymers, namely:<sup>[8-11]</sup>

- Prevention of radical formation by filtering the damaging UV light as described in Eq. (1). *UV absorbers* are appropriate for this function. An acceptor (*quencher*) can be used when a functional group in the polymer (the “chromophore”) has already absorbed energy in the form of electromagnetic radiation. The quencher destroys the excited states of the chromophore.

- Destruction of already formed radicals before damaging consecutive reactions can occur. *Radical scavengers* can be used for this purpose. *Peroxide decomposers* can be utilized especially against peroxides.

#### 8.2.1.4 Economic Importance

Light stabilizers were primarily developed for automotive coatings. Light stabilizers were the technical basis for the development of two-layer topcoats consisting of a metallic basecoat and a final clearcoat. In 1995, 50 million vehicles were produced worldwide. An assumed average topcoat use (pigmented or clear) of 5 kg per vehicle means that 250 000 ton liquid coating needs to be stabilized.<sup>[8-12]</sup>

The stabilization of industrial coatings is also of increasing significance. Examples are wood coatings for exterior use, plastic coatings, and powder coatings.

### 8.2.2 Basic Principles

#### Classification of Light Stabilizers

The basic principles of stabilizing polymers were already described in Section 8.2.1.3. Light stabilizers can therefore be classified into four different classes:<sup>[8-12]</sup>

1. *UV absorbers*: As already described, the most important task of UV absorbers is the absorption of UV light in competition with the chromophores which are part of the polymer backbone or impurities. The aim is to prevent chromophores from being transferred in their excited state, from which radicals can be formed.
2. *Quenchers*: The excited states of chromophores can be destroyed by quenchers to result in the chromophore being transferred back to its ground state. A quencher accepts the energy of the chromophore and releases the energy as harmless heat or radiation. Organic nickel compounds are examples of quenchers.
3. *Radical scavengers*: The two different classes of radical scavengers are cyclic and non-cyclic radical scavengers. Cyclic radical scavengers are nearly exclusively *Hindered Amine Light Stabilizers* (HALS). The most important non-cyclic radical scavengers are the phenolic antioxidants which are also named primary antioxidants. The chain reaction of the polymer degradation is interrupted by phenolic antioxidants which are used up during the reaction.
4. *Peroxide decomposers*: Hydroperoxides are destroyed by peroxide decomposers which are also named secondary antioxidants. The most important compounds of this class are thioethers and phosphites. The reaction mechanism is ionic and results in the additives being used up.

It should be mentioned here that UV absorbers can react as quenchers and HALS can be active as peroxide decomposers.

The combined use of UV absorbers and HALS is of major technical importance. The combination of both compound classes results in much better protection than the use of the single compounds. UV absorber and HALS are the two light stabilizer classes which will be discussed in detail in the following chapters.

### 8.2.2.1 UV Absorbers

#### UV Absorber Classes

Harmful UV light can be absorbed by different organic molecules. Some of these molecules can dissipate the absorbed energy in a way which is harmless for the polymer. The technically most important UV absorber classes are:<sup>[8-14]</sup>

- (2-hydroxyphenyl)benzotriazoles (BTZ)
- hydroxyphenyl-*s*-triazines (HPT)
- 2-hydroxybenzophenones (BP)
- oxalic anilides

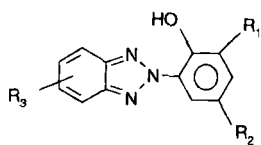
Further examples are hydroxyphenylpyrimidines, salicylic acid derivatives, and cyano acrylates. The formulae of the technically most important UV absorber classes are shown in Fig. 8.2-3.

Each of the above-mentioned UV absorber types has a characteristic spectrum. The corresponding transmission spectra can be seen in Fig. 8.2-3. At the wavelength where the polymer, which is used as a binder in coatings, has a maximum sensitivity (e. g., polyesters: 320 nm), a UV absorber needs to be able to absorb well, e. g., especially between 290–350 nm.<sup>[8-15]</sup> Depending on the substrate to be protected and impurities in the binder, an absorption at higher wavelengths may be desirable. There is an important physical limit at the beginning of the spectrum of the visible light at about 400 nm which should not be crossed. The consequence would be undesirable colour formation. It can be seen in Fig. 8.2-3 that the absorption curve of the benzotriazoles shows the strongest shift to longer wavelengths among the UV-absorber classes. This means that the benzotriazoles give the broadest protection, followed by the hydroxyphenyl-*s*-triazines. Both of these UV-absorber classes are consequently of the greatest technical importance. While oxalic anilides have only one absorption maximum, at about 300 nm, the other UV-absorber classes have two absorption maxima at longer wavelengths between 280–400 nm (benzotriazoles: > 340 nm, hydroxyphenyl-*s*-triazines: 335–340 nm, benzophenones: 320–330 nm). Tailor-made protection of the substrate is also possible with a combination of different UV absorber classes.<sup>[8-16]</sup>

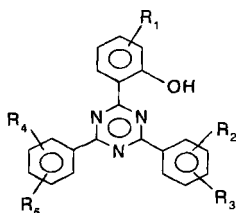
Apart from absorption characteristics of a UV absorber, the Lambert–Beer law is also an important consideration in the protection of a substrate:

$$E = \epsilon c d$$

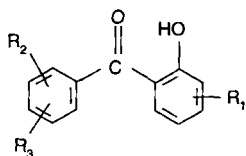
The extinction  $E$  (corresponds to the absorbance, Abs) is a measure of the filter effect of a UV absorber at a given wavelength. The Lambert–Beer law shows that the extinction depends on the extinction coefficient  $\epsilon$  ( $\text{L mol}^{-1} \text{cm}^{-1}$ ), the concentration



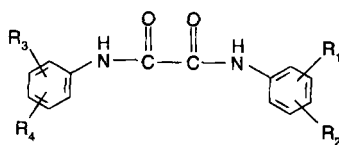
2-(2-Hydroxyphenyl)benzotriazole



Hydroxyphenyl-s-Triazine



2-Hydroxybenzophenone



Oxalic anilide

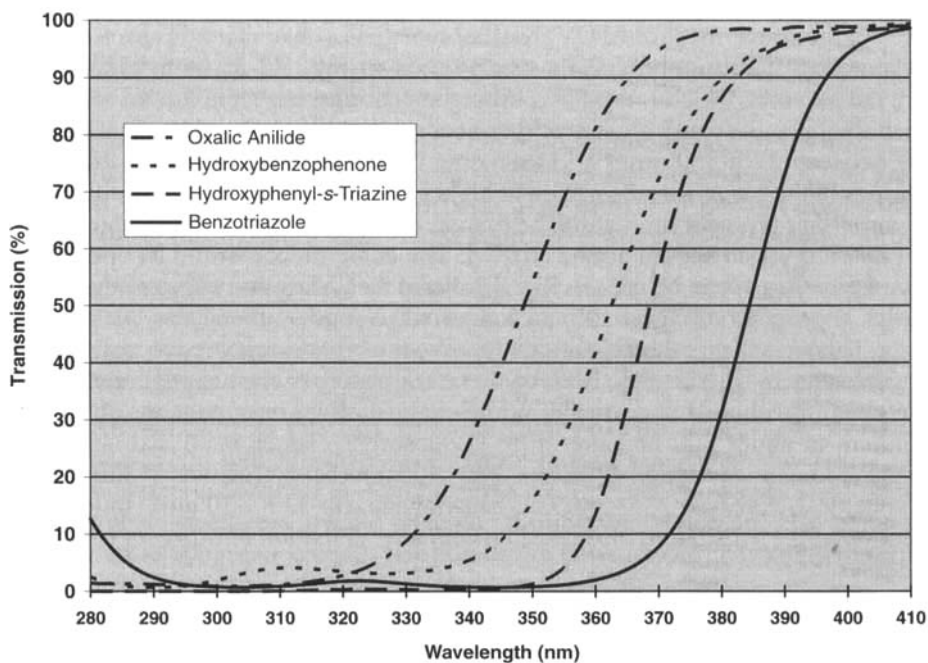


Figure 8.2-3. Formulae and transmission spectra of different UV-absorber classes (concentration:  $1.4 \times 10^{-4}$  mol L<sup>-1</sup> in chloroform)

$c$  ( $\text{mol L}^{-1}$ ) of the UV absorber, and the film thickness  $d$  (cm) of the clearcoat. The extinction coefficient  $\epsilon$  is a constant which is specific for a compound. This means that the concentration  $c$  or the film thickness  $d$  have to be increased to achieve an improved protection for the substrate.

### Mode of Action of UV Absorbers

A UV absorber has to fulfil, in principle, the following requirements: it should absorb UV light faster and better than the substrate to be protected, it must dissipate the absorbed energy quickly, and it must be able to run this cycle repeatedly. Of the technically interesting UV absorber classes, the oxalic anilides are the only ones without a phenolic OH group. Experimental results indicate an intramolecular proton transfer during the energy transformation.<sup>[8-17]</sup> To explain the energy transformation by the phenolic UV absorbers, benzotriazoles will be used as an example. It can be seen in Fig. 8.2-4 that the benzotriazole molecule is transferred from the ground state to the excited singlet state through energy uptake (energy of the UV light). This means that the nitrogen becomes more basic than the phenolic oxygen. The consequence is the “keto–enol tautomerization” shown in Fig. 8.2-4.<sup>[8-18]</sup> The absorbed energy is now dissipated very fast, preferably radiationless. The original molecule is re-established and is ready to undergo the cycle again. In the case of benzotriazoles, a long wavelength absorption maximum of 340–350 nm can be found. The exact position of the maximum depends on the polarity of the substrate and the substitution of the benzotriazole molecule.<sup>[8-19]</sup> An intact intramolecular hydrogen bond is the basis for the mechanism of the benzotriazoles described above. UV absorbers can lose their activity through disturbances like a very polar

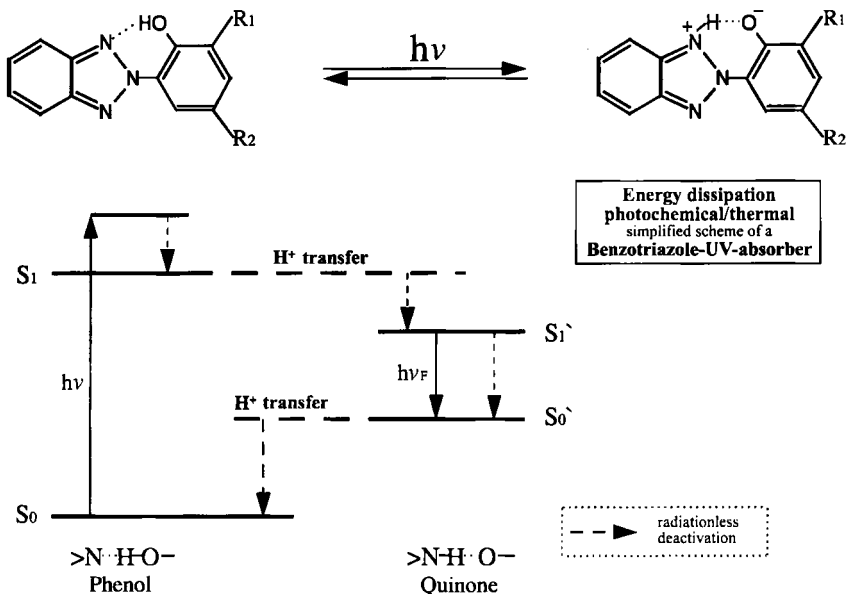
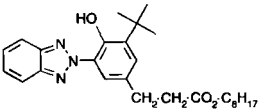
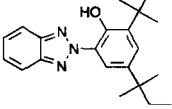
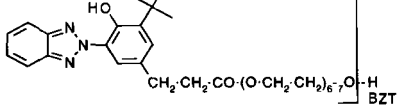
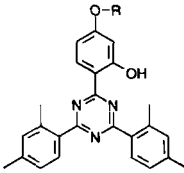
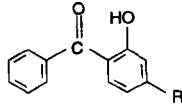
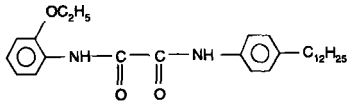


Figure 8.2-4. Mode of action of UV absorbers

Abbreviation		Structure
BTZ-1	liquid	 BTZ-1
BTZ-2	solid	 BTZ-2
BTZ-3	liquid	 BTZ-3
BTZ-4	solid	
HPT-1	liquid	 HPT-1: R = CH <sub>2</sub> ·CH(OH)·CH <sub>2</sub> ·O·C <sub>12</sub> H <sub>25</sub> /C <sub>13</sub> H <sub>27</sub> HPT-2: R = CH <sub>2</sub> ·CH(OH)·CH <sub>2</sub> ·O·CH <sub>2</sub> ·CH(C <sub>2</sub> H <sub>5</sub> )·C <sub>4</sub> H <sub>9</sub> HPT-3: R = C <sub>8</sub> H <sub>17</sub>
HPT-2	solid	
HPT-3	liquid	
BP-1	solid	 BP-1: R = O·C <sub>8</sub> H <sub>17</sub> BP-2: R = O·C <sub>12</sub> H <sub>25</sub>
BP-2	liquid	
Oxalic Anilide-1	liquid	

**Figure 8.2-5.** Structures of UV absorbers

substrate. This can also cause an increased sensitivity of the molecule against photochemical reactions.

The reaction mechanism of the hydroxyphenyl-*s*-triazines and benzophenones is similar to that of the benzotriazoles.

### Structures of Selected UV Absorbers

**Benzotriazole-1:** 2-(2-hydroxy-3-*tert*-butyl-5-propionic acid isooctyl ester)-2*H*-benzotriazole

**Benzotriazole-2:** 2-(2-hydroxy-3,5-di-*tert*-amylphenyl)-2*H*-benzotriazole

**Benzotriazole-3:** reaction product of 2-(2-hydroxy-3-*tert*-butyl-5-propionic acid methyl ester)-2*H*-benzotriazole and polyethylene glycol 300

- Benzotriazole-4: 2-[2-hydroxy-3,5-di(1,1-dimethylbenzyl)phenyl]-2*H*-benzotriazole
- HPT-1: 2-{4-[(2-hydroxy-3-dodecyloxy/tridecyloxypropyl)oxy-2-hydroxyphenyl]}-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine
- HPT-2: 2-[4-(2-hydroxy-3-(2-ethylhexyl)oxy-2-hydroxyphenyl)]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine
- HPT-3: 2-(4-octyloxy-2-hydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine
- Benzophenone-1: 2-hydroxy-4-octyloxybenzophenone
- Benzophenone-2: 2-hydroxy-4-dodecyloxybenzophenone
- Oxalic anilide-1: *N*-(2-ethoxyphenyl)-*N'*-(4-isododecylphenyl)ethanediamide

The corresponding structures are shown in Fig. 8.2-5.

### 8.2.2.2 Hindered-Amine Light Stabilizers (HALS)

#### Mechanism of HALS

The 2,2,6,6-tetramethylpiperidine group is the basic structure of all the technically relevant HALS compounds. The active compounds are the nitroxide radicals which are formed from the basic compounds. Fig. 8.2-6 shows a modified Denisov cycle, which describes the basic reaction scheme of HALS.<sup>[8-20, 8-21, 8-22]</sup> The original 2,2,6,6-tetramethylpiperidine group is converted into a nitroxide radical under the influence of oxygen and light. Investigations indicate that this can be a direct reaction or a reaction via the NH-intermediate. Steric hindrance in the  $\alpha$ -position of the nitroxide radical is required for the formation of a stable radical. The next step is the formation of an aminoether by recombination of radicals. The aminoether reacts

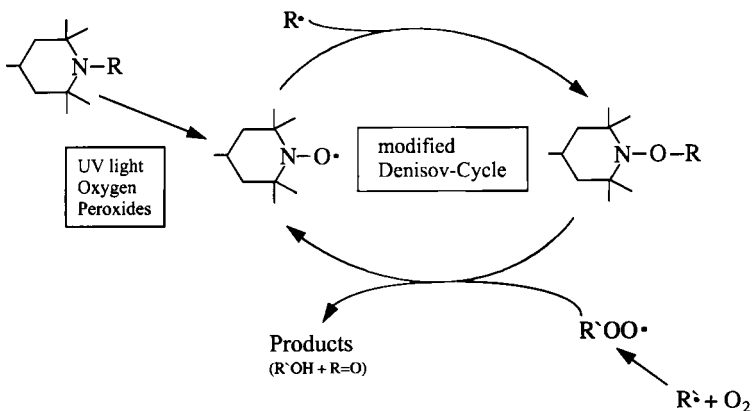


Figure 8.2-6. Mode of action of HALS – modified Denisov cycle

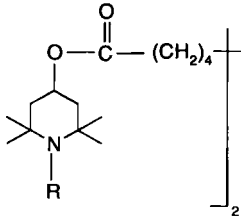
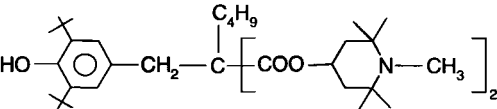
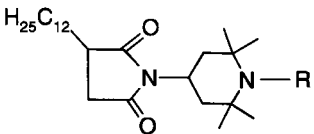
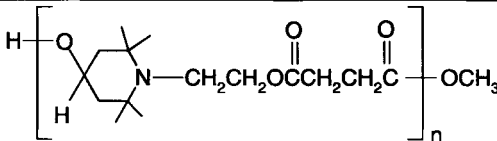
Abbreviation	pK <sub>b</sub> value	Structure
HALS-1 HALS-2 HALS-3	5.0 5.0 9.6	 <p>R = H (solid) R = CH<sub>3</sub> (liquid) R = OC<sub>8</sub>H<sub>17</sub>(iso) (liquid)</p>
HALS-4	5.3	 <p>(solid)</p>
HALS-5 HALS-6	5.3 11.5	 <p>(liquid) R = CH<sub>3</sub> R = COCH<sub>3</sub></p>
HALS-7	7.5	 <p>(solid)</p>

Figure 8.2-7. Structures of HALS compounds

with peroxy radicals which again leads to the formation of nitroxide radicals. The destruction of the peroxy radicals results in the formation of alcohols or carbonyl groups. The type of products that are formed depends on the substrate.<sup>[8-23]</sup> Stable nitroxide radicals cannot be used directly because of their red colour. This would result in unacceptable colour formation in the substrate at concentrations >0,5%.

The formation of nitroxide radicals reduces the concentration of peroxy radicals in the coating significantly. This could be proven by experiments in acrylate/melamine clearcoats.<sup>[8-24]</sup> At the same time, a reduced formation of carbonyl groups could be observed. The formation speed of nitroxide radicals is significantly influenced by the substitution at the piperidine nitrogen of the HALS molecule. The formation of nitroxide radicals is much faster for N-CH<sub>3</sub> than for N-COCH<sub>3</sub> compounds.<sup>[8-25]</sup> This explains the superior protection with HALS containing N-CH<sub>3</sub>.

### Structures of Selected HALS

- HALS-1: bis(2,2,6,6-tetramethyl-4-piperidiny)sebacate  
 HALS-2: bis(1,2,2,6,6-pentamethyl-4-piperidiny)sebacate  
 HALS-3: bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidiny)sebacate  
 HALS-4: bis(1,2,2,6,6-pentamethyl-4-piperidiny)[3,5-bis(1,1-dimethylethyl-4-hydroxyphenyl)methyl]butylpropandioate  
 HALS-5: *N*-(1,2,2,6,6-pentamethyl-4-piperidiny)-2-dodecyl succinimide  
 HALS-6: *N*-(1-acetyl-2,2,6,6-tetramethyl-4-piperidiny)-2-dodecylsuccinimide  
 HALS-7: *N*-(2-hydroxyethyl-2,2,6,6-tetramethylpiperidin-4-ol succinic acid copolymer

The corresponding structures are shown in Fig. 8.2-7.

## 8.2.3 Properties of Light Stabilizers

### 8.2.3.1 Requirements for Light Stabilizers

#### Automotive Coatings

The main application of light stabilizers is in automotive coatings. This means that most of the results with light stabilizers were generated in transportation coatings. The composition of automotive coatings is as follows: phosphate pre-treatment, electrocoating, primer surfacer, topcoat. The topcoat can be a one-coat solid shade or a clearcoat/colourcoat system. Clearcoat/colourcoat systems consist of a pigmented basecoat with a clearcoat applied on top of the basecoat.

The most important resin technologies for automotive coatings are described below:<sup>[8-26, 8-27]</sup>

- thermosetting acrylic resins with melamine cross-linking (thermosetting acrylics = TSA); high-solids TSA (HS-TSA) contain a high ratio of binder and a reduced solvent level; an acid catalyst is required for the high-solids technology
- two-pack polyurethane coatings (2P-PUR); the acrylic polyol reacts with an isocyanate cross-linker
- one-pack polyurethane coatings (1P-PUR); an acrylic polyol reacts with a blocked isocyanate cross-linker

Other resin technologies of technical importance are alkyd/melamine coatings and coatings based on epoxy acrylate/anhydride or carbonic acid. Powder coatings and UV-curable coatings are totally solvent-free and have been introduced recently. They are partly based on the above-mentioned binder systems.

In clearcoat/colourcoat systems a combination of UV absorbers and HALS is widely used. The benefit of the use of UV absorbers is mainly colour retention and the adhesion of the clearcoat or the complete topcoat. The use of HALS guarantees

long-lasting gloss retention and prevents the coating from cracking. Typical use levels in clearcoats of 40  $\mu\text{m}$  film thickness are 1.5–2% UV absorber and 1% HALS, calculated on binder solids. The stabilization of basecoats can also improve the weatherability, depending on the binder technology and the weatherfastness of the pigments used in the basecoat.

Requirements for UV absorber and HALS:

- primary requirements for UV absorbers: high extinction coefficient, broad absorption band between 290–380 nm, steep absorption curve in the near-UV light range and photochemical stability
- primary requirement for HALS: high efficiency
- secondary requirements for UV absorbers and HALS: good solubility in typical solvents used in coatings, preferably liquid; resistance against extraction; low volatility between 80–160 °C; good compatibility with the binder; no interaction with other coating components; ease of incorporation in waterborne coating systems (preferably without co-solvents) or with powder coatings (melting point close to the extrusion temperature)

### 8.2.3.2 Solubility and Compatibility of Light Stabilizers

Light stabilizers should dissolve well in solvents frequently used for coatings (e. g., methyl ethyl ketone, *n*-butanol, ethyl acetate). Liquid light stabilizers are especially easy to handle. An example of limited solubility is BTZ-4 (0.4% in *n*-butanol and 4% in ethyl acetate). Liquid light stabilizers such as BTZ-1, BTZ-3, HPT-1, HALS-2, and HALS-3 have excellent solubility of >50% in the above-mentioned solvents. The incorporation in waterborne coatings requires, as a rule, liquid light stabilizers. They can be added to the binder before the addition of water or post-added later by dispersion. Solid light stabilizers with a melting point close to the extrusion temperature (70–100 °C) are preferred for powder coatings. Higher melting points can cause insufficient distribution of the light stabilizer or recrystallization. Light stabilizers should generally be compatible with the polymer matrix of the binder. Incompatibilities can lead to layer formation on the coating surface after bake or storage at elevated temperatures.

### 8.2.3.3 Volatility of Light Stabilizers

An automotive topcoat has to withstand various thermal stresses. Temperatures of significantly above 120 °C can be reached upon bake which can apply for a longer time when production lines are stopped. Elevated air temperatures in combination with dark colours can result in extremely high surface temperatures of the car body. This means that the volatility of light stabilizers should be low. Apart from the polymer matrix and the cross-link density of the binder, the side chains of the light stabilizer mainly determine the volatility. A higher molar mass normally reduces the volatility but can also lead to solubility problems. The following volatilities

have been measured in a TSA clearcoat (film thickness: 20  $\mu\text{m}$ , bake: 130 °C, 30 min + overbake: 150 °C, 60 min): BTZ-2, BP-1 > 80%; BTZ-3 1–2%; HPT-1, HPT-2 < 1%. Another possibility for reducing the volatility of light stabilizers is the co-reaction with the polymer matrix. Examples are HPT-1, HPT-2, and BTZ-3 which have reactive OH groups. These OH groups can react with isocyanate or melamine cross-linkers.

#### 8.2.3.4 Influence of the Own Colour of a Light Stabilizer

UV absorbers have a yellowish aspect in contrast to HALS which do not absorb at wavelengths of more than 250 nm. The influence of this own colour on the colour of the coating can be investigated after bake and overbake of a TSA clearcoat over a white basecoat. As expected from the Lambert–Beer law the yellowing of the clearcoat (characterized by the yellowness index, YI) increases with increasing UV absorber concentration and increasing film thickness. The yellowing can be minimized with oxalic anilide-1 or HPT-1.

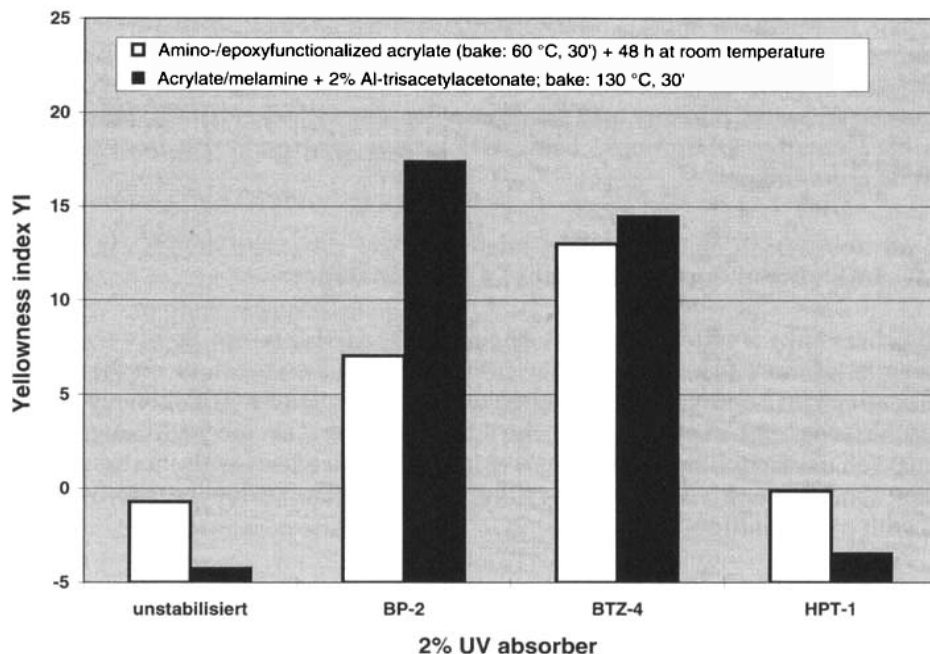
#### 8.2.3.5 Interaction of UV Absorbers with Other Coating Components

Reactive coating components such as amines or metal catalysts can react with UV absorbers. This can result in undesirable yellowing of the clearcoat. UV absorbers with phenolic OH groups can interact with these reactive coating components due to a possible disturbance of the intramolecular hydrogen bond leading to the formation of chinoid structures. Fig. 8.2-8 demonstrates the interaction tendency of phenolic UV absorbers as obtained from model experiments.

- The yellowing of a 2P epoxy clearcoat (film thickness 30  $\mu\text{m}$ ) after bake and 48 h storage at room temperature can be monitored by measuring the increase of the yellowness index, YI. While benzophenones and benzotriazoles show strong yellowing, this interaction tendency is nearly completely missing with hydroxyphenyl-*s*-triazines.<sup>[8-14]</sup> This behaviour is also found in strongly basic amines.
- 2% Aluminium trisacetylacetonate is added to a TSA clearcoat which is applied over a white basecoat and cured at 130 °C for 30 min (film thickness 40  $\mu\text{m}$ ). The result is comparable with a 2P epoxy clearcoat. HPT-1 is close to the unstabilized sample. With BP-2 and BTZ-4 strong yellowing is observed. Interactions can also be found with catalysts such as zinc octanoate or tin catalysts.

#### 8.2.3.6 Permanence of UV Absorbers

The retention of UV absorbers in a coating depends mainly on their volatility, compatibility, extractability, and photochemical stability. Fig. 8.2-2 shows the



**Figure 8.2-8.** Interaction trend of phenolic UV absorbers in basic and metal-catalysed coatings

most important reaction steps during the photooxidation of polymers. UV absorbers are organic molecules which can be part of the photooxidative degradation themselves.<sup>[8-28]</sup> This underlines the importance of the radical density in the binder for the permanence of UV absorbers. The radical density differs strongly depending on the binder class. A high radical density can be found in HS-TSA and TSA clearcoats. The conditions during the acrylate synthesis is the other important factor for the radical density.<sup>[8-29]</sup> Residual solvent and remaining catalysts are important for the radical formation. Significantly less radicals are formed in 1P-PUR and 2P-PUR clearcoats which means less radical attack on UV absorbers. The radical density in a coating also depends on the radiation energy and the addition of HALS. The lifetime of a UV absorber can be markedly increased by the addition of HALS.<sup>[8-30]</sup> Another very important factor is the film thickness of the clearcoat. A higher film thickness causes an increasing internal filter effect. This results in better protection of UV absorber molecules which are in the deeper layers of the clearcoat.<sup>[8-31]</sup> Oxalic anilides and benzophenones are photochemically less stable than benzotriazoles, as is known from the literature.<sup>[8-32, 8-33]</sup> The consequence is insufficient adhesion after five years Florida exposure when oxalic anilide-1 is used in clearcoats. In contrast to oxalic anilides, complete adhesion was found with benzotriazole-3. The photochemical permanence of the most important UV absorber classes can be ranked as follows: hydroxyphenylbenzotriazoles  $\gg$  oxalic anilides  $\approx$  hydroxybenzophenones.<sup>[8-13]</sup> Hydroxyphenyl-*s*-triazines are comparable to benzotriazoles.

### 8.2.3.7 Side Reactions of HALS

The tendency of HALS to interact with other coating components is mainly influenced by their basicity. The basicity depends decisively on the substitution of the piperidine nitrogen. The lower the  $pK_b$  value, the higher the basicity of the compound is. The stronger basic HALS with H- or  $CH_3$  substitution of the nitrogen have  $pK_b$  values of around 5. HALS with acyl- or *O*-alkyl substitution have no basic reactivity. More strongly basic HALS may occasionally cause problems:

- When *H*-substituted HALS are used instead of HALS-1, the pot life of 2P-PUR coatings that are catalysed by bases can be reduced.
- When basic HALS are used, salt formation may occur with the catalyst in acid-catalysed coatings such as HS-TSA coatings. The consequence is that the coating is insufficiently cured.

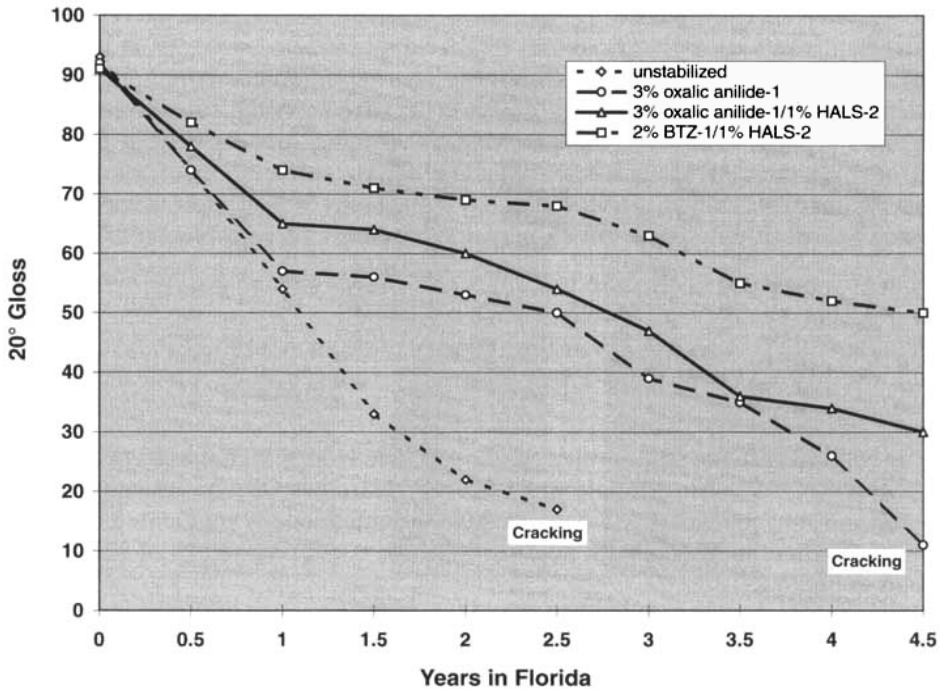
These coating systems require the use of non-basic HALS. Examples are HALS-3 or HALS-6.<sup>[8-34, 8-35]</sup> An example are HS-TSA clearcoats which are catalysed by *p*-toluene sulfonic acid. HALS-3 can also be recommended for pigmented one-coat solid shades where pigments with acid surfaces are used.  $pK_b$  values of HALS can be found in Fig. 8.2-7.

## 8.2.4 Use of Light Stabilizers

### 8.2.4.1 Stabilization of Clear Coatings/Colour Coatings

The make-up of automotive coatings was discussed in Section 8.2.3.1. The following examples describe the use of light stabilizers in more detail. The corresponding evaluation methods and evaluation criteria can be found in Section 8.2.5.1.

Fig. 8.2-9 shows the effectiveness of UV absorbers and HALS in a TSA clearcoat over a silver metallic basecoat after outdoor exposure in Florida. The evaluation criteria used for this coating are the 20° gloss and time before cracking occurs. A significant loss of gloss after short exposure times can be found when no light stabilizers are used. Cracking occurs after 2.5 years. The single use of a UV absorber cannot prevent the coating from strong loss of gloss and cracking after 4.5 years in Florida. This is demonstrated with the use of oxalic anilide-1 which is even employed at elevated concentration (3% based on binder solids). The addition of 1% HALS-2 results in a slightly improved gloss retention and time before cracking. The best result could be achieved with a combination of 2% BTZ-1 and 1% HALS-2. The loss of gloss can be slowed down from the beginning. The 20° gloss remains on a high level even after several years of Florida exposure. This could be achieved with less BTZ-1 than oxalic anilide-1. The broader-spectrum coverage of benzotriazoles which was discussed in Section 8.2.2 is seen here. This can also be shown by evaluating the adhesion after 5 years Florida exposure. A standard test method is additional humidity exposure of the coating (40 °C, 48 h) followed by the



**Figure 8.2-9.** Stabilization of two-layer topcoats: Florida exposure of a TSA clearcoat over a waterborne silver-metallic basecoat

cross-cut test. Complete adhesion could only be achieved with 2% BTZ-1 and 1% HALS-2 as stabilizers of the clearcoat.

The filter effect of different UV absorber classes can also be monitored with the colour change  $\Delta E$  of the topcoat after exposure. Table 8.2-1 shows the colour change of a topcoat consisting of a TSA-clearcoat applied on basecoats of different pigmentation after 54 months Florida exposure. The protection is worst with oxalic anilide-1. The improvements achievable with benzophenone-2 are minor; this is surprising because of the slightly better spectrum coverage of benzophenones (see

**Table 8.2-1.** Filter effect of different UV-absorber classes in a TSA clearcoat over basecoats with different pigmentations (exposure: 54 months in Florida)

Stabilization	Colour change, $\Delta E$		
	Red metallic	Yellow metallic	Violet metallic
Unstabilized	31.3	28.9	38.2
2.5% Ox. anilide-1	23.8	14.6	21.1
2.5% BP-2	19.2	15.1	18.5
2.5% BTZ-3	10.1	4.3	3.0

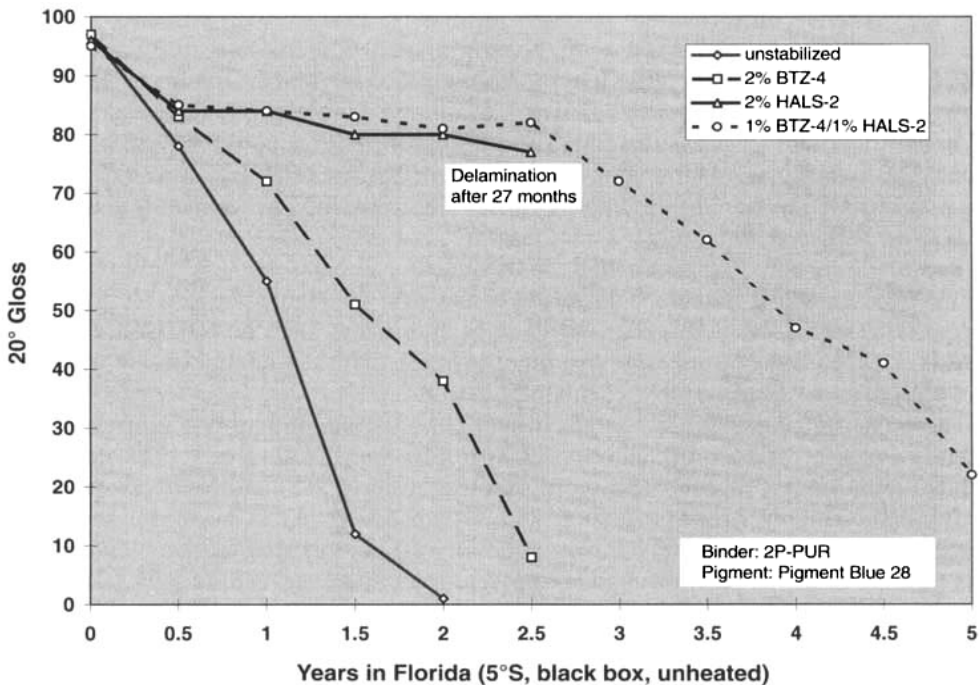
Fig. 8.2-3). The colour change is much lower with BTZ-3. The best protection of the basecoat can be achieved with benzotriazoles due to their absorption edge which is shifted to longer wavelengths compared with that of oxalic anilides and benzophenones. An additional benefit is the much higher photochemical stability of benzotriazoles. Best results regarding colour retention could be attained with blends of hydroxyphenyl-*s*-triazines and benzotriazoles. This can be explained by the combination of the high extinction of HPT at 300 nm with the better absorption of BTZ at longer wavelengths.

These results can also be transferred to waterborne clearcoats. A combination of BTZ-3 and HALS-2 is widely used due to the ease of incorporation. Good results can also be achieved with other liquid light stabilizers such as HPT-1, BTZ-1, or HALS-3. Solid light stabilizers have the drawback that they cannot be incorporated in waterborne systems in most of the applications.

The question of the benefit of additional basecoat stabilization is addressed frequently but a clear recommendation is difficult. Stabilization of the basecoat depends on its binder, pigmentation, use of additives and the coating layers over it or underneath. The improved protection with UV absorbers in the basecoat can also be achieved with an accordingly higher amount of UV absorber in the clearcoat. In this case the focus is on improved colour retention and long-lasting adhesion of the basecoat on a substrate which is sensitive to UV light. The recommendations for the use of HALS are different. The addition of HALS-2 or HALS-3 can improve the stability of the basecoat when light-sensitive basecoat binders and non-weather-fast pigments are used. Especially gloss retention and adhesion could be improved. The evaluation of additional basecoat stabilization should start with 1% HALS.

#### 8.2.4.2 Stabilization of One-Coat Solid Shades

One-coat solid shades are pigmented topcoats that have no protecting clearcoats applied over them. The sedimentation of pigments before the bake of the coating results in a very thin pigment-free film on top of the coating. Because this film is so thin, it is impractical to stabilize it with UV absorbers. This would require extremely high UV absorber concentrations according to the Lambert–Beer law. In one-coat solid shades the use of UV absorbers is normally not required due to the fact that pigments absorb UV light. A basic stabilization with 1.5–2% HALS can be recommended here. This results in the protection of the binder and prevents it from early matting or chalking caused by binder degradation. But it can also make sense to use UV absorbers in one-coat solid shades. Fig. 8.2-10 shows a typical example. The pigmented 2P-PUR topcoat contains a cobalt spinel pigment which is not completely impermeable to UV light. It can be seen in Fig. 8.2-10 that the unstabilized coating is completely dull after 2 years Florida exposure. As expected the use of 2% BTZ-4 alone does not result in significant improvements. Much better protection is achieved with 2% HALS-2, but delamination occurs after 27 months Florida exposure. The delamination occurs between the pigmented topcoat and the light-sensitive epoxy primer. The transparent pigment could not prevent the binder from



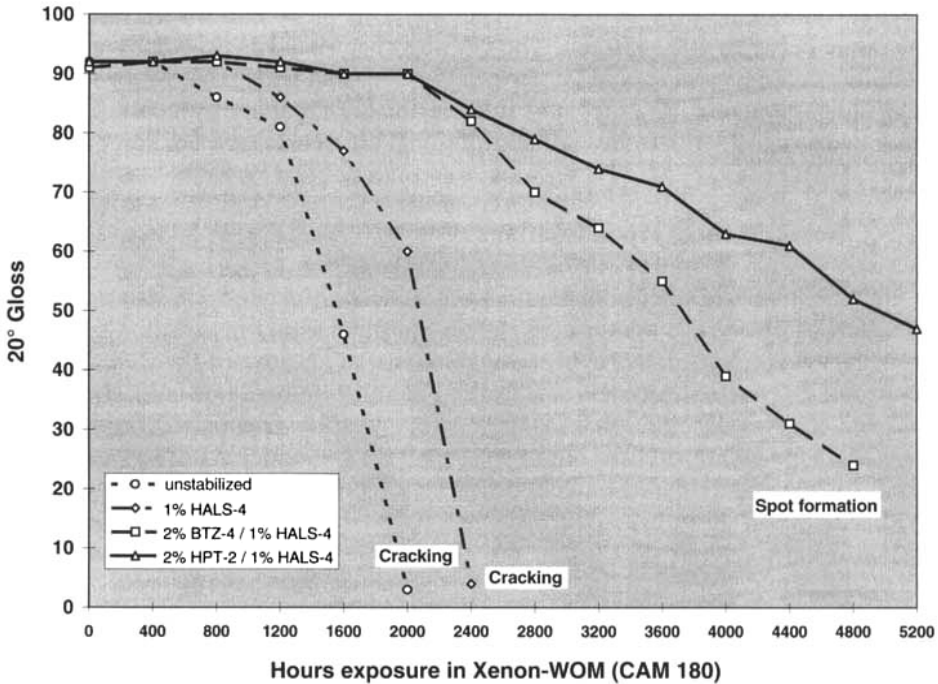
**Figure 8.2-10.** Use of UV absorbers in one-coat solid shades: Florida exposure of a blue-pigmented 2P-PUR topcoat

the degradation caused by UV light. This problem could be solved by a combination of 1% BTZ-4 and 1% HALS-2. The other area where UV absorbers should be used in addition to HALS are in one-coat solid shades with low pigment volume concentration.

These findings can be transferred to industrial coatings. The protection of the binder with HALS in pigmented topcoats can result in distinctively improved corrosion protection.

### 8.2.4.3 Stabilization of Powder Coatings

Powder clearcoats for automotive coatings are still a niche application, but interest in this has grown recently. The considerations regarding stabilization are the same as for clearcoat/colourcoat systems (see Section 8.2.4.1). The main differences to liquid coatings are the higher film thicknesses of powder clearcoats (60–80  $\mu\text{m}$ ), the extrusion process applied to incorporate additives, and the coating application. In contrast to liquid coatings, light stabilizers for powder coatings should be solid and melt close to the extrusion temperature (70–110  $^{\circ}\text{C}$ ). Higher melting points can lead to problems during incorporation of the light stabilizers. Fig. 8.2-11 shows the stabilization of an epoxy acrylate cross-linked with carbonic acids. A Xenon



**Figure 8.2-11.** Stabilization of a powder clearcoat: accelerated weathering of a topcoat consisting of an epoxy acrylate cross-linked with carbonic acids

weatherometer was used for the accelerated weathering. The unstabilized powder coating cracked after 2 000 h. The addition of 1% HALS-4 cannot significantly improve the stability. Much better protection is achieved with a combination of 2% UV absorber with 1% HALS-4. The best results were with HPT-2. Another advantage of HPT-2 is the least yellowing in this coating system after bake and overbake. HPT-2 can also be used to stabilize polyester-based powder coatings, e. g., polyester cross-linked with blocked isocyanates or TGIC (Trisglycidyl isocyanurate). HALS-4 which is especially suitable for polyacrylates, should be replaced by HALS-7 in polyester-based powder coatings. Typical use levels are 0.5–2% UV absorber (depending on the pigmentation) and 1–2% HALS.

#### 8.2.4.4 Stabilization of UV-Curable Clear Coatings

The combined use of photoinitiators and UV absorbers was considered to be impossible for a long time due to competitive UV absorption. It is known today that UV-curable clearcoats can also be stabilized.<sup>[8-36, 8-37]</sup> The absorbance spectra of the UV absorber and the photoinitiator do not overlap completely. The photoinitiator can absorb enough light to be cleaved and start the curing reaction even when a UV absorber is used. The best photoinitiator recommendation is the combination of a

bisacylphosphin oxide with an  $\alpha$ -hydroxyketone. This blend can absorb visible light in the range between 400–450 nm. The UV absorber HPT-1 is especially useful for UV-curable coatings and should be used in combination with HALS-2 or HALS-3. Liquid light stabilizers are especially suitable for UV-curable clearcoats. The typical use levels correspond to those of conventional clearcoats (see Section 8.2.4.1).

### 8.2.4.5 Stabilization of Wood Coatings

The use of clearcoats on wood requires the stabilization with UV absorbers and HALS. Typical use levels are the same as for automotive coatings. Some additional aspects have to be considered with coatings for wood because of the difference between wood and other substrates. The use of phenolic antioxidants or HALS in pre-treatments can have a direct stabilization effect on the wood (typical use level is 1% on total formulation). The combination of BTZ-1 and HALS-3 is especially suitable for clearcoats based on long-oil alkyd resins. The UV absorber prevents early discoloration of the wood surface. The use of HALS significantly delays the cracking of the clearcoat. The use of UV absorbers alone can be recommended for wood coatings which are used indoors (e.g., parquet or furniture).

## 8.2.5 Guidelines for the Use of Light Stabilizers

### 8.2.5.1 Evaluation Methods

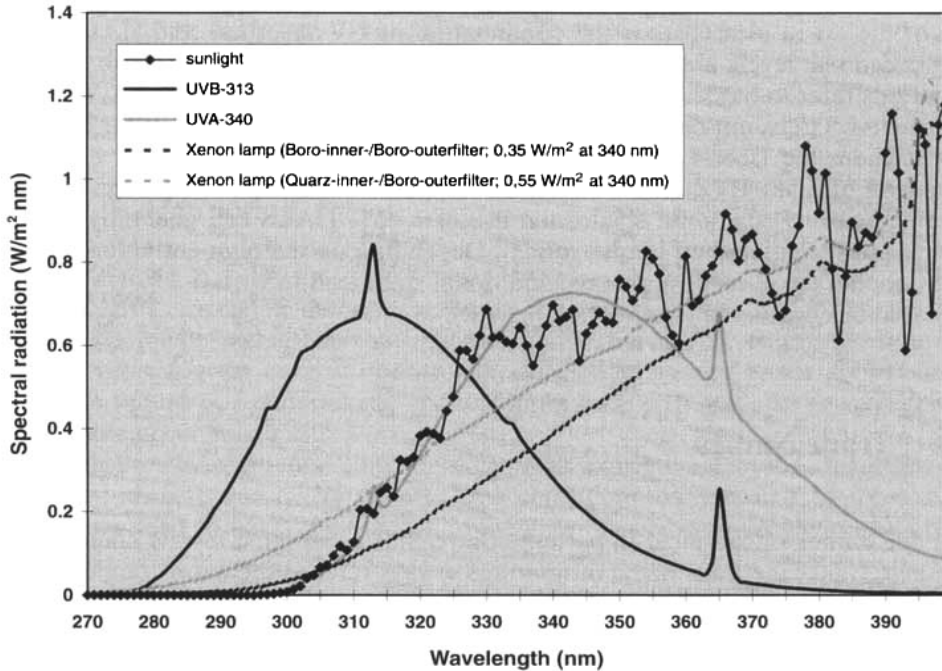
Two basic methods can be used to assess the stability of coatings towards weathering: outdoor exposure or accelerated weathering.

The outdoor exposure should correspond to the daily use of a coating and deliver fast results. Florida exposure (tropical climate) is a worldwide standard for automotive coatings. Alternative places for outdoor exposure are: Arizona (dry desert climate), Allunga/Australia (high UV doses) and Jacksonville/Florida (tropical climate + air pollution). Local outdoor exposure stations can also be used, but it depends on the substrate and the application.

Artificially accelerated weathering is used to drastically reduce evaluation times. An acceptable correlation with outdoor exposure is required. The most important methods used for accelerated weathering are listed below:

- xenon weatherometer (Atlas): CAM 180-cycle (SAE-J 1960);  $0.55 \text{ W m}^{-2}$
- xenon weatherometer (Atlas): CAM 7-cycle (102 min light at  $60^\circ\text{C}$ , 18 min light with rain at  $40^\circ\text{C}$ );  $0.35 \text{ W m}^{-2}$
- UVCON (Atlas), QUV (Q-Panel): fluorescence lamps UVB-313 or UVA-340; Cycle: 8 h UV at  $70^\circ\text{C}$ , 4 h condensation at  $50^\circ\text{C}$

The corresponding lamp spectra are shown in Fig. 8.2-12. The cracking of clearcoats can be investigated under UVB-313 conditions. A drawback is the poor corre-



**Figure 8.2-12.** Spectra of different lamp types that are used for accelerated weathering (from Q-Panel Lab Products)

lation with the outdoor exposure of one-coat solid shades or the colour retention of clearcoat/colourcoat topcoats. The best correlation of outdoor exposure and accelerated weathering can be achieved with Xenon lamps due to the similarity of their spectrum to that of sunlight. A meaningful prediction of the loss of gloss, cracking, colour change, and adhesion is possible with Xenon lamps. A disadvantage is the longer exposure times compared with UVB-313 conditions. Table 8.2-2 shows the most important evaluation criteria for coatings.

**Table 8.2-2.** Evaluation criteria for coatings

Evaluation criterion	Standard
Gloss (20°, 60°, 85°)	DIN 67530
DOI (Distinctness of Reflected Image)	ASTM E 430
Colour change $\Delta E$	DIN 6147
Yellowness index, YI	ASTM D 1925
Adhesion (cross-cut test)	EN ISO 2409
Cracking	TNO scale

### 8.2.5.2 Recommendations for the Use of Light Stabilizers

State of the art in clearcoats is the combination of UV absorbers and HALS. Recommended use levels are 1–3% UV absorber and 0.5–2% HALS. These recommendations refer to binder solids (including hardener at 2P-PUR coatings). The use level of HALS does not depend on the film thickness which is different for UV absorbers where the Beer–Lambert law has to be considered (see Section 8.2.2.1). A use level of 1.5% BTZ-1 in a 40  $\mu\text{m}$  thick clearcoat may be used as a guideline. In pigmented one-coat solid shades the use of 1–2% HALS can generally be recommended (calculated on binder solids). Depending on the pigment volume concentration and the class of pigments, additional stabilization with 0–2% UV absorber should be considered (see Section 8.2.4.2).

### 8.2.6 Trade Names

The trade names of the most important compounds mentioned in this chapter are given here (note: the trade name of mixtures always refer to the main compound of the corresponding light stabilizer):

BTZ-1:	TINUVIN <sup>®</sup> 384 (Ciba Specialty Chemicals)
BTZ-3:	TINUVIN <sup>®</sup> 1130 (Ciba Specialty Chemicals)
HPT-1:	TINUVIN <sup>®</sup> 400 (Ciba Specialty Chemicals)
HPT-2:	TINUVIN <sup>®</sup> 1545 (Ciba Specialty Chemicals)
Ox. Anilide-1:	Sanduvor <sup>®</sup> 3206 (Clariant)
HALS-2:	TINUVIN <sup>®</sup> 292 (Ciba Specialty Chemicals)
HALS-3:	TINUVIN <sup>®</sup> 123 (Ciba Specialty Chemicals)
HALS-4:	TINUVIN <sup>®</sup> 144 (Ciba Specialty Chemicals)
HALS-5:	Sanduvor <sup>®</sup> 3056 (Clariant)
HALS-6:	Sanduvor <sup>®</sup> 3058 (Clariant)

Tradenames are the property of the respective owners.

### 8.2.7 Toxicology and Waste Treatment

For questions concerning toxicology and waste treatment the safety data sheets of the producers of the light stabilizers are referred to.

## 8.3 Corrosion Inhibitors

*Adalbert Braig*

### 8.3.1 Introduction

Metal-corrosion-related damage accounts for losses of ca. 3–5% of the GNP (Gross National Product) in the industrialized nations. This enormous figure explains both the great interest in corrosion protection, as well as the significant efforts the industry is undertaking in developing both efficient and environmentally acceptable novel concepts.

Increasing environmental concern along with legislative activities regarding both solvent emissions and heavy metals (lead, chromium, barium, and, to some extent, zinc) have led to novel approaches in the area of corrosion protection by organic coatings in the past years. Amongst these are, in particular, the development of water-borne coatings and non-heavy-metal-based anticorrosive pigments, as well as that of purely organic corrosion inhibitors, specifically designed for coating applications.

#### 8.3.1.1 Basics

According to Kaesche,<sup>[8-38]</sup> the corrosion of metals can be defined as the destruction of a metal, commencing at the surface, by chemical reactions with components of its environment. The resulting corrosion products can be either solid (e. g., layer-forming oxides or carbonates) or soluble (e. g., sulphates, chlorides, nitrates).

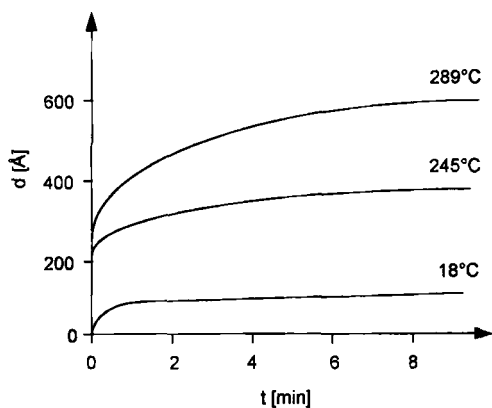
Most metals that are important for industrial or automotive applications such as steel, aluminium, or galvanized steel have a strong affinity for oxygen which leads to an almost spontaneous formation of thin oxide layers. This affinity (Table 8.3-1) can be expressed in terms of the  $G_0$  values ( $G_0$  = partial molar free enthalpy for the formation of 1 mol metal oxide under standard conditions, i. e., 298 K, standard pressure).<sup>[8-39]</sup>

The composition of these oxide layers has a major influence on the corrosion behaviour of the individual metals. In the case of, e. g., aluminium, a pore-free oxide layer forms, which is partially incorporated into the surface lattice of the metal (self-passivating, protective oxide layer). With increasing thickness of the oxide layer, the reaction with oxygen is slowed down and eventually stopped, i. e., as soon as oxygen can no longer reach the metal surface. Iron behaves quite differently, as shown in Fig. 8.3-1, within seconds oxide layers in the range of ca. 100 Å form.

These oxide layers, however, are porous in nature and adhere poorly to the metal surface. As a result, oxygen diffusion to the metal surface is greatly unhindered, leading to complete consumption of the metal through oxidation.

**Table 8.3-1.** Affinity values of various metals towards oxygen

Metal oxide	$G_{0(298)}$ in $\text{kJ mol}^{-1}$
$\text{Ag}_2\text{O}$	-11.2
$\text{Al}_2\text{O}_3$	-1582.4
$\text{Cr}_2\text{O}_3$	-1058.1
$\text{Cu}_2\text{O}$	-146.0
$\text{FeO}$	-245.1
$\text{Fe}_2\text{O}_3$	-1015.5
$\text{Fe}_3\text{O}_4$	-742.2
$\text{NiO}$	-211.7
$\text{ZnO}$	-318.3

**Figure 8.3-1.** Thickness ( $d$ ) of iron oxide layers, under normal atmosphere, as a function of temperature and time ( $t$ ) (according to Evans<sup>[8-42]</sup>)

The ability to form passivating oxide layers is closely linked to the volume ratios between the metal and its corresponding oxide. As shown in Table 8.3-2, self-passivation is possible if the molar volumes of the metal and its corresponding oxide are comparable or at least similar in size.<sup>[8-40]</sup> A volume coefficient of ca. 1 therefore allows, in the case of aluminium, the incorporation of the metal oxide into the surface lattice of the metal, i.e., the formation of a protective oxide layer. Volume coefficients  $\geq 1$  therefore mean insufficient adhesion of the oxide, whereas with volume coefficients  $\ll 1$  no or only partial coverage of the surface occurs.

**Table 8.3-2.** Volume coefficients of metals/metal oxides (Pilling–Bedworth)

Metal	MeO/Metal Volume coefficient (VC)	Volume ratio Metal/MeO
Aluminium	1.28	ca. 1 : 1
Iron	2.16	ca. 1 : 2
Zinc	1.59	ca. 1 : 1.5

This requirement is emphasized by a comparison of the lattice constants of the metal and its corresponding oxide. The larger the difference (Table 8.3-3), the less space becomes available for the metal oxide to be incorporated into the surface lattice.

**Table 8.3-3.** Lattice constants of metals and their corresponding oxides

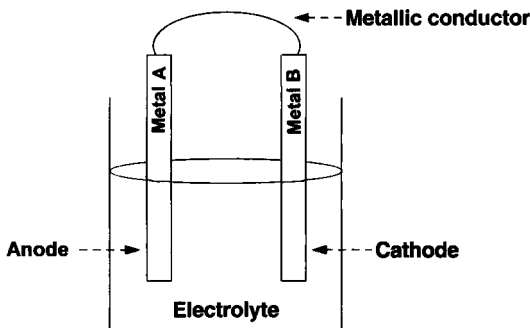
Metal	Metal oxide	Difference
Al: 4.04 Å	Al <sub>2</sub> O <sub>3</sub> : 5.15 Å	1.11 Å
Fe: 2.86 Å	Fe <sub>2</sub> O <sub>3</sub> : 5.42 Å	2.56 Å

### 8.3.1.2 Electrochemical Corrosion Processes

Most people are familiar with visibly corroding materials and the potential consequences resulting thereof, e. g., when the good old car is falling apart. This visible rusting of a metal or of different metals that are in contact with each other is related to electrochemical corrosion processes.

This topic is covered extensively in the scientific literature<sup>[8-41–8-44]</sup> and will not be described in great detail here.

Generally speaking, an electrochemical corrosion process consists of an anodic and cathodic reaction which occurs in the presence of an electrolyte. Electrons are exchanged between the anode and the cathode, resulting in the flow of current. This can be described in a simple way with a corrosion cell (Fig. 8.3-2) as a model.



**Figure 8.3-2.** Corrosion cell

A metal A (e. g., iron) and a metal B (e. g., copper) are thereby immersed in an aqueous electrolyte solution. Because iron is the more electronegative of the two metals in the electrochemical series it assumes the role of the anode. The two metals are connected through a metallic conductor and the electrolyte solution. In such a cell, a current will flow due to oxidation of the anode (metal dissolution) and a reduction reaction at the cathode (e. g., hydrogen formation).

In a simplified way these electrochemical processes can be summarized as follows:

Anodic reaction:

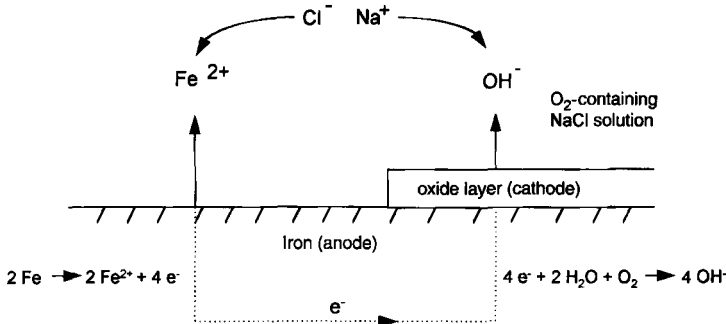


Cathodic reactions:



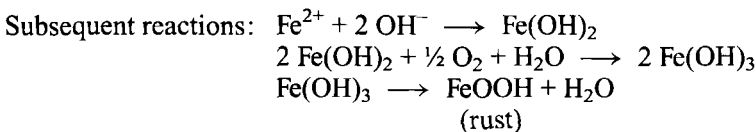
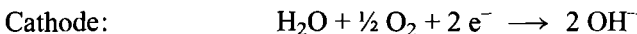
Because of the existence of minute corrosion cells (so-called localized galvanic cells), the above corrosion processes are in real-life conditions typically not locally separated, but occur at the same surface. Impurities at the surface, inhomogeneous composition of the metal, as well as mechanical deformation of the crystal lattice through processing are responsible for their formation.<sup>[8-45]</sup>

The mode of action of such cells is schematically shown (according to Bukowiecki<sup>[8-46]</sup>) in Fig. 8.3-3. The oxide layer functions thereby as the cathode, whereas the anodic dissolution of the metal occurs at the defect sites of the oxide layer.



**Figure 8.3-3.** Mode of action of a galvanic local element during the corrosion of iron in an aqueous NaCl solution (according to Bukowiecki<sup>[8-46]</sup>)

The corrosion products formed are ferrous chloride and sodium hydroxide, i.e., water-soluble products. Under atmospheric conditions, however, solid corrosion products (rust) form mostly:



The composition of these corrosion products can vary greatly and depends on a variety of factors, such as temperature, oxygen and electrolyte concentration, composition of the electrolyte, as well as the pH value of the environment. Depending on the parameters mentioned before, iron oxide hydrates such as  $\alpha$ -,  $\beta$ -,  $\gamma$ -,  $\delta$ -FeOOH, as well as Fe<sub>3</sub>O<sub>4</sub> (magnetite) and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> or  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> can be formed. Additionally, under real-life conditions, the existence of so-called sulphate or chloride nests plays an important role. The various rust modifications and the conditions leading to their formation are described in greater detail in the literature.<sup>[8-47-8-51]</sup>

### 8.3.1.3 Corrosion Protection by Organic Coatings

The protection of metal surfaces by organic coatings (paints) is traditionally achieved with the following methods:

- the use of anticorrosive pigments
- the application of barrier coatings
- the application of zinc-rich coatings

The various classes of anticorrosive pigments can be divided into chemically inert pigments (e. g., mica) and chemically or electrochemically active pigments. Inert pigments improve the barrier function of the coating by increasing the diffusion pathways for water, oxygen and corrosion-promoting ions. Chemically active pigments work by stabilizing the pH value of the coating (buffer function), whereas electrochemically active pigments passivate the metal surface (e. g., by forming protective layers at anodic defect sites or by slowing down the rust formation at the cathodic areas through their high oxidation potential). The most important representatives are based on phosphates, borates, silicates, molybdates, and chromates.<sup>[8-52]</sup>

Barrier coatings are formulated in such a way that water, oxygen, and corrosion-promoting ions are kept away from the metal surface as much as possible. The increase of the diffusion pathways for these components is thereby decisive for the whole concept. This can be achieved through the selection of suitable pigments/flakes (e. g., mica), sufficiently high cross-linking capability of the binder materials used and the application of thick film layers.<sup>[8-53]</sup>

In the case of zinc-rich coatings, zinc functions as a sacrificial anode, because, in the electrochemical series, zinc is more electronegative than iron. Steel surfaces are thereby cathodically protected.<sup>[8-54]</sup>

The development of new resin technologies (e. g., waterborne coatings), increasing legislative activities regarding solvent emissions and heavy metals, as well as increasing performance requirements, are challenging the industry to develop novel concepts beyond the existing ones. The use of anticorrosive additives (corrosion inhibitors) for long-term protection is, today, a true alternative (Section 8.3.2).

### 8.3.2 Corrosion Inhibitors

Corrosion inhibitors comprise a broad field, both in terms of the different chemical compound classes, as well as the variety of applications involved. Inhibitors are widely used in, e. g., liquid media such as lubricants, oil/water emulsions, or cooling/circulating systems. Other important applications include the protection of metal parts in the packaging industry through volatile inhibitors (vapour-phase inhibitors) and the inhibition of acid-induced corrosion upon the transport of strongly acidic media.

According to a study conducted in the US<sup>[8-54]</sup> between 1987–1992, an annual growth rate of 6.7% was found for the corrosion inhibitor market. In the early 1990s the turnover was in the range of  $800 \times 10^6$  USD. It is believed that this figure will be doubled by the year 2000, whereby a significantly higher growth rate is expected for organic inhibitors than for inorganic inhibitors.

The usefulness of organic inhibitors for long-term protection in coating applications was for some time controversial. Both high activity and suitable secondary properties (which are significantly different to those required for liquid systems) are needed (Section 8.3.2.3).

#### 8.3.2.1 Definition

A substance, which can prevent or slow down a chemical reaction is considered an inhibitor. By this definition, a corrosion inhibitor is a substance, which once added to a system at low levels can effectively reduce the corrosion rate of a metal or slow down the individual corrosion reactions.<sup>[8-55]</sup>

#### 8.3.2.2 Inhibition Mechanisms

In a corrosion cell, three out of its four components, the anode, cathode, electrolyte, and metallic conductor (see Section 8.3.1.2), can be influenced by inhibitors to impede the corrosion process. Amongst these are:<sup>[8-55, 8-56]</sup>

- shift of the potential at the anode (anodic inhibition)
- shift of the potential at the cathode (cathodic inhibition)
- adsorption onto the metal surface or formation of protective layers

Additional possibilities with respect to coatings are:

- reduction of the porosity and the permeability of a coating towards water, oxygen, and corrosion-promoting ions (e. g., chlorides and sulphates<sup>[8-57]</sup>)
- improvement of the adhesion, especially of the wet adhesion between the coating and the metal surface

A clear assignment of the various mechanisms is not always easy, as, especially in the case of organic inhibitors, anodic or cathodic activity may overlap with adsorption and other effects.

### **Anodic Inhibition**

The group of anodically passivating inhibitors can be divided in oxidizing and non-oxidizing substances<sup>[8-58]</sup>. Classic representatives of oxidizing materials would be, e. g., nitrites or chromates, whereas non-oxidizing compound classes are best represented by phosphates, tungstates, molybdates, and carboxylates (see Section 8.3.3).

As far as the mode of action is concerned, the two above classes are differentiated (amongst others) in such a way, that oxidizing substances such as chromates do not require oxygen for inhibition purposes (the protection is achieved by a combination of adsorption and localized oxide layer formation, i. e., the repair of defect sites which occurs in parallel with reduction of the inhibitor). Non-oxidizing inhibitors such as carboxylates, however, do require the presence of oxygen. Such compounds allow efficient inhibition by promoting the adsorption of oxygen at the anode, which is therefore considered the true passivator.<sup>[8-58]</sup> As, under atmospheric conditions, oxygen is always present, such inhibitors are considered very suitable for use in coating applications.

Certain carboxylic acids, which do have the ability to form insoluble salts or complexes at the anodic defect sites (pore plugging), thereby preventing further dissolution of the metal, can also be considered anodic in nature (see Section 8.3.3.2).

### **Cathodic Inhibition**

Cathodic inhibitors either slow down the cathodic corrosion as a whole or selectively form insoluble precipitates at the cathodic sites. Under conditions leading to atmospheric corrosion an inhibition mechanism based on oxygen reduction might be possible from a conceptual point of view. The vast majority of cathodic inhibitors, however, work by forming insoluble precipitates utilizing the increasing alkalinity at the cathodic sites. Compounds with this ability predominantly play a role in the water-treatment area.

### **Layer Formation**

Generally, inhibitive layers have an impact on the metal surface as a whole, i. e., they indirectly influence both anodic and cathodic processes. A clear differentiation between, e. g., the role of protective layers and that of anodic activity through salt formation at defective sites is not always possible. Here, however, protective layers will be discussed as a separate subject.

Inhibitive layers can be divided into layers simply covering the surface, passivating layers, and layers formed through adsorption.<sup>[8-59]</sup> The processes leading to layer formation through adsorption were thoroughly investigated by, e. g., Schultze<sup>[8-60]</sup> who focused on benzimidazole derivatives. According to these investigations, different orientations are possible for the inhibitors once adsorbed onto the metal surface or onto the oxide layer. Amongst these are a parallel or vertical orientation relative to the metal surface of the heterocyclic portion of the molecules, the co-adsorption of anions in the case of inhibitor salts, the adsorption or incorporation into the oxide layer and film formation (polymerization), e. g., by anodic oxidation.

Layers which are formed through salt formation of the inhibitor with e. g.  $\text{Fe}^{2+}$  (or  $\text{Fe}^{3+}$ ) ions can function as straightforward surface-covering layers, whereas passivating layers are considered as monolayers that are created by an oxidation or reduction process.

Both surface-covering and passivating layers can be regarded as interface barriers, which keep oxygen and/or corrosion-promoting ions away from the metal surface. There are a number of prerequisites for the efficiency of such layers (Ruf [8-59]):

- Surface-covering layers are only then efficient, if the formed salts are sufficiently insoluble and are hydrolytically stable, adhere strongly to the surface, and form a dense barrier against both oxygen and ions.  $\text{Fe}^{2+}$  salts, sensitive towards oxidation, are generally not considered to be suitable, as the resulting  $\text{Fe}^{3+}$  salts are easily hydrolysed to form poorly adhering iron oxides.
- Passivating layers are only then efficient, when the reaction leading to their formation is not reversible, i. e., oxidatively formed layers should not be sensitive towards reduction processes and vice versa.

### Permeability

As mentioned in Section 8.3.2.2, a clear assignment of the mode of action of organic inhibitors is often difficult, as the overall protection may be a result of overlapping effects. An example is the action of certain carboxylate-based inhibitors

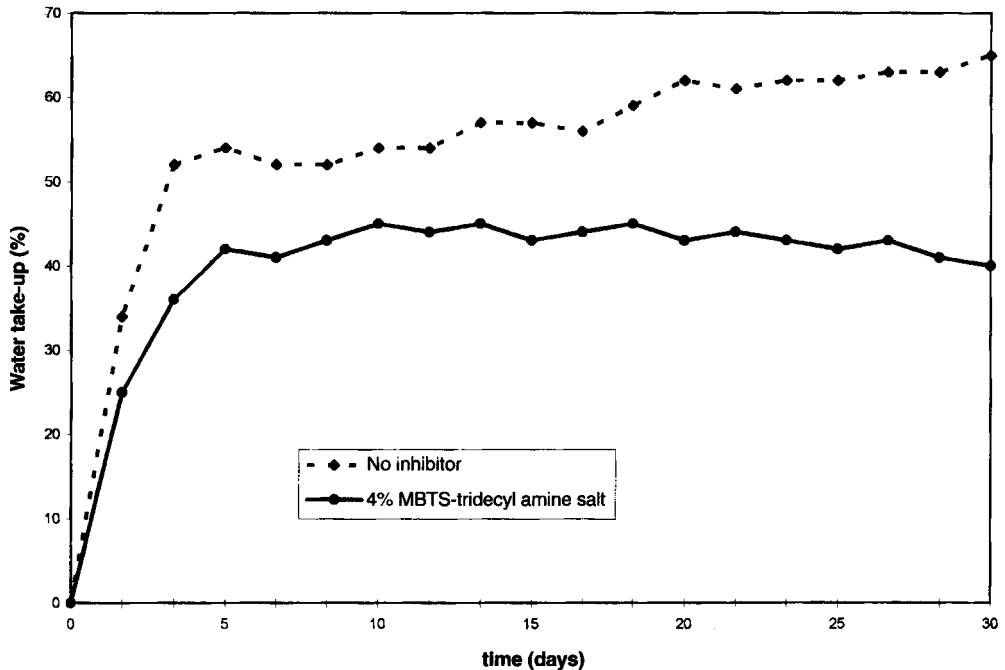


Figure 8.3-4. Influence of the tridecylamine salt of MBTS on the water absorption of 2K-epoxy-resin primers

such as the tridecylamine salt of (2-mercaptobenzothiazolyl)thiosuccinic acid (MBTS), which, in addition to its proven anodic activity, can improve the barrier properties of the coating (Fig. 8.3-4).

A similar influence on the barrier properties can generally be expected for all anodically or cathodically active inhibitors that are also hydrophobic in nature. Important for their usefulness is the right balance between hydrophilicity and hydrophobicity, i. e., purely hydrophobic compounds almost certainly prevent the build-up of polar interactions between the paint film and the substrate, which subsequently leads to poor adhesion.

### Adhesion Improvement

Adhesion, in particular in the presence of high humidity or water (wet adhesion) is one of the most important parameters in coating applications. As long as the adhesion is not negatively influenced by exterior conditions, no underrusting should occur.<sup>[8-61]</sup>

Apart from inhibitors, organometallic coupling agents based on zirconates and titanates play a role as adhesion promoters.<sup>[8-62]</sup>

#### 8.3.2.3 Inhibitor Classes/Characteristics

Numerous organic compounds exhibit inhibiting properties. These include (Trabainelli<sup>[8-63]</sup>) acetylene derivatives and cyclic aromatic systems, amines, nitrogen, sulphur- and/or oxygen-containing heterocycles, long-chain aldehydes and ketones, carboxylic acids and their derivatives, as well as nitrogen/sulphur compounds such as thiourea derivatives and thiophosphates. The inhibiting properties are determined by both the steric characteristics and the charge distribution throughout the whole molecule.

Inhibiting properties alone do not necessarily translate into applicability of these compounds in coating applications. As indicated in Section 8.3.2, for such applications the right balance between activity and suitable secondary properties needs to be achieved. An efficient and modern inhibitor for long-term protection should therefore meet the following requirements:

- high activity at low concentrations
- low water solubility
- sufficiently high thermal stability
- no sensitivity towards oxidation (ageing)
- high activity at pH 5–8 (ideally pH 2–14)
- high purity
- low toxicity
- compatibility with a broad range of resin technologies

One should in addition strive for ease of incorporation and usefulness as the sole inhibitor.

Low water solubility plays an important role for long-term protection in coatings. A too high solubility quickly leads, at the required usage levels (Section 8.3.3.1), to

increased water sensitivity of the coating and, as a consequence, osmotic blistering and delamination. With the exception of water-emulsifiable inhibitors, compounds that were specifically developed for temporary corrosion protection in waterborne coatings (i. e., flash-rust inhibitors) are exempt from this rule. Such inhibitors (Section 8.3.3.1) need to be sufficiently soluble in water in order to temporarily protect the substrate, i. e., to prevent corrosion during the drying time of the paint. The usage levels for these products, however, are significantly below those needed for long-term protection, which in turn minimizes the risk of increased water sensitivity.

High purity is of importance, since impurities may be surface-active as well, thereby competing with the inhibitor for the metal surface.

The demand for products with low toxicity is growing in importance in view of both legislative activities and increasing environmental awareness. Acute toxicity, ecotoxicological behaviour, as well as questions regarding future waste disposal are, amongst others, determining factors in new product development and material selection today; therefore the use of certain heavy metals such as lead, chromium, barium, and increasingly zinc is to be avoided.

Of the numerous compounds with inhibiting properties the following classes were found to be suitable for coating applications:

- organic acids and their salts
- basic compounds such as organic bases and amines
- oxidizing organic compounds

### 8.3.3 Products and Product Characteristics

As mentioned in Section 8.3.2.3, one has to differentiate between flash-rust inhibitors, for temporary corrosion protection, and inhibitors designed for long-term protection.

#### 8.3.3.1 Flash-Rust Inhibitors

Flash-rust inhibitors are either water-soluble or water-emulsifiable substances, which when added to waterborne coatings prevent, at very low levels, the corrosion of ferrous metals during the drying time of the paint. Another application would be the prevention of in-can corrosion upon storage of aqueous systems.

In practice, such inhibitors are often used in combinations to achieve flash-rust inhibition on particularly difficult substrates (e. g., along weld seams). One of the oldest and best-known representatives of this product class is sodium nitrite. It should be mentioned, however, that the industry is increasingly trying to replace sodium nitrite by alternative products, since in combination with the amines used for neutralization of the resins, nitrosamines can be formed.

Some of the most important commercially available products as well as their characteristics are summarized in Table 8.3-4. In some cases, the detailed chemical composition is only generically disclosed by the manufacturers. The trade names and the suppliers are listed at the end of Section 8. Due to their low water solubility, water-emulsifiable inhibitors can also contribute to long-term corrosion protection. Some application guidelines for flash-rust inhibitors are summarized in Section 8.3.4.

**Table 8.3-4.** Characteristics and usage levels of important flash-rust inhibitors (for trade names see Section 8.3.6)

Composition	Supply form	Usage level	Emulsifying/ water-soluble
2-Aminomethoxypropanol <sup>a)</sup>	liquid	0.2–0.5%	soluble
Basic ammonium benzoate <sup>b)</sup>	crystalline	0.1–1%	soluble
Ba salt of dodecyl-naphthalenesulfonic acid <sup>c)</sup>	liquid	0.25–3%	emulsifying
Ca salt of dodecyl-naphthalenesulfonic acid <sup>d)</sup>	liquid	0.8–3%	emulsifying
Alkene adduct compound <sup>e)</sup>	liquid	1–2%	soluble
Organic Zn complex <sup>f)</sup>	liquid	0.3–1%	emulsifying
Amine-neutralized (2-mercaptobenzo-thiazolyl)thiosuccinic acid <sup>g)</sup>		0.2–0.5%	soluble

Footnotes: The superscripted references in this table refer to the suppliers and trade names given in Section 8.3.6

### 8.3.3.2 Inhibitors for Long-Term Corrosion Protection

Inhibitors for long-term protection are, in contrast to most flash-rust inhibitors, substances with low water solubility. The products commercially available today were mostly developed as a replacement for traditional anticorrosive pigments, and are, in practice, used either as the sole inhibitor or in combination with pigments to, for example, enhance the anodic protection.

One can expect the importance of such inhibitors to increase significantly in the coming years, especially in view of the fast development of waterborne coatings. In these systems, compatibility problems and, according to the assessment of the coating industry, insufficient performance are often observed with traditional anticorrosive pigments.

The required usage levels for these inhibitors are higher than that of flash-rust inhibitors, but are, however, significantly lower than that of anticorrosive pigments. This may allow more formulating freedom, particularly in the development of new systems. The most important commercially available products and the recommended usage levels (based on total formulation) are listed in Table 8.3-5. Table 8.3-6 summarizes the recommended applications for these products.

**Table 8.3-5.** Characteristics and recommended usage levels for important inhibitors for long-term corrosion protection (for trade names see Section 8.3.6)

Composition	Supply form	Recommended usage level
Aminocarboxylate(metal salt) <sup>h)</sup>	liquid	1–6%
Zn salt of 5-nitroisophthalic acid <sup>i)</sup>	crystalline	1–2%
Zn salt of cyanuric acid <sup>k)</sup>	crystalline	1–2%
Zn salt of dodecyl-naphthalenesulfonic acid <sup>l)</sup>	liquid	1–3%
Mg salt of dodecyl-naphthalene sulfonic acid <sup>m)</sup>	liquid	0.5–5%
(2-Mercaptobenzothiazolyl)thiosuccinic acid <sup>n)</sup>	crystalline	0.5–1.5%
Tridecylamine salt of (2-mercaptobenzothiazolyl)thiosuccinic acid <sup>o)</sup>	liquid	1–3%
Amine complex of toluylpropionic acid <sup>p)</sup>	crystalline	1–2%
Zr complex of toluylpropionic acid <sup>q)</sup>	crystalline	0.5–1%

Footnotes: The superscripted references in this table refer to the suppliers and trade names given in Section 8.3.6

**Table 8.3-6.** Recommended applications of important inhibitors for long-term corrosion protection (for trade names see Section 8.3.6)

Composition	Recommended applications
Aminocarboxylate(metal salt) <sup>h)</sup>	Solvent-based systems
Zn salt of 5-nitroisophthalic acid <sup>i)</sup>	Conventional alkyd-, epoxy-, polyester-, PU-, vinyl-, acrylic resins in combination with Zn phosphate
Zn salt of cyanuric acid <sup>k)</sup>	Waterborne and solvent-based systems in combination with Zn phosphate
Zn salt of dodecyl-naphthalenesulfonic acid <sup>l)</sup>	Waterborne systems, HS coatings
Mg salt of dodecyl-naphthalene sulfonic acid <sup>m)</sup>	Waterborne systems, HS coatings
(2-Mercaptobenzothiazolyl)thiosuccinic acid <sup>n)</sup>	Polyvinylbutyral combinations, acrylic-, polyester-, epoxyester resins (solvent-based)
Tridecylamine salt of (2-mercaptobenzothiazolyl)thiosuccinic acid <sup>o)</sup>	Conventional alkyd-, epoxy resins, HS coatings
Amine complex of toluylpropionic acid <sup>p)</sup>	Aqueous dispersions, water-reducible systems, hybrid systems
Zr complex of toluylpropionic acid <sup>q)</sup>	Aqueous dispersions, water-reducible systems, hybrid systems

Footnotes: The superscripted references in this table refer to the suppliers and trade names given in Section 8.3.6

### 8.3.4 Practical Hints, Formulation Guidelines

For the successful application of inhibitors in coatings a number of formulation guidelines should be kept in mind; these are summarized below.

#### 8.3.4.1 Flash-Rust Inhibitors

Upon application of waterborne coatings, flash rust is preferably formed in the presence of high relative humidity or low temperatures, i. e., the drying of the coating is slowed down. Blasted, rough surfaces are particularly sensitive, whereas welds are considered rather difficult to protect. Flash-rust inhibition along welds can often only be achieved by a combination of different products. The following procedure is recommended for the development of new formulations:

- identification of the suitable product(s)
- determination of the required usage level(s) by variation of the drying conditions
- evaluation of the coating properties when exposed to humidity, to ensure no increase in water-sensitivity of the system (in particular when water-soluble flash-rust inhibitors are being used)

#### 8.3.4.2 Inhibitors for Long-Term Protection

Inhibitors for long-term corrosion protection can basically be applied according to one of the following two principles:

- use as the sole inhibitor (e. g., replacement of anticorrosive pigments)
- combined with anticorrosive pigments (e. g., enhancement of certain protective properties)

The easiest way of combining inhibitors with anticorrosive pigments is its addition to an existing formulation. Typically the addition of small quantities is sufficient, but this procedure will obviously lead to a cost increase of the formulation. If anticorrosive additives are used as the sole inhibitors, the following formulation guidelines have to be considered:

- most inhibitors exhibit a system-dependent performance optimum, and an evaluation of the concentration-related performance is therefore recommended
- usage levels higher than recommended typically do not lead to additional improvements
- in formulation calculations (e. g., the pigment-volume concentration), crystalline products are generally, despite their additive character, regarded as pigments, although they might be completely soluble in the formulation

Due to the significantly different usage levels, the replacement of anticorrosive pigments by inhibitors is performed in such a way that the inhibitor is used in combination with an increased quantity of extender pigment or inert pigment.

It is the usual practice to keep only the pigment volume concentration (PVC) at a constant level when different formulations are compared. This, however, is not adequate, since the substitution products for, e. g., pigments may have a significantly higher binder demand (higher oil-absorption value). As a result, the content of free binder in the formulation is lowered, which in turn may lead to a dramatic change in the coating properties, e. g., the anticorrosive behaviour. For correct replacement the ratio of the pigment volume concentration (PVC) and the critical pigment volume concentration (CPVC) should be kept at a constant level. Crystalline inhibitors are thereby considered as pigments.

The PVC and CPVC can be determined as follows. The pigment volume concentration depends on the density of the raw materials used and can easily be calculated according to the formula below:

$$\text{PVC (\%)} = V_p \times 100 \times (V_p + V_b)^{-1}$$

( $V_p$ : volume of all pigments, extender pigments, and crystalline inhibitors;  
 $V_b$ : non-volatile resin components)

The critical pigment-volume concentration depends largely on the oil-absorption value of the crystalline raw materials. It can be defined as the limit at which no excess or no more free binder is available between the individual pigment or extender pigment particles. The experimental determination of the critical pigment volume concentration often requires too much effort for practical purposes. It can be, however, calculated to a good approximation from the oil-absorption value<sup>[8-64]</sup> of the pigment/extender pigment/inhibitor blend applied:

$$\text{CPVK (\%)} = V_{pf} \times 100 \times (V_{pf} + OZ_{pf} \times 0.93^{-1})^{-1}$$

( $V_{pf}$ : volume of all pigments, extender pigments, and crystalline inhibitors;  
 $OZ_{pf}$ : oil-absorption value of the pigment/extender pigment/inhibitor blend)

According to this formula, correct substitution of, e. g., pigments by alternative pigments or by a combination of inhibitors and extender pigments can be easily determined by the ratio of PVC to CPVC.

The evaluation of the anticorrosive properties of such coatings is typically performed with accelerated-exposure tests such as salt-spray exposure (ASTM B 117) or humidity exposure (DIN 50017 KK).

More recently, cyclic-exposure tests were developed, which are claimed to give a much better correlation between spray results in particular and the coating performance in exterior exposure.

The toxicity data and guidelines related to disposal of these products are mentioned in the material safety data sheets of the individual manufacturers.

### 8.3.5 Toxicology and Disposal

The known toxicity of chromates and lead compounds, in particular, has had a major influence on the development of the inhibitors that are commercially available today. The goal of the industry in these developments is to offer only safe products to the market.

### 8.3.6 Manufacturers and Trade Names

The trade names and the manufacturers/suppliers of the products listed in Tables 8.3-6 to 8.3-8 are summarized below:

- a) ® AMP-90: Angus Chemie GmbH, D-49479 Ibbenbüren
- b) ® Cotrol AMB: CasChem, Inc., Bayonne, NJ (USA)
- c) ® Nacorr 1151: King Industries, Norwalk, CT (USA)
- d) ® Nacorr 1351: King Industries, Norwalk, CT (USA)
- e) ® Lanco-Rustgard FW: Georg M. Langer & Co., D-27721 Ritterhude
- f) ® Ser AD FA 579: CONDEA-Servo BV, NL-7490 AA Delden
- g) ® Irgacor 252 FC: Ciba Specialty Chemicals Inc., CH-4002 Basel
- h) ® Cotrol 18-8: CasChem, Inc., Bayonne, NJ (USA)
- i) ® Sicorin RZ: BASF AG, D-67056 Ludwigshafen
- k) ® Alcophor 827 W: Henkel KGaA COC-Coating, D-40589 Düsseldorf
- l) ® Nacorr 1552: King Industries, Norwalk, CT (USA)
- m) ® Nacorr 1651: King Industries, Norwalk, CT (USA)
- n) ® Irgacor 252 LD: Ciba Specialty Chemicals Inc., CH-4002 Basel
- o) ® Irgacor 153: Ciba Specialty Chemicals Inc., CH-4002 Basel
- p) ® Irgacor 1405: Ciba Specialty Chemicals Inc., CH-4002 Basel
- q) ® Irgacor 1930: Ciba Specialty Chemicals Inc., CH-4002 Basel

## 8.4 Biocides

*Jürgen Klaus Glaser*

### 8.4.1 Introduction

The use of biocides as paint additives is currently giving rise to heated discussions. These discussions concern the protection of the environment and the consequences regarding environmental compatibility and eco-balance. The sometimes idealized “new” formulations that are based on water instead of other solvents necessitate the use of biocides to prevent fast deterioration of the paint. For well-documented reasons, the use of highly effective chemical substances such as organomercury compounds is now forbidden in most countries. Despite the extremely broad spectrum of activity of these substances and the small concentrations used, their eco-toxicological evaluation is extremely unfavourable. In connection with modern active ingredients and their preparation, the general term microbicides is often used. Depending on their specific effects, they can be separated into bactericides, fungicides, and algicides. These biologically active ingredients often have a very specific spectrum of activity. From the eco-toxicological point of view, most of them can be considered less harmful than the substances used previously, and they satisfy the requirements alone or in combination with other biologically active substances. Depending on their area of application, they are called in-can and/or film preservatives. Even with the introduction of these “new generation” substances the discussions about their environmental impact continues, and the biologically active substances are still being criticized. While some people question whether these active substances are really necessary, others try to find out why there are still microbial problems despite the use of these chemical substances. To come to the most important point first: the environmental impact of modern microbicides (quantities used: 0.05 to 4%, except antifouling), when they are used according to the instructions, is very low.

It is clear that we need to use microbicides; the consequences of not using them can be seen in everyday life: cans of smelly paints which cannot be used anymore, mouldy walls and exterior surfaces covered by algae – undesirable results because they have a negative effect on the image of the manufacturer and render the efforts made in production and processing worthless. The portion of microbicides in the total formulation is very small and not a decisive cost factor for the paint. In order to maintain its function and value, however, the microbicide is essential. In this chapter bactericides, fungicides, and algicides, which are used in both in-can and film preservation, will be described. To prevent any misunderstanding, the most important terms used hereafter will be described in brief.

## 8.4.2 Definitions

### Algae

Algae are a group of plants that consist of organisms of different colours; from the evolutionary point of view, they are characterized by great originality. Algae are capable of feeding independently, through the process of photosynthesis. The vegetative bodies of algae consist of one or more cells; they have thread-like or flat shapes; the higher forms have a relatively complicated internal organization, transportation canals are, however, absent. The cells always contain nuclei. They occur in the sea, in freshwater, in humid places such as on wet walls, on the floor, and on snow. Algae that live in symbiosis with fungi are called lichens.<sup>[8-65]</sup>

### Bacteria

These are, mainly, unicellular micro-organisms without a nucleus (their diameter is sometimes less than 0.001 mm). They multiply by means of simple division or in some cases through sprouting. Some bacteria are characterized by flagellae, with which they move actively. With a few exceptions, bacterial cells are surrounded by a rigid or semi-rigid cell wall, which gives them a stable form. According to their various forms, bacteria can be grouped into the following categories: cocci (spherical), rod-like bacteria, and spirilla (spiral-like). The categorization of bacteria according to Gram's staining method into gram-positive and gram-negative bacteria is based on structural differences in the cell wall. Some species of bacteria can form endospores, popularly known as spores. Spores are permanent forms of bacteria which are of particular importance because of their extraordinary resistance to unfavourable environmental conditions (heat, cold, dryness, chemical influences). Different bacteria have different feeding methods. As with green plants, some species use light as an energy source and satisfy their need for carbon with carbon dioxide from the air. Other species derive the necessary energy from the oxidation of inorganic substances (e.g., ammonia is oxidized to nitrite by the bacterial species *Nitrosomonas*). However, most bacterial species satisfy their need for energy and carbon with organic substances alone, such bacteria are found in substrates with neutral to slightly alkaline pH values. With regard to temperature, the lower limit for their growth is the freezing point of their cell sap and the upper limit is the boiling point of water. Due to their various feeding methods, bacteria are found almost everywhere.<sup>[8-65]</sup>

### Preservatives

Preservatives are defined as substances which maintain the quality of (i.e., preserve) products that are not intended for immediate use. These substances may have a biostatic and/or biocidal action in an environment infested by micro-organisms. This needs to be stated, because substances preventing chemical or physical processes, such as oxidation, hydrolysis, polymerization, phase separation, and drying are also considered to be preservatives, in the wider sense of the word.

Preservatives are substances which, even in low concentrations, inhibit the multiplication of micro-organisms. The micro-organism does not necessarily have to be killed, it is sufficient to inhibit its multiplication. When one considers the importance of cleanliness in production facilities, however, it is obvious that it is in most cases desirable to destroy the micro-organisms as quickly as possible. The list of requirements of a preservative also includes a broad spectrum of activity (i. e., effectiveness against all microbes which reduce the durability of the products) as well as good compatibility with paints, chemical stability, low toxicity for mammals, and generally favourable eco-toxicological properties. The possible ways in which antimicrobial substances are applied in the coatings and paint industry is discussed below.

#### *As In-Can or In-Tank Preservatives*

An in-can preservative should be highly water-soluble, because its function is to preserve aqueous products in their containers. Micro-organisms – in particular bacteria and fungi – multiply in the aqueous phase. After having served its purpose, the preservative should then no longer be analytically detectable and it should completely, that is, without any undesirable by-products, degrade.

#### *As Film Preservatives*

The spectrum of activity of film preservatives should include fungi and, if used outdoors, algae. As opposed to in-can preservatives, the solubility in water, ultraviolet sensitivity, and volatility should be as low as possible. This prevents early loss of the active ingredients (particularly when used outdoors) and ensures long-term film protection.

### **Microbes**

Microbes is the general term used for many different micro-organisms such as algae, bacteria, and fungi.

### **Microbistatic Substances**

Microbistatic substances are chemical compounds that, due to their specific effects, inhibit the growth and multiplication of micro-organisms. After the microbistatic substance has been removed and or used up, the micro-organisms continue to grow and to multiply. However, depending on its concentration, one and the same substance can have both microbistatic and microbicidal effects. One distinguishes between, for example, bacteriostats and fungistats on the basis of their specific action on the different micro-organisms.<sup>[8-65]</sup>

### **Microbicidal Substances**

Microbicidal substances are chemical substances that kill micro-organisms. Depending on the specific action on different micro-organisms, one can distinguish between, for example, bactericides, fungicides, and algicides.<sup>[8-65]</sup>

## Fungi

Fungi are a heterogeneous group of micro-organisms that are considered to belong to the thallophytes. They are non-chlorophyllic organisms with genuine nuclei; the walls of their nuclei consist of chitin and/or cellulose. There are unicellular and multicellular forms. They multiply both sexually and asexually, in many different forms, in particular through the formation of flagellated and unflagellated spores. Fungi occur in all climatic zones of the earth, especially in the humid ones. There are two forms of fungi: those developing on water and those developing on solid substrates. As non-chlorophyllic organisms, they depend on organic carbon. Apart from the fungi living on dead organic material, there are also parasites which may cause diseases in human beings, animals, and plants. Some fungi live in symbiosis with algae (lichens), higher plants (mycorrhiza), or insects.<sup>[8-65]</sup>

### 8.4.3 In-Can or In-Tank Preservation

All systems containing water and biodegradable substances provide a possible nutritive medium for micro-organisms. These organisms grow in both synthetic and natural products. In a natural environment, there are certain chemical substances which have a microbicidal action and thus inhibit biodeterioration. The problems with synthetic products are almost the same as those associated with natural products, with the exception that man has to ensure sufficient and reasonable protection of the substances used. Water, in every case, is the limiting factor for microbe infestation. However, even very low humidity is sufficient to establish a potential habitat for micro-organisms. This is illustrated with the following example: Water is soluble to some extent in mineral oil products such as petrol and kerosine. The water, in particular the interface between the water and the relevant product, as well as the water which condensates from air humidity in the fuel tanks and migrates to the bottom of these tanks, serves as a nutritive medium for hydrocarbon-oxidizing microbes. There is no serious damage to the product itself, but a biofilm forms which may block the suction filter. If the biofilm becomes too thick, bacteria may form which produce hydrogen sulphide, and this may lead to the corrosion of fuel injection systems.<sup>[8-66]</sup> To avoid this, mineral-oil products are preserved similarly to coatings and paints.

It is important to use the preservatives sparingly and to check their corrosion potential before usage. Coatings and paints which have been infested by microbes are usually characterized by reduced viscosity, discoloration and bad odours. Most of the deterioration is caused by gram-negative bacteria of the species *Pseudomonas*, whose optimal growth conditions are at a pH value of 7–9. The products infested by fungi are mostly highly-pigmented ones. In general, the preservation of acidic products is easier than that of neutral or alkaline products. This can to some extent be attributed to the effect and stability of chemical preservatives at different pH values. Another potential obstacle for successful preservation may be posed by ingre-

dients with a large surface area, such as organic pigments and activated charcoal, since the preservatives are deactivated by surface phenomena such as adsorption. Due to their chemical structure and the resulting reactivity, many of the biocides available on the market are unstable with regard to oxidizing and reducing agents such as sodium sulphite. The active substance is decomposed and this results in insufficient in-can preservation. A high portion of residual monomers, however, may prove favourable, because they also have a microbicidal action, even if they are undesirable for toxicological reasons. In order to be able to make reliable statements about the concentration, type and composition of the preservative for a particular product, a microbiological test has to be carried out in most cases.

There are different test methods for these preservation tests. In most cases, a mixture of various bacterial and fungal strains is used. It can be an advantage if these microorganisms are taken directly from the degraded products. The sample is inoculated with a standard quantity, usually 1 mL/50 g sample, of this "biococktail" (approx.  $1.0 \times 10^9$  germs/mL) and checked for viable germs after certain intervals. This simple test allows the evaluation of the actual level of preservation after production. However, in order to be able to make a reliable statement about the quality of in-can or in-tank preservation, the test has to be repeated, that is, the sample is repeatedly inoculated, possibly with increasing bacterial and fungal concentrations. Based on the result of this repetitive test, as opposed to the simple test, a reliable statement may be made regarding the efficiency of the biocidal substances and thus the reliability of the preservation of the products subject to repeated microbial contamination. Repeated microbial contamination is far too often disregarded. Microbial infestation may occur if containers have not been hermetically sealed, if infected condensation water is dripping from the contaminated inside of the cap onto the surface of the product, if a storage tank has not been cleaned properly, or when a container is dirty, when thinning water is contaminated, when a painter immerses his dirty brush in the product, or when the product with other contaminated products (pigment pastes). The undesirable consequences are bad odour, discoloration and/or reduced viscosity.

In-can preservatives protect paints from the storage of the raw material through to production and processing. Proper plant hygiene is also an important factor in preventing claims and in reducing the increased quantity of biocides and/or the related effort involved, as well as in reducing costs.

#### **8.4.4 Plant Hygiene**

Proper plant hygiene is a vital factor in guaranteeing efficient preservation. A high initial microbial balance can be avoided and the concentration of preservatives required thus reduced. The importance of the initial microbial balance is often disregarded. This leads to problems in production and subsequently in the product itself.

In-can preservatives are capable of destroying particular species of germs. However, these preservatives are irreversibly consumed in this process and are thus not available for storage protection.

Apart from the problems with the germs of bacteria and fungi described before, there are also difficulties caused by enzymes. In general, enzymes provide evidence of ongoing or past activity of micro-organisms and can only be controlled to a limited extent by using common decontamination methods. Most biocides are ineffective against enzymes, or only effective if used in excessive concentrations. Their ineffectiveness is also the reason for the sudden viscosity reduction of a product, even if it is sterile. To prevent this reduction, it is essential to use high-quality raw materials, that is, to try to achieve the lowest possible microbial contamination. Some of the raw materials analysed as well as their microbial contamination are listed in Table 8.4-1. The water used in the production should be absolutely sterile, and it should be treated with ultraviolet light or biocides before the production phase, to kill all germs. Water in storage tanks is usually chemically treated. This ensures long enough contact between biocide and micro-organisms, to destroy the latter. The sterility of the water should be checked at regular intervals, because if

**Table 8.4-1.** Cell number of raw materials [8-67]

Material	Number of germs/g
<b>Emulsions</b>	
Acrylic emulsion (100%)	$5.3 \times 10^5 - 1.0 \times 10^6$
Vinyl acetate-butyl acrylate copolymer	$1.0 \times 10^4$
Vinyl acetate copolymer	$1.0 \times 10^7$
<b>Pigments</b>	
Copper phthalocyanine paste	$1.5 \times 10^3 - 1.75 \times 10^6$
Halogenated phthalocyanine paste	$4.4 \times 10^5$
Halogenated cobalt phthalocyanine	$1.0 \times 10^5$
Titanium dioxide	$1.0 \times 10^2$
Chromium powder	$6.1 \times 10^2$
Barium chromate	$3.1 \times 10^2$
<b>Fillers</b>	
Amorphous calcium carbonate	$2.0 \times 10^8$
Precipitated calcium carbonate	$1.5 \times 10^7$
Magnesium aluminium silicate	$1.3 \times 10^7$
Kaolin	$1.0 \times 10^1$
China clay	$1.0 \times 10^8 - 3.0 \times 10^{11}$
Crystalline calcium carbonate	$3.0 \times 10^{11}$
Barium sulphate	$1.0 \times 10^2$
<b>Additives</b>	
Casein	$3.4 \times 10^6 - 1.1 \times 10^7$
Carboxymethylcellulose	$7.0 \times 10^8 - 1.0 \times 10^{10}$
Hydroxymethylcellulose	$2.9 \times 10^4$
Process water	$4.4 \times 10^4 - 2.8 \times 10^5$
Ion-exchanger water	$1.0 \times 10^4$
Drinking water	$< 1.0 \times 10^2$
Water from storage tanks	$1.0 \times 10^4 - 1.0 \times 10^7$

the concentration of one single substance is too low, germs which are tolerant to that substance may develop. Subsequently, these “cultivated” microbes can hardly be controlled at all or only with other biocidal substances with chemically different structures and modes of action. The same effect occurs in medical applications if treatment with antibiotics is stopped too early or if the concentration was too low. Other causes for infection are stock solutions such as thickening solutions. It is of utmost importance to preserve them in case they are not immediately processed after production. Regular cleaning of the production plant is also part of proper plant hygiene. For cleaning, process water, or, even better, water treated with biocides can be used. Depending on the preservative used, it may then be integrated into production. To be absolutely sure, the sterility and possibly also the in-can stability of the products should be checked at regular intervals.

### 8.4.5 In-Can Preservatives

For reasons of simplicity, the following explanations will be based on the division of the different mechanisms of activity into two categories: membrane-active and electrophilically active biocides. Some molecules cannot be clearly assigned to one of the two categories, because, due to their chemical structure, they may have several modes of activity. Some of the active substances or categories of substances outlined below may also be used as film-preservative additives because they cannot be clearly distinguished with regard to their effects on the target organism. The differentiation here is based on the frequency of use. The modes of action of the preservative substances can be summarized as follows:

#### *Membrane-Active Substances*

- nonspecific adsorption on the cell membrane
- disturbance of the function of embedded proteins
- loss of semi-permeability of the membrane: penetration of ions and organic molecules
- inhibition of substrate transport and ATP synthesis

These substances include, for example, alcohols, carbanilides, quaternary ammonium compounds, phenols, acids, biguanides, and guanidines.

#### *Electrophilically-Active Substances*

- reaction with nucleophilic functional groups of cell parts in particular
- blocking of amino acids and enzymes

These substances include, for example, aldehydes and aldehyde-releasing compounds, substances with activated halogen compounds, isothiazolinones, and organometallic compounds.<sup>[8-68]</sup>

### 8.4.5.1 Formaldehyde

The destructive and/or deactivating effect of formaldehyde is attributed to its reactions with carboxyl, amino, hydroxyl, and/or sulphhydryl groups of the cell proteins. Its antimicrobial spectrum of activity is mainly limited to bacteria and, to a lesser extent, also mould fungi and yeasts. Therefore, formaldehyde and formaldehyde-releasing compounds are usually reinforced by a fungicide component. The range of activity is between pH 3–10. A special characteristic of formaldehyde is its sporicidal action. It is compatible with anionic, cationic, and non-ionic detergents without losing its efficiency. Formaldehyde is not compatible with ammonia, casein, alkali, proteins, oxidizing substances, and salts of heavy metals. Its reactivity and volatility may be regarded as negative factors, as they cause the bad odour, incompatibility, and instability of the substance. On the other hand, formaldehyde's volatility ensures its vapour-phase effect. This characteristic is successfully applied in the preservation of aqueous liquids in the head-space of containers or tanks. Gaseous formaldehyde is difficult to handle, therefore liquid or solid compounds, such as the most simple form, formalin (30–45% aqueous solution of formaldehyde), or paraformaldehyde (polyoxymethylene  $\text{HO}(\text{CH}_2\text{O})_n\text{H}$ ;  $n = 8\text{--}100$ ), a crystalline white polymer, are preferred.<sup>[8-67, 8-69]</sup>



Formaldehyde; CAS no. 50-00-0

### 8.4.5.2 Formaldehyde-Releasing Compounds

Formaldehyde-releasing compounds are less volatile, more stable, and have a less intensive odour than formaldehyde. However, their microbicidal effects are also due to the release of formaldehyde. Compounds capable of releasing formaldehyde but with a completely different mode of action, such as Bronopol, are excluded. The antimicrobial action of Bronopol is considerably stronger than can be attributed to the theoretical contribution of formaldehyde.<sup>[8-69]</sup> Because formaldehyde-releasing compounds are available, formaldehyde itself – even when not used in its pure form – is frequently used as an in-can preservative and is often one of the active ingredients in a biocide formulation. These compounds, liquids or powders, can be grouped into the following important main categories:

#### *O*-Hydroxymethyl Compounds (Hemiformals)

These compounds are produced by the reaction between an alcohol and formaldehyde. In this case, water can also be considered to be an alcohol, and here the reaction product is formalin. Under acidic conditions, formals are formed; in these formals, formaldehyde is so strongly bound that it can no longer be used as an antimicrobial substance.<sup>[8-67–8-69]</sup>

*Amino-Formaldehyde Addition and Condensation Products*

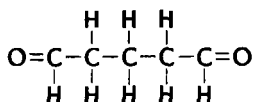
These products result from the reaction between formaldehyde and amines, with the formation of water. The microbial action of these compounds is based on the formaldehyde portion that they release in aqueous media. Examples are 1,3-oxazolidines, dioxazolidinyl methanes, hexahydro-*s*-triazines or tetrahydro-1,3-oxazines.<sup>[8-67-8-69]</sup>

*Amide-Formaldehyde Addition Products*

The addition of formaldehyde to amides or substances with amide configurations may produce substances with microbicidal action based on the release of formaldehyde, for example, *N*-hydroxymethyl chloracetamide or *N,N'*-bis(hydroxymethyl) urea.<sup>[8-67-8-69]</sup>

**8.4.5.3 Glutaraldehyde**

This oily liquid is approximately twenty times more effective than formaldehyde. It kills bacteria, fungi, spores, and viruses. This is why glutaraldehyde is often used as a disinfectant. However, its metal-corroding effect should not be underestimated. Its mode of action is based on the reaction with sulphhydryl and amino groups of the cell of the micro-organism. Its reactivity increases with a rising pH value. In aqueous solutions, glutaraldehyde is polymerized, in particular at higher pH values (>9). Due to this polymerization, many aldehyde groups are eliminated, and with them, the effects of glutaraldehyde. In terms of stability, the optimum pH value is 5.0, and with regard to bactericidal effects, the optimum is reached at pH 7.5–8.5. The substance is deactivated by ammonia and primary amines at neutral and alkaline pH, as well as by sodium bisulphite.<sup>[8-67-8-69]</sup>



Glutaraldehyde; CAS no. 111-30-8

**8.4.5.4 Phenol Derivatives**

Of the microbicides that are still important today, phenol used to be the most important one. However, phenol itself has been replaced by its more effective alkylated and/or halogenated derivatives. Phenol derivatives are antimicrobially active in their undissociated form. When aliphatic or aromatic groups are introduced, the acidity and water solubility are reduced, and this results in more efficient solubility of lipids and thus stronger antimicrobial effects. The activity of halogenated phenols increases with the number of halogen substituents and the increasing atomic weight of the halogen; the increased activity is more distinct in *para*-substitution than in *ortho*-substitution. Phenol derivatives belong to the membrane-active group of mi-

crobiocides. In low concentrations, they have a microbistatic action, because they adsorb onto the cell membranes. Upon dilution, this effect is reversible. In higher concentrations, they have a microbicidal action, but are not consumed by this. [8-67-8-69]

Combined with cellulose ethers, all phenols produce thickening; this limits their application concentration possibilities. To prevent flocculation, phenol derivatives should be added to pigment pastes or dispersion paints as diluted solutions or should be provided in the aqueous portion. In dispersion paints, phenolic substances migrate into the binding agent; *p*-chloro-*m*-cresol is the substance which shows the most favourable action in this respect. [8-70]

Phenol derivatives, in particular the halogenated ones, are known to be extremely toxic and detrimental to the environment. This may be true for a number of compounds, but there are also some positive examples such as *p*-chloro-*m*-cresol. This substance has an oral LD<sub>50</sub> of 5129 mg/kg rat, is not sensitizing, does not accumulate, is neither mutagenic nor teratogenic, and decomposes in surface water and in the atmosphere. [8-67]

#### 8.4.5.5 Acids

Acids play a particularly important role among preservatives. They are mostly used in the preservation of nutrients, cosmetics, pharmaceuticals, and medicine. The mode of action of acids, apart from the reduction in the pH value and subsequent inhibition of bacteria multiplication as well as spore germination, is based on their ability to act in their undissociated forms as membrane-active microbicides. They enter into the cell of the micro-organism where they disrupt metabolic functions. The portion of undissociated acid and thus also membrane activity decreases with a rising pH value. Organic acids can thus only be used in the acidic range, whereas inorganic acids, except for sulphurous acid, are to a larger extent also present in undissociated forms in the neutral pH range. In Table 8.4-2, the most important preservative acids are listed together with their degree of dissociation and pH values. [8-67-8-69]

**Table 8.4-2.** Dissociation constants and pH values of preservative acids [8-69]

Preservative substance	Dissociation constant	pK <sub>a</sub> value
Sulphurous acid	$1.54 \times 10^{-2}$	1.81
Salicylic acid	$1.07 \times 10^{-3}$	2.97
Formic acid	$1.77 \times 10^{-4}$	3.75
<i>p</i> -Chlorobenzoic acid	$9.3 \times 10^{-5}$	4.03
Benzoic acid	$6.46 \times 10^{-5}$	4.18
<i>p</i> -Hydroxybenzoic acid	$3.3 \times 10^{-5}$	4.48
Acetic acid	$1.76 \times 10^{-5}$	4.75
Sorbic acid	$1.73 \times 10^{-5}$	4.76
Propionic acid	$1.32 \times 10^{-5}$	4.88
Dehydroacetic acid	$5.3 \times 10^{-6}$	5.27
Hydrogen sulphite	$1.02 \times 10^{-7}$	6.99
Boric acid	$7.3 \times 10^{-10}$	9.14

### 8.4.5.6 Carbonic Acid Amides

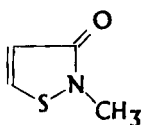
The most important substances of this microbicide group in the area of technical in-can preservation are *N*-methylolchloracetamide and 2-chloracetamide. Their antimicrobial action is not due to the amide group, but is due to the activated halogen in the  $\alpha$ -position. The distinct electrophilic character of these molecules enables them to react with nucleophilic groups in the cell of the microbe and so produce their microbicidal action. The above-mentioned substances of this group are compatible with anionic, cationic, and non-ionic detergents. They are not compatible with strong acids and alkalis. Their action is somewhat weaker against bacteria than against fungi. The advantages of these substances are lack of odour, high solubility, as well as a favourable distribution factor.<sup>[8-68-8-70]</sup>

### 8.4.5.7 Quaternary Ammonium Compounds (QACs)

This class of compounds is characterized by a positively charged hydrophilic group in the form of an ammonium group. This group allows for the adsorption on the negatively charged surface of the cell of the micro-organisms (i.e., they are membrane-active microbicides). Due to this, the outer membrane is affected to such an extent that it can no longer fulfil its function as a protective barrier. Subsequently, further active ingredients penetrate as far as the cytoplasmic membrane, where they interact. In order to achieve optimum effectiveness, one of the four radicals has to have a chain length of  $C_{12}$  to  $C_{16}$ . The spectrum of activity of QACs is a very broad one; however, gram-positive bacteria are destroyed at considerably lower concentrations than gram-negative bacteria are. The antimicrobial action of QACs increases with an increasing pH value ( $>7$ ) but they have no antimicrobial action whatsoever at a pH value of  $<3$ . They are incompatible with anionic surfactants, emulsifiers, and many other substances. Therefore, they can only be used in low concentrations and mostly in combination with other active ingredients.<sup>[8-67-8-69]</sup>

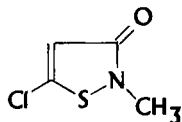
### 8.4.5.8 Isothiazolinone Derivatives

The antimicrobial action of these compounds is based on the activated N-S bond in the ring. Upon reaction with nucleophilic cell components (amino acids, proteins, enzymes), the ring opens, and the microbicidal action is thus produced. The electrophilically active substance is consumed irreversibly. The effectiveness of these microbicides decreases with the increasing stability of the molecule.



2-Methyl-4-isothiazolin-3-one (MIT); CAS no. 2682-20-4

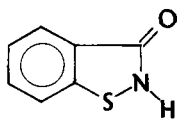
A particularly reactive example of this class of substances is 5-chloro-2-methyl-4-isothiazolin-3-one (CMIT). The reason for the high effectiveness of CMIT is the additional vinyl-activated chlorine atom.



5-Chloro-2-methyl-4-isothiazolin-3-one (CMIT); CAS no. 26172-55-4

In contrast to 2-methyl-4-isothiazolin-3-one (MIT), which is not chlorinated and more stable, CMIT contains two toxophoric groups in one single molecule. The differences in the effectiveness of CMIT and MIT can easily be detected by determining the minimum inhibition concentration. Another advantage of CMIT is that it is more effective than other preservatives against *Pseudomonas*. However, it has no rapid or head-space action; thus, the formation of condensation water may result in local dilution effects and subsequent mould formation. This can be avoided by combining CMIT with a vapour-phase effective preservative. Another negative aspect of the use of CMIT is its critical stability. The substance decomposes relatively quickly or deactivates in the presence of oxidizing or reducing agents, at pH values above 8, at temperatures over 40 °C, as well as by sodium thioglycolate, amines, mercaptans, sulphides, and sulphites. Bivalent ions such as  $\text{Cu}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  can be added to CMIT to stabilize it and protect it against nucleophilic attack outside the microbial cell.

The most stable compound amongst the isothiazolinone derivatives is 1,2-benzisothiazolin-3-one (BIT). Compared to CMIT, its heat tolerance and storage stability over a wide pH range (3–11) are relatively high, however, its effectiveness is rather low and its spectrum of activity is not balanced. High concentrations of BIT are required to inhibit or destroy *Pseudomonas* and some species of fungi such as *Aspergillus niger* and *Trichoderma viride*. In combination with iron salts, BIT causes discoloration.



1,2-Benzisothiazolin-3-one (BIT); CAS no. 2634-22-5

2-Methyl-4,5-trimethylene-4-isothiazolin-3-one (MTIT) is more stable than CMIT, but not as stable as BIT. In contrast to BIT, its antibacterial action is considerably stronger and also includes the *Pseudomonas*. To ensure fungicidal action, however, higher concentrations of MTIT are necessary.

All isothiazolinone derivatives – in particular CMIT and BIT – are skin sensitizing.<sup>[8-67-8-69]</sup>

### 8.4.5.9 Alcohols

Alcohols are biocides with rapid action; however, compared to other active substances, higher concentrations are required in most cases. In general, the microbicidal action of alcohols improves with increasing molecular weight and chain length – the maximum length is 5–8 C atoms. Their disinfectant action is mainly based on the denaturation of proteins, which depends on the water portion present (optimum with ca. 30% water). In the case of absolute alcohols, the dehydrating action is the main one. Alcohols act fast and are thus often used as disinfectants; another advantage is that they do not leave any undesirable chemical residues on treated objects and surfaces. The group of alcohols also includes other molecules that, apart from the OH group typical of alcohols, contain additional biocidal structure elements. Important examples in preservation are 2-bromo-2-nitropropane-1,3-diol (Bronopol), 2-bromo-2-nitropropan-1-ol (BNP) and 5-bromo-5-nitro-1,3-dioxane (Bronidox). These compounds are electrophilically active substances with antimicrobial action that is not based on the release of formaldehyde, but on the reaction with thiol groups in enzymes and presumably a certain impact on the cell wall synthesis. Together with metal ions such as iron or aluminium, these substances can form nitrosamines.<sup>[8-67–8-69]</sup>

### 8.4.6 Film Preservation

Every surface and every substrate serves as a suitable nutritive medium for micro-organisms, provided there is enough humidity. As opposed to in-can preservation where enough water is available, there is not always sufficient water on surfaces. Different species of micro-organisms, other than bacteria, are specialized to thrive in this particular ecological habitat: fungi, algae, and lichens. Their humidity requirements are not as demanding as those of bacteria. Fungi use – like bacteria – organic carbon sources to obtain their energy. Algae only need a suitable source of light and carbon dioxide to feed. Due to their green or orange colour, they can be identified more easily than fungi. The mostly brown-blackish fruiting body and spores of fungi are often not identified as such, or are mistaken for dirt, or vice versa. In contrast to algae, fungi grow not only on the film, but also in and under the paint film on or in the substrate (e. g., blue-stain fungi in timber). There are several types of growth:

- The fungus grows in the film and uses the latter as nutrient (primary growth).
- It grows on the dirt particles deposited on the film surfaces and uses them as nutrients (secondary growth).
- The fungus grows under the film in the substrate, and after breaking through the paint film it forms strongly coloured spores. The fungus grows through the paint film which thereby becomes porous and no longer adheres to the surface.

Many types of fungi grow both inside and outside buildings. Algae are mostly found outdoors because, with only a few exceptions, they need a strong light source

for their growth. This also applies to lichens. Based on these considerations, and depending on the individual field of application, there are different requirements for film preservatives:

*Indoor application:* The products that are used should above all have a fungicidal or fungistatic action. In most cases, leaching of the substance(s) can be prevented by applying a water spray to the film surface; thus, the water solubility of the microbicides used is of minor importance. Low water solubility, however, is very important in rooms with high room humidity. Through condensation of air humidity at the cooler walls, condensation water may be formed and thus the portion of active ingredients in the film is considerably reduced by leaching. Due to the reduced concentration of active substances in the area of the film surface, the substrate will be attacked by fungi after a short time. This applies in particular to paints in dairies, in breweries, and in cheese dairies, where the proportion of fungal spores is naturally very high, where condensation water continuously wets the walls, and where walls are often additionally cleaned with water after the different manufacturing steps.

*Outdoor application:* The products used should be effective against both fungi and algae. If this requirement is not fulfilled, some selected species of algae or fungi may be "cultivated" unintentionally on the film. Moreover, the solubility of the active ingredients in water should be relatively low in order to achieve optimum long-term protection. Despite the low water solubility, the substances can migrate in the slightly swollen paint film, and the biocidal preservative develops its full action over the desired period of time.

The pH values of the exposed coatings have a decisive influence on the behaviour of the biocides. Problems are particularly posed by cements, plasters, or paints with high pH values (>10). Even under these extreme conditions, the preservative must not degrade. For permanent protection, the type of the paint or coating system is also very important. Based on the findings in systematic documentation regarding the individual active ingredients, the influence of the binding agent and pigmentation, relatively precise predictions can be made concerning the suitability of a fungicidal paint or coating and the duration of preservation. Lacquers generally need more biocidal additives than dispersion paints or plasters. However, in paints and plasters, the action is insured for a longer period of time. The acute effectiveness of film preservatives is higher in highly pigmented systems than in systems rich in binding agents, and in particular, their remote action is stronger. Long-term protection is stronger in systems rich in binding agents because the film only allows for limited migration of the active substances. Under extreme conditions, with microbicides with very low water solubility, and a high portion of binders, the preservatives may be blocked in the film, and thereby produce none of the desirable surface activities.

To take all factors in consideration and to simplify the choice of a suitable film preservative, several test methods have been developed to check the effectiveness of the microbicide in the film, its leaching resistance, as well as its chemical stability.

Since it may be difficult for laymen to use the test results and methods to decide which system meets their requirements most effectively, the most important criteria for a critical evaluation are listed below:

- For how long and at what temperature were the uncoated wet samples stored prior to application?
- What was the applied thickness of the film?
- What is the substrate made of?
- How long and at what temperature was the applied film dried?
- What kind of loading tests, such as leach-out stability and ultraviolet resistance, were carried out on the dry film?
- What micro-organisms were used to check microbiological activity?
- At what temperature and for how long were the samples incubated?
- How were the samples evaluated?

On the basis of the test results, the best-suited biocidal system for the analysed conditions can be selected; long-term development, however, can only occur through practical usage. Many real-life natural processes cannot be copied or can only be imitated to a limited extent in the laboratory. In the case of strong pollution, for example, there may be fungal infection despite sufficient application of a fungicide if a substance with very low water solubility is used. However, the action can be reactivated by the removal of the dirt layer. To avoid cleaning and/or to compensate for its effects, coatings with a certain remote action are preferred. Because the fungicide penetrates slowly into the dirt layer, this layer can also be kept fungus-free. This remote action, however, is at the cost of long-term protection if the film preservative contains only one active substance. Since this is a well-known problem, most microbicides for film preservation are mixtures of several active ingredients, with one or more components that have high water solubility to thus ensure remote action, and the other components have low water solubility to ensure long-term protection.

#### **8.4.7 Restoration of Surfaces**

Analysis of an infested surface and the determination of its cause often leads to the following conclusion: To save costs, no film preservative or an insufficient amount of preservative was used. Another reason for fungal and algal infestation may also be found in the incomplete spectrum of activity of the microbicide used. In all cases, it is essential to determine what kind of organism has caused the deterioration and – by means of a test series in a laboratory – what preservative is best used and in what concentration. However, before the infested surface is recoated with the microbiccidal paint, the biofilm has to be destroyed and removed. This prevents reinfestation of the newly applied layer from below and also prevents the appearance of the colour pigments produced by the micro-organisms. To this end, oxidizing chemicals or special restoration substances are used. The following steps are recommended in order to successfully restore infested surfaces:

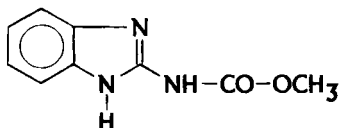
- The biofilm should be treated with a suitable restoration substance. After a contact time of 12 hours, the destroyed micro-organisms should be removed mechanically. This prevents fungal spores from spreading into the air.
- Subsequently, the prepared surface should be treated again with the substance to ensure that any persistent micro-organisms in cracks and micro-splits are also destroyed.
- After the surface has completely dried, the microbicidal paint should be applied, to prevent reinfestation.

### 8.4.8 Film-Preserving Substances

The simplified division of active ingredients into membrane-active and electrophilically active biocides outlined in Section 8.4.5 regarding in-can preservation is also applied to film-preserving substances. Some of the active ingredients are used both as in-can and film preservatives in different formulations. These sometimes complicated formulations consisting of different active and auxiliary substances are developed depending on their field of application and special requirements. In the following section, the most important substances or categories of substances currently used will be outlined.

#### 8.4.8.1 Benzimidazoles

The most important substance of this product category is carbendazim. This technical fungicide is characterized by a high chemical and physical stability. Its action is based on the inhibition of DNA synthesis. Carbendazim is a pure fungicide and thus ineffective against algae and bacteria. Unfortunately, its spectrum of activity is somewhat incomplete: the growth of the fungus species *Alternaria*, *Mucor*, *Geotrichum*, *Candida* and *Streptoverticillium*, for example, is hardly inhibited at all, or only inhibited with the application of very high concentrations. However, this lack of effectiveness can be compensated for through combination with other active ingredients. Due to its extremely low water solubility, carbendazim is perfectly suitable for the protection of strongly exposed surfaces.<sup>[8-67-8-69]</sup>



Carbendazim; CAS no. 10605-21-7



and with an S-CCl<sub>2</sub>F toxophoric group have optimum microbicidal activity. These substances are mainly used as fungicides in paints, where they have the advantage of low water solubility. In terms of ecological requirements, the chlorine and fluorine in the molecules are of disadvantage. Important examples of this substance class are Folpet, Fluorfolpet, Captan, Dichlofluanide, and Tolyfluanide.<sup>[8-68]</sup>

#### 8.4.8.4 2-*n*-Octyl-4-isothiazolin-3-one (OIT)

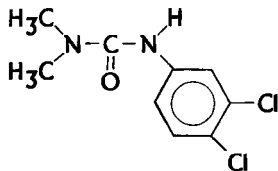
This compound belongs to the isothiazolinone derivatives outlined in section 8.4.5.8. OIT is effective against fungi, algae, and bacteria. Since its fungicidal effectiveness is extremely strong, it is mainly used as a film preservative, and also as a preservative in cutting and drilling oils. A negative aspect of OIT is its high water solubility and therefore its fast leaching out of the substance of the paint film in outdoor applications.<sup>[8-68, 8-69]</sup>

#### 8.4.8.5 Zinc Pyrithione

Zinc pyrithione is a membrane-active microbicide which also forms complexes. It is primarily effective against fungi; its effectiveness against bacteria is considerably lower. At a pH value of >8, zinc pyrithione is converted into alkaline salts which are more water-soluble. If ions of heavy metals, such as iron or copper ions, are available, coloured complexes may be formed. This may cause undesirable discoloration in white paints.<sup>[8-67, 8-68, 8-70]</sup>

#### 8.4.8.6 Diuron

This urea derivative is a pure algicide. Its effects are based on the interruption of photosynthetic electron transport and thus inhibition of photosynthesis. Diuron is light-resistant, nonvolatile, almost insoluble in water, and it has good toxicological properties. In order to achieve satisfying protection of the paint, Diuron has to be combined with a fungicide.<sup>[8-67, 8-68]</sup>



Diuron; CAS no. 330-54-1

### 8.4.9 Conclusion

The worldwide trend towards water-based paint systems due to ecological considerations was not possible before preservatives were introduced. They allow the use of biodegradable products because they inhibit or prevent the growth of micro-organisms. Paint technologists have a wide range of preservatives at their disposal. It is their task to choose the optimum product for the paint system. They are supported by the manufacturers of biocides, who are aware of both microbiological and paint-specific problems. Due to their close cooperation, customized products are being developed for the finished product. These formulations contain combinations of active substances which, due to the enlarged spectrum of activity, allow for lower concentrations. A competent supplier of biocides is capable of identifying microbial problems, finding the suitable active ingredients and developing a user-friendly product. During the manufacture of the paint, the quantity of microbicides can be strongly reduced if production hygiene is maintained. Thus, costs and the environmental impact can be reduced.

The use of microbicides is a temporary compromise with nature. We delay the natural mechanisms of deterioration for a certain time and thus have to bear the expense of the preservatives.

### 8.4.10 Commercial Products

Metatin	(Acima)
Proxel	(ICI)
Preventol	(Bayer)
Mergal	(Troy Mergal)
Nuosept	(Creanova)

## 8.5 Flame Retardants

*R. Spang*

### 8.5.1 General Information

Flame retardants are used as additives in coating systems; they are decomposed by heat to produce non-flammable components which are able to slow the flame spread and retard or even suppress the combustion process by inhibiting the combustion reaction in the flame, or by other mechanisms such as suppression of the oxygen flow and the build-up of protective layers.

#### 8.5.1.1 Flammability Classification and Testing Methods

Each year many human lives and material of large values are destroyed by fires (e. g., in Germany in 1980, 500 people died and damages of DM 2500 million were caused by fires); therefore, great importance is attached to preventive fire protection measures.

To make it possible to compare and evaluate the inherent fire hazards of different materials used for building, furniture, decoration, and other purposes, classification systems for the assessment of properties such as inflammability, flame spread, etc., were created.

Depending on the country and type of use, there are various regulations and testing methods for the classification of materials.<sup>[8-71-8-73]</sup> In Germany, for example, the fire protection regulations for building purposes divide building materials and composites into five fire-performance classes (DIN 4102): classes A1 and A2 (non-combustible), which is only valid if the material consists almost entirely of inorganic components, class B1 (low flammability), B2 (moderately flammable) and B3 (highly flammable). In these last three classes, the basic material may consist of combustible (organic) components, but for classes B1 and B2 inflammability and flame spread rate must be within a certain range, and the material should have self-extinguishing properties after removal of the heat source. Building compounds (which may be composed of different material types) are divided into fire-resistance classes in which a denominator indicates the time (in minutes) that the compound can withstand a standardized fire without losing its functional properties (ratings up to F 60 are called fire-retardant, F 90 and F 120 fire-resistant, F 180 highly fire-resistant).

Highly flammable materials (B3) should not be used in buildings, except if processed into composites with a rating of B2 or better. Layers of coatings up to 0.5 mm thickness on massive mineral substrates need not necessarily conform to

these regulations. Building materials classed B2 (such as wood, polystyrene, sealants) are allowed for many building applications, but the requirements for multi-storeyed buildings are more stringent, and for them B1-type materials (such as plaster board, polyvinyl chloride pipes, oak parquet) are mostly required.

Many applications (e. g., transportation, electrical engineering, furniture, and furnishings) have their own, mostly nationally different testing regulations. One of the most important, widely used and adapted testing methods is the UL 94V Flammability Test of Underwriter Laboratories (USA) in which vertically suspended samples are exposed at their lower edges to a Bunsen burner flame for 10 seconds and then divided into flammability classes according to their burning behaviour:

	Afterflame time	Afterglow time	Burning drippings
94V-0	≤ 5 s	≤ 30 s	no
94V-1	≤ 25 s	≤ 60 s	no
94V-2	≤ 25 s	≤ 60 s	yes

Depending on their basic chemical make-up, many plastics need to be equipped with flame-retardant substances if they are to fulfil fire protection regulations. These additives normally cannot prevent ignition of a material (except in the case of very weak ignition sources), but they slow the velocity of the flame spread and thus retard the progression of a conflagration; this gives threatened persons an opportunity to escape, or allows time for the fire brigade to fight and suppress the fire.

### 8.5.1.2 The Combustion Process

The burning behaviour of a material is determined by external conditions such as:

- temperature
- ignition source (flame strength)
- oxygen supply
- the thickness of the substance layer and the geometry of its parts
- influence of adjoining materials

Innate properties such as the following material properties have an even greater influence on the burning behaviour:

- decomposition temperature (start of pyrolysis)
- ignitability (flash- and self-ignition temperature)
- heat of combustion
- thermal conductivity
- tendency towards char formation
- type of generated combustion gases

The course of the combustion process may be divided into two parts:

- firstly, the pyrolysis reaction occurs in the condensed phase (the solid substrate)
- this is followed by oxidation of the pyrolysis products in the gas phase<sup>[8-74, 8-75]</sup>

The necessary preliminary step for the combustion of solid plastics is the thermal decomposition of the material. For this, the bond energy of the polymers, which lies between 200 to 400 kJ mol<sup>-1</sup> has to be surmounted and the bonds have to be cracked; the energy for this endothermic process has to be provided by an external heat source (radiation or open flame), either in the latter stages of a fire, or by the exothermic energy of the combustion process itself.

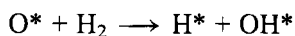
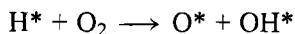
In the condensed phase, the pyrolysis of the polymers generates partly charred solid products in the case of duromeric plastics or a polymer melt in the case of thermoplastics; due to the low oxygen concentration at the interface of the condensed/gas phase, only smouldering and glowing processes occur there.

In contrast to this, the combustible pyrolysis gases in the gas phase are mixed with atmospheric oxygen, ignite, and burn in a strongly exothermic reaction; the heat of combustion generated in this manner supplies the energy needed for further pyrolysis of the substrate surface, and combustion can progress without further energy supply from the outside. Then flame spread occurs, with temperatures of up to about 1200 °C in the gas phase, and about 500 °C in the surface layer of the condensed phase (Table 8.5-1).

**Table 8.5-1.** Combustion process in the gas- and condensed phase

	Initial state		Start of combustion		Flame spread
Gas phase	Air (O <sub>2</sub> )		Air (O <sub>2</sub> ) Non-combustible gases Combustible gases		$\xrightarrow[\text{Combustion}]{\text{Oxidation}}$ 1200 °C
Condensed Phase	Polymer	$\xrightarrow[250\text{ °C}]{\text{Pyrolysis}}$	↑ Combustible liquids Charred solid residues		$\xrightarrow[\text{Smouldering}]{\text{Glowing}}$ 500 °C
Energy balance			Endothermic (-Q <sub>1</sub> )		Exothermic (+Q <sub>2</sub> ) (where Q <sub>2</sub> >Q <sub>1</sub> )

The gas-phase reaction in the flame consists of a radical chain reaction which starts with the radicals or molecular fragments released by pyrolysis of the polymer, and continues rapidly due to the very “hot” (extremely reactive) radicals OH\* and H\*, which are generated in great amounts by the so-called branching reaction with oxygen:



The gases set free by the combustion process are what represent the greatest danger to humans, because the inhalation of toxic and hot fumes, as well as lack of oxygen were found to be the most frequent cause of death in fires. It is the carbon monoxide, generated in high concentrations at each fire, that is the main factor in fatal poisonings.

### 8.5.1.3 Mechanism of Flame Retardance

The modes by which flame retardants interfere with the combustion process depend on their type of mechanism (physical or chemical) and the phase in which they operate (condensed or gas phase). Table 8.5-2 gives an overview of the different principles of combustion inhibition.<sup>[8-74-8-76]</sup>

**Table 8.5-2.** Modes of action of flame retardants

	Type of action		Place of action	
	phys.	chem.	Gas phase	Condensed phase
(A) Dilution of combustible mass	×		×	×
(B) Endothermic decomposition	×			×
(C) Charred layer formation	×	×		×
(D) Radical scavenging		×	×	

#### Dilution of the Combustible Mass

The presence of inorganic fillers in the condensed phase reduces the concentration of combustible material and thus lowers the “heating value” (the potential gain of combustion energy) of the substrate. Pyrolysis of the substrate or decomposition of fillers in the solid phase, as well as the combustion reaction itself generate inert gases which, in a similar manner, dilute the concentration of flammable substances in the gas phase, thus reducing the exothermic energy of the combustion reaction in the flame.

These inert compounds have the effect of a ballast at the site of the fire; they have to be heated up too, so they consume part of the energy of the fire, without contributing their share to the combustion energy.

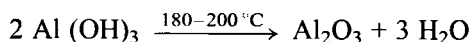
Inert decomposition gases that evolve in the condensed phase and enter the gas phase may also form a sort of protective layer at the interface, thereby lowering the concentration of oxygen there and reducing the extent of smouldering and glowing processes – this also means a decrease in exothermic energy.

#### Endothermic Decomposition

This mechanism interferes with the energy balance of the combustion process. The condensed phase (substrate) contains fillers that decompose under the influence of heat in an endothermic reaction, thereby evolving inert gases such as vaporous water.

The energy  $Q_d$  used up thereby is withdrawn from the combustion process; this lowers the amount of combustion energy  $Q_c$  which could otherwise have been used for pyrolysis of the substrate (another endothermic process, consuming  $Q_p$ ). As soon as the resulting energy amount  $\Delta Q$  in the energy balance  $Q_c - Q_p - Q_d = \Delta Q$  sinks below zero, the substrate involved cannot maintain the progress of its combustion by itself – the material is combustible but self-extinguishing. In such a case, a fire can spread only if external input of energy continues, that is, if an external heat source continues contributing energy.

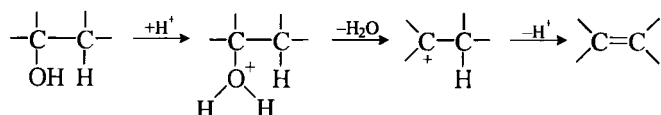
A typical representative of this class of flame retardants is aluminium trihydroxide (ATH), which eliminates water in a strongly endothermic reaction ( $Q_d = 298 \text{ kJ mol}^{-1}$ ):



### Char Formation

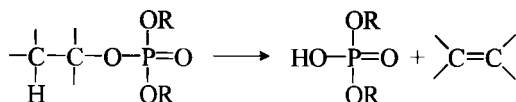
If the substrate contains substances favouring char formation, such as aromatic or other organic structures rich in C=C double bonds or hydroxyl groups, a carbonization reaction may occur at the surface of the condensed phase in the case of fire. A charred layer with low ignitability forms, covering the substrate like a lid or glaze and retarding further combustion in two ways: by impeding the heat transfer into the substrate, and thus hampering the further progress of pyrolysis into deeper layers of the substrate, and by barring the transition of combustible pyrolysis products from the condensed into the gas phase, thus limiting the supply of combustible materials in the flame.

In organic compounds rich in hydroxyl groups, the charring reaction occurs in two steps: firstly the hydroxyl-containing substances are dehydrated by acid catalysis and C=C double bonds are formed:



These are converted by radical reactions into highly cross-linked carbon-rich layers.

Phosphoric and phosphonic esters undergo similar processes, to decompose into acids and compounds with C=C double bonds:

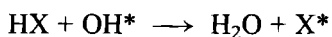
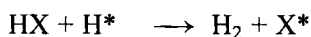
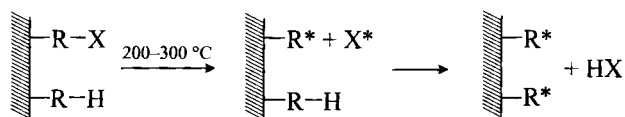


The phosphoric acid derivatives thus formed act as dehydrating agents, and may also condense to form polyphosphoric acid, forming a sort of additional protective glaze. Boric acid acts in a similar way.

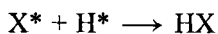
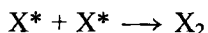
### Radical-Scavenger Reaction

This effect occurs in the flame itself and functions by converting the “hot” radicals present in the flame into “cool” (less reactive) ones.

The radical scavengers used in most cases are halogen radicals ( $X^*$ ) which are eliminated by the influence of heat from the flame retardant contained in the condensed phase; the scavengers enter the gas phase and react there with the “hot” radicals  $H^*$  and  $OH^*$ , thus eliminating them from the radical chain reaction:



The “cool” halogen radicals formed as products of this scavenging reaction are stable enough to survive in the gas phase without starting another chain reaction until they recombine with one another (in a three-body collision with, e.g., soot particles; the presence of a third particle is necessary to provide a “wall effect” to dissipate the collision energy and avoid the immediate re-decomposition of the recombined radicals), thus terminating the reaction chain.



## 8.5.2 Common Flame Retardants – Structure, Mode of Action, Properties

### 8.5.2.1 Inorganic Flame Retardants

The most widely used material of this type is aluminium trihydroxide  $\text{Al}(\text{OH})_3$ .<sup>[8-77]</sup> Magnesium hydroxide,  $\text{Mg}(\text{OH})_2$ , as well as boric acid, and their derivatives are used to a much lesser extent.

These substances have a flame-retardant action mainly due to their endothermic decomposition reaction (mode B); their dilution effect (mode A) also plays a lesser role. Boric acid acts additionally by char formation (mode C).

It is important that the decomposition temperatures of such flame-retardant inorganic fillers lie in the range between 200 and 300 °C. This allows them to be effective in the starting phase of a fire. This is the reason why chalk (calcium carbonate), with its elimination of carbon dioxide only at temperatures of about 900 °C, is not suitable.

The disadvantage of these flame retardants is that high filler loads (normally above 60%) are necessary for good results. Their great advantage lies in the fact that they produce no toxic or corrosive gases, so that they can be considered as physiologically harmless.

Other inorganic flame retardants are ammonium polyphosphates as well as micro-encapsulated red phosphorus; their effectivity is mainly due to their char-formation tendency (mode C). The scope of application of some ammonium polyphosphate types is limited by their solubility in water; but long-chained, as well as micro-encapsulated types with very low solubility are available.<sup>[8-78]</sup>

A ceramic material which sinters in fire to form a glassy protective layer on the substrate is useful only in special cases due to its high sintering temperature of 800 to 900 °C;<sup>[8-79]</sup> the same holds for an expandable type of graphite.

All inorganic flame retardants are solids and thus not suitable for transparent materials. Table 8.5-3 summarizes the properties of the most important inorganic flame retardants.

**Table 8.5-3.** Inorganic flame retardants

Substance		Decomposition temperature
Aluminum trihydroxide	Al(OH) <sub>3</sub>	180–200 °C
Magnesium hydroxide	Mg(OH) <sub>2</sub>	approx. 340 °C
Boric acid	H <sub>3</sub> BO <sub>3</sub>	2 steps: 130–200 °C 260–270 °C

### 8.5.2.2 Halogen-Containing Flame Retardants

This class of flame retardants is, quantity-wise, second only to the inorganic one. Consumption of the halogen-containing retardants makes up approximately one third of the total use of flame retardants.

In most cases, bromine- and chlorine-containing compounds are used, either as additives and plasticizers or as reactive compounds that are able to be incorporated during the curing process into the binder matrix and thus covalently bond to the polymer-network structure.

Halogenated systems work by the radical-scavenging mechanism (mode D). Hydrogen bromide or hydrogen chloride is eliminated from the substrate under the influence of heat, they enter the gas phase and there inhibit the radical chain reaction in the flame.

In principle, all halogen-containing retarder types are effective as radical scavengers, but their differing ease of elimination (that is, their different carbon-halogen bond strengths) determines their practical applicability as it is important that they act early, at the lower temperatures in the initial phase of the combustion process. The bonding energy of fluorine to organic carbon (R-F) is too high for practical use, that of iodine (R-I) is again too low, so that iodine compounds are not stable enough at

normal temperatures. The bromine to carbon bond (R-Br) breaks more easily than the chlorine to carbon bond (R-Cl), and because the aromatic halogen compounds are more stable than the aliphatic ones, aromatic bromine compounds and aliphatic chlorine compounds have proved to be the most suitable types for flame retardation. Because the bromine compounds decompose rapidly in a narrow temperature range that is typical of the early stages of a fire, a high concentration of hydrogen bromide is formed in the gas phase in that critical starting phase; therefore bromine-containing flame retardants are even more effective than most of the chlorinated types. Due to their satisfying thermal stability they are well suited for use in thermoplastic materials.

Liquid chlorinated paraffins are widely used as plasticizers.

To avoid "bleeding" of liquid flame retardants by migration out of the substrate, halogen-containing compounds with additional reactive groups are used in many reactive synthetic resin systems such as polyurethanes, epoxides, unsaturated polyesters, and alkyd resins; they are able to take part in the curing reaction, thus the flame retardant molecules are bound solidly into the polymer matrix structure and are prevented from migrating. Table 8.5-4 shows a selection of the most common halogenated flame retardants.

Due to the very good flame-retarding effect of halogenated compounds, concentrations of 15 to 20 weight percent are usually sufficient to reach an adequate fire-pro-

**Table 8.5-4.** Halogenated flame retardants

			Thermally stable up to	Remarks
<b>as additive:</b>				
Chlorinated paraffins	$\text{H}-(\text{CH})_n-\text{H}$ 	30-70% Cl	220 °C	inexpensive, light stable, liquid, plasticizer
Polybromodiphenyl oxides		up to 83% Br	400 °C	expensive, limited light-stability, solid, very effective for thermoplasts
Polybromodiphenyls		up to 80% Br		
<b>as reactive components (integrated):</b>				
Cl- and Br-containing Polyols (Cl up to 7%, Br up to 46%)				for polyurethanes
<b>as binder components:</b>				
Dibromoneopentylglycol			<220 °C	for UPE, epoxides, alkyd resins
Tetrabromobisphenol-A			400 °C	
HET acid anhydride			260 °C	
Tetrabromophthalic acid anhydride			400 °C	

tection classification. Their efficiency may be enhanced by simultaneous use of antimony trioxide, because this metal oxide evaporates in the heat of the fire and intervenes in the radical-scavenging action of the hydrogen halides in a synergistic manner by the formation of intermediate  $SbX_3$  molecules. Antimony trioxide dust is, however, considered to be potentially carcinogenic, so its use is not recommended, for physiological reasons. Zinc hydroxy stannates, as well as zinc borates, are discussed as potential alternatives.<sup>[8-80]</sup>

In fire, halogenated compounds generate corrosive and physiologically hazardous acidic gases. The corroding action on metallic parts and electrical wiring may, especially, present serious problems. The toxic effect of hydrogen halides is normally not as serious as the danger presented by carbon monoxide, which in most fires is the main cause of lethal poisonings. Presently, the potential generation of dioxins by aromatic bromine-containing compounds such as polybrominated diphenyl oxides is under discussion as being a very serious problem; this also strongly hinders the possibility of recycling or easily disposing of plastic housings and electronic conduits that are often flame-protected in this manner.<sup>[8-81]</sup>

### 8.5.2.3 Phosphorus-Containing Flame Retardants

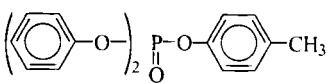
This is the third-most commonly used class of flame retardants, but its importance is bound to grow. Phosphorus-containing compounds (usually phosphoric and phosphonic acid esters) act by forming protective layers of char (mode C). They are especially effective with binder systems containing many hydroxyl groups. Liberating phosphoric acid by decomposition, they promote the acid-catalysed dehydration and formation of structures rich in C=C double bonds, which by radical reaction build up a thermally stable protective carbon layer; in addition, they may form a flame-retarding glaze-like phosphoric acid melt on the surface of the substrate.

Most phosphorus-containing flame retardants are used as plasticizers, in which case care needs to be taken that low-volatility types are used, to guarantee lasting fire protection of the material. Compounds such as diethyl phosphate are therefore less suitable, despite their good flame-retarding performance, because they tend to evaporate gradually from the substrate. Diphenyl cresyl phosphates and similar compounds are preferable, instead.

Some of these phosphorus compounds are halogenated additionally, and the radical scavenging action of the halogens is used as a supplementary effect. There may also be some synergistic effect between phosphorus and halogens by the intermediate formation of  $PX_5$  and  $POX_3$ . Table 8.5.-5 shows some important representatives of this class.

Non-halogenated phosphorus compounds generate no acidic gases in the case of fire and are thus less harmful with regard to corrosion and toxicity risks than halogen-containing systems are. But with some widely used phosphorus-containing flame-retardant plasticizer types, a potential physiological risk has come to be suspected recently, e. g., with tris(chloroethyl) phosphate and dimethyl methylphosphonate.<sup>[8-78]</sup>

**Table 8.5-5.** Phosphorus-containing flame retardants**as additive (plasticizer):**

Phosphoric acid esters, e. g., triethylphosphate	$(\text{CH}_3\text{-CH}_2\text{-O})_3\text{P=O}$
Diphenylcresylphosphate	
Tris-β-chloro-ethylphosphate	$(\text{Cl-CH}_2\text{-CH}_2\text{-O})_3\text{P=O}$
Phosphonic acid esters, e. g., dimethylmethylphosphonate	$(\text{CH}_3\text{O})_2\text{P(=O)-CH}_3$

**as reactive components (integrated):**

P-containing Polyols, e. g., diethyl- <i>N,N</i> -bis-(2-hydroxyethyl)-aminomethylphosphonate (7–10 % P) or	$(\text{CH}_3\text{-CH}_2\text{-O})_2\text{-P(=O)-CH}_2\text{-N(CH}_2\text{-CH}_2\text{-OH)}_2$
Dibutyl-dihydroxyethyl-diphosphate	$(\text{HO-CH}_2\text{-CH}_2\text{-O})_2\text{P(=O)}_2\text{OC}_4\text{H}_9$

**Advantages:** liquid, effective, partly halogenated (synergistic effect)**Disadvantages:** price, partly low hydrolysis stability**8.5.2.4 Char-Forming Flame Retardants**

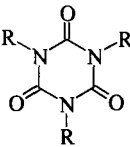
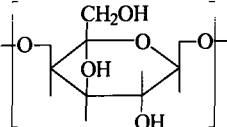
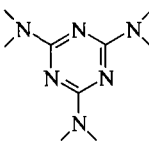
Compounds with a high content of C=C double bonds, aromatic structures, and hydroxyl, ether, and ester groups are especially suited for char-formation, the build-up of interconnected layers of carbon substrate (mode C). They may be part of the binder system (e. g., aromatic polyesters in polyurethane and unsaturated polyester systems, or cellulose and sugar derivatives in polyurethane resins and textiles), they may be introduced as fillers (e. g., solid melamine resins), or they may be generated during the curing reaction of reactive resins, e. g., in so-called PIR foams, where, in addition to the polyurethane groups (formed by reaction of isocyanate and polyol), isocyanurate ring structures are produced by catalytic trimerization of surplus isocyanate groups<sup>[8-82]</sup> (Table 8.5-6).

**8.5.2.5 Intumescent Systems**

Intumescent systems (Latin *intumescere* “to swell up”) are used above all in fire-protective coatings for wooden and metallic structures, but components thereof may also be utilized in synthetic resin systems.

In the heat of the fire, these intumescent coatings expand to a hundred-fold of their initial volume, and build up a porous layer which acts as thermal insulation and, by the presence of non-flammable gases in the foam pores, prevents the inflow of oxygen.

**Table 8.5-6.** Flame-retardant compounds rich in double bonds, hydroxyl groups, and aromatic structures

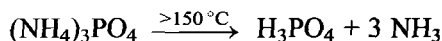
Aromatic polyester Aromatic polycarbonic acids (phthalic acids)		for PU, UPE for UPE
Polyisocyanurate-generating formulations →		for PU foam
Cellulose } combined with Sugar derivatives } P-compounds		as polyol components in PU, Textiles
Melamine resins, etc.		as fillers
<b>Effect:</b> Formation of thermally stable highly crosslinked structures (charred layers)		

Intumescent systems consist of:

- a carbon source (char promoters such as pentaerythritol, starch, urea resins, etc.)
- an acid source (e. g., ammonium polyphosphate)
- a foaming agent, a source of non-combustible gases to bring about the expansion of the system
- a binder resin (preferably thermoplastic) which melts under the heat of fire, contains the foaming gases in its viscous mass, and builds up the insulating carbon foam layer together with the remnants of the carbon source

When a fire breaks out, the following reactions will occur in the intumescence layer:

- The “acid source” decomposes and forms non-flammable gases (e. g., ammonia) and the acid:



- The phosphoric acid now catalyses the dehydration of the “carbon source”, promoting the elimination of water and the formation of a charred layer (probably by intermediate esterification of the polyhydroxy compounds and subsequent decomposition of these phosphates into phosphoric acid, water, and carbon residue)
- Simultaneously, the binder resin melts and is blown up into a foam layer by the gases freed by the thermal decomposition of the “foaming agent”. Whereas formerly chlori-

nated paraffins and similar compounds (acting as blowing agents and radical scavengers at once) were preferred for this purpose, melamine and guanidine (iminourea) derivatives are used nowadays, to avoid the generation of corrosive gases.

Intumescent systems are very efficient fire-protection agents. For example, steel structures (which lose their load-bearing capacity beyond 500 °C) covered with a 0.5 mm layer of intumescent coating are able to reach the fire-resistance class F 90, and wood treated in this way may be classified as B1 materials (low flammability).<sup>[8-83]</sup>

### 8.5.3 Use and Consumption

The yearly consumption of flame retardants amounts to approximately 700 000 tons, of which approximately 40% is used in the U.S.A., and Western Europe and the Far East approximately consume 30% each. This total may be divided into the separate classes of flame retardants as follows:<sup>[8-84]</sup>

- inorganic 47%
- halogen-containing 34% (including 18% bromine  
7% chlorine  
9% antimony trioxide as synergist)
- phosphorus-containing 14% (including 4% with additional halogen)
- others 5%

Overall, the bromine compounds are regarded as the most effective and are a still relatively inexpensive class of flame retardants. They are therefore still used in most thermoplastics as the standard means of fire protection, but due to physiological considerations and the need to avoid corrosive gases in the case of fire, the demand for alternative materials is increasing. However, in many areas of application, the replacement of halogenated flame retardants by other types would only be possible if the fire-protection requirements were lowered.

In reactive systems, phosphoric acid derivatives are a good, if not always quite equivalent choice (less so in thermoplastic systems that are processed via the molten stage and therefore need higher thermal stability).

For highly filled systems, the inorganic flame retardants (aluminium trihydroxide as a standard, with magnesium hydroxide next) is an inexpensive and physiologically harmless choice.

**8.5.4 Suppliers, Commercial Products**

Albright & Wilson (GB):	phosphoric acid esters, phosphorus-containing compounds
Bayer AG (D):	phosphoric acid esters
Dead Sea Bromine Co. Ltd. (Israel):	brominated compounds
Great Lakes Chemicals (USA):	brominated compounds
Hoechst AG (D):	phosphorus-containing compounds, chlorinated paraffins
Martinswerk GmbH (D):	aluminium trihydroxide
Nordmann, Rassmann (D):	various systems
Vereinigte Aluminiumwerke AG (D):	aluminium trihydroxide

## 8.6 Photoinitiators as Additives in UV-Curable Lacquers

*Manfred Köhler, Andreas Valet*

### 8.6.1 Introduction

UV curing is an environmentally friendly coating technology which avoids solvents. The liquid film changes, under UV exposure, within seconds into the completely cured coating. This reaction is based on complex photo-, radical-, and polymer chemical processes in the condensed phase, in which the photoinitiator, an “additive for lacquers”, plays a key role. It converts the incoming radiation energy into a chemical reaction and plays a central role in the curing process. In contrast to conventional additives, which are optionally added to a formulation to optimize its properties, the photoinitiator is an absolutely necessary ingredient in an UV-curable formulation.

#### 8.6.1.1 Difference Between Photoinitiators and Other Coating Additives

Additives for coatings are substances that in relatively small concentrations influence the properties of a coating before and after solidification. Flow and wetting agents, dispersants, antifoaming agents, or additives for the improvement of surface properties and adhesion are classical additives (see Chapter 1). Their activity is usually based on physical interactions with the other components of the formulation or with the substrate.

Light stabilizers, corrosion inhibitors, or biocides act as protecting agents. They inhibit chemical or biological processes that lead to the destruction of the coating or the substrate.

In contrast to inhibitors, catalysts or initiators start a reaction. In the case of the curing of lacquers, this reaction results in the formation of a solid coating. Catalysts, for example, cobalt salts, are used in air-drying systems. They accelerate a chemical reaction, but they themselves remain unchanged (see Section 7.1). Initiators behave in a different way. Their reaction products (radicals, for instance) add to the unsaturated components and become a part of the polymer layer. A well-known example of this type is benzoyl peroxide, which, when heated, decomposes into phenyl radicals and carbon dioxide.

As opposed to peroxides, photoinitiators exclusively react to light and their compounds are very stable and easy to handle. Lacquer formulations are ready to be applied if they are stored under the exclusion of light. They are generally stable against temperature increases. Such formulations are applied as a layer under nor-

mal room light conditions and they cure only when exposed to intensive UV light.

The following discussion deals exclusively with radical UV curing, which is most important type today. There are also photoinitiators which act by an ionic mechanism.

### 8.6.1.2 Development of UV Curing

UV curing is based on the photopolymerization of vinyl monomers.<sup>[8-85]</sup> The development of UV curing as a technology is closely related to the invention of photoinitiators. The photochemical cleavage reactions of benzoin ethers<sup>[8-86, 8-87]</sup> and benzil dimethyl ketal<sup>[8-88]</sup> were discovered between 1973 and 1975. Benzil ketals are useful as photoinitiators for the curing of clear coatings on wood, paper, and plastics.<sup>[8-89]</sup> The introduction of hydroxyketones as highly reactive and non-yellowing photoinitiators in 1982 opened further possibilities for new applications.<sup>[8-90, 8-91]</sup>

A further development is the chemical class of aminoketones. Compared to benzil ketals or hydroxyketones, they absorb light in the longer wavelength range and they are especially useful in thin, pigmented layers, for instance in UV-curable printing inks.<sup>[8-92, 8-93]</sup> For a while thick, pigmented layers with a good covering power for furniture coatings were a challenge. Because of the low transparency of such systems, only a reduced amount of light is available for the photoinitiator at the bottom layer. Recently, acylated phosphine oxide derivatives were shown to be especially useful for such applications.<sup>[8-94-8-97]</sup> They result in good through-curing and do not cause yellowing. The present state of photoinitiators and UV curing is summarized in reviews and monographs.<sup>[8-98-8-103]</sup>

A list of examples in Table 8.6-1 shows the completely different application areas of curing with photoinitiators.

**Table 8.6-1.** Different application areas of UV curing

- 
- Coatings for furniture and flooring
  - UV curing of printing inks
  - Prints on plastic containers and bags
  - High-gloss overprint varnishes on magazines and postcards
  - Glass-fibre-reinforced composites for containers and pipes
  - Lacquers for skis
  - Printed circuit boards in home appliances
  - Manufacturing of printing plates for newspaper printing
  - Manufacturing of compact discs
  - Photoresists for computer chips
  - Curing of dental materials
  - Coatings for optical fibres in communication technology
  - Manufacturing of complex three-dimensional models (stereolithography)
- 

The photocuring applications can be separated into full-plane (lacquers and printing inks) or image-wise exposure (photoimaging). The most important advantage

of UV curing in the industrial coatings area these days is that it is an environmentally friendly technology, which saves energy, space and time compared to conventional processes.<sup>[8-104, 8-105]</sup>

UV-coated objects are mainly used indoors. Outdoor applications are still in a developmental stage. It was shown that UV curing in the presence of light stabilizers as well as stabilization of UV-cured coatings against weathering is possible.

## 8.6.2 Main Components of UV-Curable Coatings

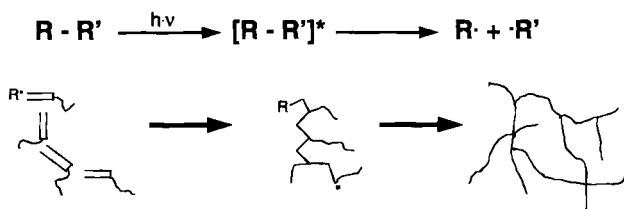
### 8.6.2.1 Photoinitiators

For a classification of the well-known photoinitiators and as a guideline for the development of new products, relationships between initiator action and chemical structure have been established.

Most photoinitiators contain a benzoyl group, which is mainly responsible for the absorption of the energy from the light. By the absorption of radiation energy, the initiator molecule is promoted to an excited state, from where the formation of a radical pair takes place. Photochemically formed radical pairs are available in a so-called triplet state. During UV curing these radicals add to the double bonds of the unsaturated reaction partner. Figure 8.6-1 schematically represents a polymerization process which is triggered by photoinitiators.

The photochemical formation of a radical pair can result of either the cleavage of one molecule (monomolecular reaction) or the reaction two molecules with each other (bimolecular reaction).<sup>[8-106-8-108]</sup> Photoinitiators of the monomolecular type are more effective than bimolecular combinations (for instance benzophenone/amine), because there is no need for a second reaction partner. In Table 8.6-2 the most important photoinitiators that form a radical pair by a cleavage reaction are listed. In each case a benzoyl- or acyl radical emerges ( $R^1\cdot$ ). The second radical type contains a different leaving group ( $R^2\cdot$ ).

Photoinitiators derived from phosphine oxides (mono- and bisacyl phosphine oxides) are of special interest these days. Investigations of a monoacyl phosphine oxide showed that the phosphine oxide radical is more reactive than the acyl radical.<sup>[8-109]</sup> Unlike in monoacyl phosphine oxides, the two acyl groups in bisacylphosphine oxides are photochemically split off.<sup>[8-110]</sup>



**Figure 8.6-1.** Schematic representation of a cross-linking reaction which is triggered by photoinitiators

**Table 8.6-2.** Examples of monomolecular-type photoinitiators

$R^1-R^2 \xrightarrow{h\nu} R^1\cdot + R^2\cdot$		
Photoinitiator	$R^1\cdot$	$R^2\cdot$
Benzoin ether	Benzoyl	Alkoxybenzyl
Benzil dimethyl ketal	Benzoyl	Dimethoxybenzyl
Diethoxy acetophenone	Benzoyl	Diethoxymethyl
Hydroxyketones	Benzoyl	2-Hydroxyalkyl
Aminoketones	Substituted benzoyl	2-Aminoalkyl
Monoacyl phosphine oxides	Substituted benzoyl (acyl)	Disubstituted phosphine oxide
Bisacyl phosphine oxides	Substituted benzoyl (acyl)	Monosubstituted phosphine oxide

### 8.6.2.2 Reactive Resins and Diluents

Acrylate-modified oligomers and unsaturated polyesters are mainly used as the reactive resins. Acrylate resins are epoxy, polyester, or polyurethane oligomers that have acrylate end groups. Unsaturated polyesters are condensation products of dicarboxylic acids and diols, and contain polymerizable double bonds, which mostly originate from maleic or fumaric acid.

(Co)polymerizable liquids with relatively low viscosity are used as reactive diluents. Examples of the most important resins and reactive diluents are given in Table 8.6-3.

**Table 8.6-3.** Most important reactive resins and diluents

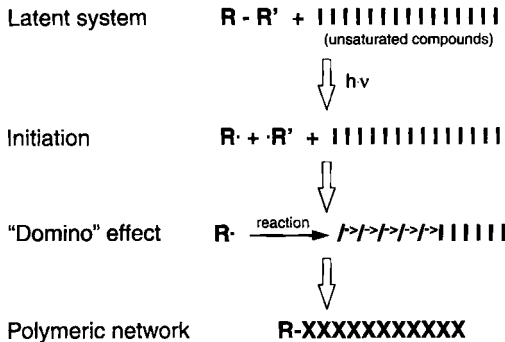
Designation	Abbreviation
Epoxy acrylate	EPOA
Polyester acrylate	PESA
Polyurethane acrylate	PURA
Unsaturated polyester	UPES
Hexanediol diacrylate	HDDA
Trimethylolpropane triacrylate	TMPTA
Tripropyleneglycol diacrylate	TPGDA
Styrene (diluent for UPES)	St

The most commonly used resins systems are continuously developed further. New developments concentrate on reducing toxicity,<sup>[8-111]</sup> improving adhesion to the substrate,<sup>[8-112]</sup> and developing systems which can be diluted with water.<sup>[8-113]</sup>

### 8.6.3 Radical Photocuring

#### 8.6.3.1 Mechanism

The mechanism of the photochemical curing process can be described with the terms latency, initiation, and “domino effect” (Figure 8.6-2).



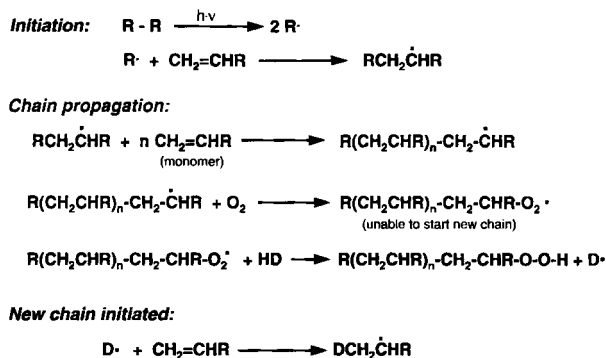
**Figure 8.6-2.** Latency, initiation and domino effect in UV-curable systems

In this context, latency means that, after the application of the coating, the reaction is initiated in a relatively convenient way by an external effect (the irradiation). The intensive exposure generates a high concentration of radicals from the photoinitiator molecules in a certain time and area. The addition of these radicals to the double bonds of the resins and diluents initiates a chain reaction which proceeds by a “domino effect” due to the direct contact of the reaction partners in the condensed phase. In this way one initiator radical triggers the reaction of a multitude of double bonds. The final product of the reaction is a cross-linked network.

The oxygen in the air inhibits radical polymerization, because the oxygen molecule as a biradical has the tendency to add to the growing polymer chain. The peroxides formed in this way are not reactive enough to continue the chain reaction and lead to termination. The inhibiting activity of oxygen is seen in incomplete curing and a tacky surface. Amines with a CH group adjacent to the nitrogen act as chain-transfer agents.<sup>[8-114]</sup> Figure 8.6-3 schematically represents oxygen inhibition through chain termination, and the action of amines.

Initiation and curing only takes place at the parts exposed to the light. The reaction cannot proceed on non-exposed areas, because the polymerization chain length is within molecular dimensions. The imaging process where exposure takes place through a mask, with subsequent washing out of unexposed (uncured) areas, is based on that feature.

During exposure, the initiator molecule is cleaved. The formed radicals can recombine or add to reactive double bonds and trigger an initiation. In the final state of the reaction, where the remaining photoinitiator molecules are trapped in a highly cross-linked polymer, recombination will dominate.



**Figure 8.6-3.** Chain termination by oxygen inhibition and new chain start by chain transfer  
 HD = Hydrogen donor (amine)

### 8.6.3.2 Investigating the Reaction Kinetics

There are different methods by which the kinetics of the photoinitiated polymerization can be followed and recorded quantitatively. The most important techniques include photo-differential-scanning calorimetry (Photo-DSC)<sup>[8-115, 8-116]</sup> and real-time infrared spectroscopy (RTIR)<sup>[8-117-8-119]</sup>. With these methods it is possible to measure the reaction behaviour of UV-curable formulations under different conditions.

The calorimetric measurement registers the heat of polymerization as a function of the exposure time. The shape and size of the emerging peak is related to the progression of the reaction. RTIR spectroscopy registers the consumption of double bonds and allows insights into the initial state of the reaction. Both methods show that polymerization starts spontaneously after a short inhibition period and reaches a maximum within a short time. The so-called Trommsdorf- or gel effect results in self-acceleration of radical polymerization, because with increasing viscosity the termination rate decreases.<sup>[8-120]</sup> In the rigid material, the velocity of the reaction slows down during continued exposure, even though there are still double bonds and photoinitiator molecules. The mobility of the reaction partners is strongly restricted and the necessary contact is not possible.

The reaction behaviour of systems containing white pigments<sup>[8-121]</sup> or light stabilizers<sup>[8-122]</sup> was also investigated with the RTIR method.

### 8.6.4 UV-Curing Technique

UV curing is especially useful for planar objects, which can be passed in front of a light source. Three-dimensional parts (e. g., chairs) are surrounded by lamps, in a closed chamber, so that uniform illumination of all coated parts is ensured.

An often-used lamp type is the 80 W/cm medium-pressure mercury lamp, which emits a broad spectrum in the short wavelength range from 200 to 320 nm but also

at discrete wavelength numbers of 360, 410, and 430 nm. Special doping substances are able to shift the spectrum to the longer wavelength region. The performance of the lamp is usually given in W per cm length of the bulb, for instance, 80 W/cm.

The curing units are designed for an optimal exploitation of the light and for shielding of harmful UV radiation or ozone which is formed by the short-wavelength UV light. The exposure time is regulated by the speed of the conveyor belt on which the coated substrate is passed under the lamps. A belt speed of 10 m/min under two lamps is equal to an exposure time of four seconds. Due to the short curing period, it possible to stack already cured parts only a short time after the application of the coating.

For a continuous process it is important to immediately ascertain a decrease in lamp performance or any other disturbance that may lead to an interference in the curing result. Minor changes in the curing conditions have a big impact on the result.

Crucial criteria for the control and evaluation of the curing are properties such as sweep- and scratch resistance, solvent resistance, abrasion resistance, hardness, and adhesion on the substrate.

Photochemical processes in polymers often leads to discoloration (yellowing). Because of this, a constant yellowness value (yellowness index) is of special importance for clear coatings on bright substrates or white lacquers.

Due to the fast congelation of the viscous liquid coating during UV curing, the gloss values are high. The surface remains smooth and undisturbed, similar to a liquid.

### 8.6.5 Examples of Photoinitiator Use

In the following examples, two hydroxyketones (HK-1 and HK-2) and one bisacylphosphine oxide (BAPO) are used. Their chemical structures are shown in Figure 8.6-4.

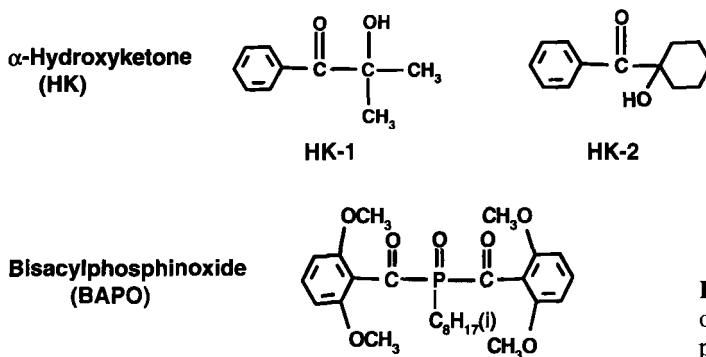
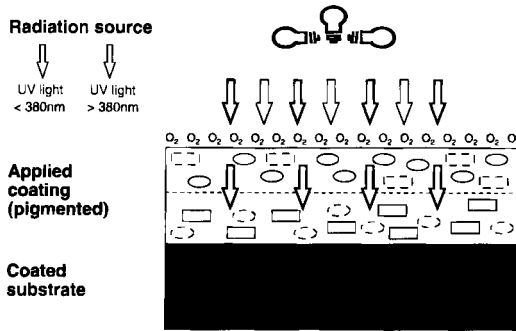


Figure 8.6-4. Examples of photoinitiators used in practice



**Figure 8.6-5.** Surface curing and through-curing with HK/BAPO mixtures in pigmented lacquers  
 □ = HK  
 ○ = BAPO  
 □□, ○○ = photocleavage

Figure 8.6-5 schematically shows how hydroxyketones mainly act on the surface, and how bisacylphosphine oxides cause through-curing. It should be kept in mind that there is a homogeneous distribution of both photoinitiators in the entire coating.

The following practical examples should serve as guidelines for the application of photoinitiators in different areas. Such lacquers are especially useful for coating wood or plastics. Tests and measurements for the evaluation of the curing result are listed in Table 8.6-4.

**Table 8.6-4.** Tests and measurements

Curing rate	The maximum belt speed in m/min for obtaining a tack-free and through-cured coating
Koenig pendulum hardness	The method is described by DIN 53 157 and the units of measurement are seconds
Yellowness index	The colour difference between the sample and a white standard as a reference is measured according to ASTM D-1925-88
Gloss	The gloss measurement is performed with a reflectometer according to DIN 67 530 at reflection angles of 20° and 60°

### 8.6.5.1 Clear Coatings

The difference in the reactivities of the acrylate resins EPOA, PESA, and PURA become obvious in an experiment which is described in Table 8.6-5. Epoxy acrylates are highly reactive, and they result in hard, but relatively brittle coatings. Polyurethane acrylates are significantly less reactive (a tack-free surface is obtained only after increasing the photoinitiator concentration), but they form more flexible coatings. Polyester acrylates are positioned between epoxy and polyurethane acrylates.

UPES/Styrene formulations have been used in the wood-coating industries for more than 25 years.<sup>[8-123]</sup> In these systems, benzil dimethyl ketal is more reactive than hydroxyketones. From the results in Table 8.6-6 it is clear that the addition of

**Table 8.6-5.** Curing speeds of different acrylate clear lacquers (Formulation: resin and TPGDA in a weight ratio of 4:1. Photoinitiator: 2% HK-1; film thickness (wet): 150  $\mu\text{m}$ . Exposure: two 80 W/cm medium-pressure mercury lamps)

Formulation	Curing speed (m/min)	Pendulum hardness (s)
EPOA + TPGDA	60	132
PESA + TPGDA	10	55
PURA + TPGDA	<10	—

**Table 8.6-6.** Curing of an UPES/styrene clear lacquer (Formulation: 66% UPES resin in styrene. Film thickness (wet): 300  $\mu\text{m}$ . Exposure: two 80 W/cm medium-pressure mercury lamps. Curing speed: 3 m/min)

2% Photoinitiator	Pendulum hardness (s)	Yellowness index
Benzil dimethyl ketal	133	19.8
HK-1	56	9.6
95% HK-1 + 5% BAPO	109	12.0

only 5% BAPO to the hydroxyketone leads to a significant increase in the hardness. The yellowing is also less than with benzil dimethyl ketal.

For the outdoor use of UV-cured lacquers, the addition of light stabilizers (UV absorbers and/or radical scavengers, see Section 8.2) is necessary.

The UV absorber competes with the initiator for the light and can diminish its activity. Therefore the absorption behaviour of initiator and absorber have to be adjusted. UV absorbers of the hydroxyphenyl-*s*-triazine type are especially useful for application in UV-curable formulations.<sup>[8-124]</sup> Addition of the UV absorber to the pure hydroxyketone results in a marked reduction in the hardness of the lacquer; this increases under the influence of bisacylphosphine oxide which absorbs at longer wavelengths (Table 8.6-7). The mixture of 95% hydroxyketone and 5% BAPO already results in a sufficient pendulum hardness. With higher BAPO amounts, the yellowness value increases slightly.

**Table 8.6-7.** Curing in the presence of an UV absorber of the hydroxyphenyl-*s*-triazine type (Formulation: EPOA/HDDA/PEGDA + 2% UV absorber. Film thickness (wet): 100  $\mu\text{m}$ . Exposure: two 80 W/cm medium-pressure mercury lamps. Curing speed: 10 m/min)

2% Photoinitiator	Pendulum hardness (s)	Yellowness index
HK-1 (without UV absorber)	183	8.2
HK-1	74	6.2
95% HK-1 + 5% BAPO	148	7.1
75% HK-1 + 25% BAPO	174	9.1
BAPO	188	17.0

### 8.6.5.2 Pigmented Coatings

Unlike with clear lacquers, the through-curing of the thicker sections in pigmented lacquers is a problem, because of their low penetrability for the light. Here acyl phosphine oxide initiators are of special advantage. In the following examples, mixtures composed of three parts hydroxyketone and one part BAPO (HK/BAPO) are used. Table 8.6-8 shows curing results in two acrylate white lacquers containing 25% titanium dioxide of the rutile type. Both photoinitiator mixtures, i.e., either with HK-1 or with HK-2 and BAPO, give very similar results. The epoxy acrylate white lacquer is more reactive because it results in a higher pendulum hardness at a higher belt speed (5 m/min) than the polyester acrylate white lacquer (3 m/min).

**Table 8.6-8.** Curing of two acrylate white lacquers (Formulation: see table. Photoinitiator: HK-1/BAPO and HK-2/BAPO. Film thickness (wet): 100  $\mu\text{m}$ . Curing speed: 3 m/min and 5 m/min)

Formulation/photoinitiator	Pendulum hardness (s)	Yellowness index	Gloss 20°/60°
<b>PESA/HDDA/TMPTA/TiO<sub>2</sub>:</b>			
HK-1/BAPO	148	2.9	76/89
HK-2/BAPO	151	3.0	78/89
<b>EPOA/HDDA/TiO<sub>2</sub>:</b>			
HK-1/BAPO	169	4.4	81/93
HK-2/BAPO	174	4.3	82/94

An UPES/styrene-based white lacquer containing 25% titanium dioxide of the same type was cured at two different belt speeds (Table 8.6-9). The better curing of the lacquer at the lower belt speed is indicated by the pendulum hardness as well as the higher gloss values.

**Table 8.6-9.** Curing of an UPES/styrene white lacquer at two different belt speeds (Formulation: UPES/St/TiO<sub>2</sub>. Photoinitiator: 3% HK-2/BAPO. Film thickness (wet): 150  $\mu\text{m}$ . Exposure: combination of a doped 120 W/cm and a 80 W/cm medium-pressure mercury lamp)

Belt speed	Pendulum hardness (s)	Yellowness index	Gloss 20°/60°
4 m/min	49	2.2	76/88
2 m/min	81	2.6	82/90

By combining titanium dioxide with different colour pigments, coloured lacquers with great hiding power, and that were also curable with 3% of the HK-2/BAPO mixture, were prepared (Table 8.6-10).

**Table 8.6-10.** Curing of coloured lacquers (Formulation: PESA/HDDA/TMPTA/TiO<sub>2</sub>/Pigment. Photoinitiator: 3% HK-2/BAPO. Film thickness (wet): 100 µm. Exposure: combination of a doped 120 W/cm and a 80 W/cm medium-pressure mercury lamp. Curing speed: 3 m/min)

Titanium dioxide/Pigment	Pendulum hardness (s)
9% TiO <sub>2</sub> /1% Pigment Blue, 15:4	154
8% TiO <sub>2</sub> /2% Pigment Blue, 15:4	143
7% TiO <sub>2</sub> /3% Pigment Blue, 15:4	131
9% TiO <sub>2</sub> /1% Pigment Orange, 73	149
9% TiO <sub>2</sub> /1% Pigment Yellow, 74	86
9% TiO <sub>2</sub> /1% Pigment Green, 36	90

### 8.6.6 Toxicology and Disposal

Data about toxicology and disposal of the commercially available products can be found in the data sheets of the respective manufacturers.

### 8.6.7 Trade Names

Darocur 1173 (HK-1), Irgacure 184 (HK-2), Irgacure 149 (HK-1/BAPO 95/5), Irgacure 1800 (HK-2/BAPO 75/25), Irgacure 819 (new BAPO photoinitiator), all from Ciba Specialty Chemicals Inc., CH-4002, Basel, Switzerland

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## 9 Industrial Hygiene and Environmental Management

*Aljan Postma*

### 9.1 Introduction

The biological behaviour of chemical substances, including that of the additives of the paint and lacquer industry, plays an important role in our environment.

During production, use and disposal of additives and end products, it is not only the dermatological and toxicological properties that have to be taken into account. The biological effects on our environment, that is, possible air pollution caused by solvent emission or biological degradation of water-soluble additives should also be considered for responsible application of these raw materials.

### 9.2 Commonly Used Terms

- Dermatology:** Science dealing with skin diseases.
- Responsible care:** A worldwide commitment of the chemical industry to the continuous improvement in all aspects of health, safety, and environmental performance and to openness in communication about its activities and achievements. It manifests the will to improve the conditions for the protection of employees and society, independent of regulatory requirements. It is also the obligation of every single employee of a company to devote his or her personal competence to the benefit of people and environment.
- Product stewardship:** The responsible and ethical management of the health, safety, and environmental aspects of a product throughout its life cycle. Product stewardship is “responsible care” applied to products. The purpose is to prevent harm to human health and damage to the environment; to do this a continuous and cost-effective process is required, which involves:
- Reduction of actual and potential risks associated with the manufacture, packaging, distribution, handling, use, and disposal of products.

- Improvements in product design, assessment practices, advice, education, communication, and customer support.
- Oncogenicity study: A toxicity study to investigate possible tumour formation (i. e., carcinogenicity).
- Endocrine effects: Endocrine disturbances are effects that come from outside the organism (exogen) to change the hormonal balance or the hormonal action in the body.
- OECD confirmatory: A biological degradation test published by the Organisation for Economic Cooperation and Development (OECD).

### 9.3 Biological and Toxicological Properties

As a consequence of legislation, chemical substances are more and more judged and selected on the basis of their biological and toxicological effects and the systems they belong to.

In the case of additives, a large amount of different chemical compounds are involved, and they may show many different specific effects.

In Europe, selected chemical substances are classified by the European commission and are labelled according to this. Other chemicals are classified and labelled based on investigations and judgments performed by producers or importers who follow the respective European Union Directives.

“Responsible Care” and “Product Stewardship” are promoted by the chemical associations all over Europe. The authorities also require that environmental auditing should occur and that certified environmental management systems should be in place, to prove a company’s environmental concern and commitment.

These programs stimulate product responsibility and the search for alternatives with less environmental impact. It is obvious that certain substances or groups of substances that were used very frequently in the past are no longer acceptable because of new knowledge about their toxicity or environmental behaviour.

In many cases, industry voluntarily abandoned further use of such chemical compounds. Mercury is an example of this. Organic mercury compounds were used as biocides in aqueous- as well as in solvent-based paints and lacquers. The paint- and lacquer industry voluntarily abandoned this application. Biocides with improved ecological- and toxicological properties are used instead (see Section 8.4).

In many European countries, industry decided voluntarily to stop using alkyl phenol ethoxylates (APE’s) because of the supposed endocrine effects of these compounds. A further example is the driers; these are at present mainly formulated on the basis of aliphatic hydrocarbon solvents instead of aromatic solvents.

## 9.4 Safety Data

Following the tenets of “Responsible Care” and “Product Stewardship”, the producers of chemical substances and preparations cooperate on coordinating and determining the toxicological and ecotoxicological classification data. Where possible, they agree on unequivocal classification of the chemical substances.

The main result of this is that users are receiving clear information, and that there are no discrepancies between suppliers. In the safety data sheets, the user can find basic information on product-specific safety and environmental aspects.

Since 1985, European legislation is in force that requires packaging of (eco-)toxic substances or preparations to contain a label with the respective danger symbols and the so-called R- and S-phrases. The R-phrases inform the user about the risks of the chemicals whereas the S-phrases describe the necessary safety measurements. These R- and S-phrases are also put on the safety data sheets. Table 9.4-1 shows the text of the R- and S-phrases that are frequently used for additives.

More specific information on the general toxicological and biological properties of additives is found in the respective chapters of this book. Detailed information about toxicity and biodegradability of surfactants can be found in the Surfactant Science Series.

**Table 9.4-1** Explanation of some relevant R- and S-phrases

<b>R-Phrases</b>	<b>Text</b>
R20/22	Harmful by inhalation and if swallowed
R22	Harmful if swallowed
R33	Danger of cumulative effects
R36/38	Irritating to eyes and skin
R38	Irritating to skin
R40	Possible risks of irreversible effects
R43	May cause sensitization by skin contact
R48/20/22	Harmful: danger of serious damage to health by prolonged exposure through inhalation and if swallowed
R52/53	Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment
R61	May cause harm to the unborn child
R62	Possible risk of impaired fertility
R65	Harmful: may cause lung damage if swallowed
<b>S-Phrases</b>	<b>Text</b>
S20/21	When using, do not eat, drink, or smoke
S24	Avoid contact with skin
S24/25	Avoid contact with skin and eyes
S26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice

**Table 9.4-1** (continued)

S28	After contact with skin, wash immediately with plenty of ... (specified by the manufacturer)
S36/37	Wear suitable protective clothing and gloves
S36/37/39	Wear suitable protective clothing, gloves, and eye/face protection
S37	Wear suitable gloves
S45	In case of accident or if you feel unwell, seek medical advice immediately (show the label where possible)
S46	If swallowed, seek medical advice immediately and show this container or label
S51	Use only in well-ventilated areas
S53	Avoid exposure – obtain special instructions before use
S62	If swallowed, do not induce vomiting: seek medical advice immediately and show this container or label

## 9.5 Industrial Hygiene

As the respective chapters show, several additives have to be classified as dangerous substances or preparations. In most cases, skin-contact risks are involved. Rigorous hygiene is necessary, particularly when skin sensitizers are involved.

Special attention should be paid to the risks associated with solvent vapours or aerosols, especially where ventilation is insufficient.

For the safe processing of additives, the relevant safety information from the safety data sheets should be translated into internal plant instructions that can be used by the operators.

If additives labelled as dangerous are processed into a paint formulation, this may lead to the classification of the end product. In the EU-member states, the producer is then obliged to use the EU classification, packaging, and labelling directives and act accordingly.

## 9.6 Waste Disposal and Packaging

A maximum of approximately 5% of the total raw material content in a paint formulation belongs to the additive product group. Nevertheless, the residues of the additives or the produced end products must be regarded as chemical waste. The waste disposal should therefore only be undertaken by authorized companies.

The packaging containing remnants of additives should also be regarded as chemical waste and should be handled accordingly. The cleaned and eventually recycled packaging can often be reused.

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## 10 Quality Assurance

*Aljan Postma*

### 10.1 Introduction

Why quality assurance? Quality assurance is necessary to guarantee consistent quality of products and service.

The philosophy of the American quality expert Crosby is that quality is easily realized through immediate elimination of a lack of quality: "Quality is free".<sup>[10-1]</sup> If the job is done the correct way from the start, later problems can be avoided.

Quality assurance with respect to additives is expressed by the careful fulfilment of product specifications.

Lack of quality is only detected if every activity leading to a product or service is assessed and documented in such a way that misunderstandings and failures are excluded.

This can be achieved with a quality assurance system that is also accepted by the paint- and lacquer industry and their customers and is assessed according to the international standard ISO 9000.

### 10.2 Commonly Used Concepts

The main ISO-9000 standards (ISO – International Organization for Standardization) are:

- ISO 9000: Quality management and quality assurance standards
  - guidelines for selection and use
  - clarifies the distinctions and interrelationships among the principal quality concepts
  - provides guidelines for the selection and use of a series of International Standards on quality systems
- ISO 9001: Quality system – model for quality assurance in design/development, production, installation, and service
- ISO 9002: Quality system – model for quality assurance in production and installation
- ISO 9003: Quality system – model for quality assurance in final inspection and test
- ISO 9004: Quality management and quality system elements – guidelines
  - describes a basic set of elements by which quality management systems can be developed and implemented

A third version of the ISO 9001 standard is drafted and will replace ISO 9001:1994 as well as ISO 9002 and ISO 9003. After final publication of this new ISO 9001:2000 the current ISO 9002 and ISO 9003 will be withdrawn. The new quality management standard has been brought in compliance with ISO 14001:1996 Environmental Management Systems.

### **10.3 The Quality Standard ISO 9001**

In the new ISO-9001:2000 standard all observable system requirements are described in six chapters. An accredited certifying body (e.g., Lloyds, Det Norske Veritas, BVQI, TÜV, DQS, etc.) can certify companies, which have implemented such an ISO-9001 quality assurance system.

This certification takes place after an intensive audit on the documentation system and the whole primary process, in which the aspects related to the ISO-9001 standard are investigated to see if they are acceptable. If this is the case, an official certificate with a validity of three years is awarded. Within these three years, the certifying body will perform periodical audits to check the company's reliability with respect to the fulfilment of the quality system. After three years a new initial audit will be take place. The purpose of these audits is the continuous improvement of the organisation.

By means of proposals on improvements, quality circles, complaint analysis, management-review meetings, etc, the employees as well as the management are continuously stimulated and motivated to develop the quality philosophy "Do it right the first time".

### **10.4 Environment Protection and Industrial Hygiene**

Quality-assurance systems are nowadays often integrated with environmental- and industrial-hygiene management systems. In 1996 a new international standard for environmental management was introduced. Companies can be certified according to this ISO-14001 standard.

It is also possible to undergo an eco-audit according to the European EMAS guidelines (Environmental Management Audit System). In this certification, the dialogue with society is taken into account and commitments such as Responsible Care, Coatings Care and Product Stewardship (see Section 9.3) play an important role.

## 10.5 Quality Control of Additives

To verify the quality of additives, physical and chemical parameters are used. It is particularly the parameters that are easily determined, such as viscosity, specific gravity, solid content, colour index, acid value, infrared spectrum, etc. that are focused on. Internationally accepted or standardized methods such as ISO, DIN, or ASTM standards are predominantly used to establish these data.

These standards are verifiable, easily reproducible determination methods. There is a broad palette of additives available. Depending on the application, the chemical compositions can diverge significantly. For this reason there is no one single concept or specific list of quality determination methods for additives. A selection of current test methods for quality control of additives is listed in Table 10-1. (See Ref. [10-2] for the equivalent German standards).

**Table 10-1.** Characteristic test-method standards for paint- and lacquer additives

Standard	Edition	Explanation
ASTM E 70-97	1997	Standard glass-electrode test method for the pH of aqueous solutions
ISO 1065	1991	Non-ionic surface-active agents obtained from ethylene oxide and mixed non-ionic surface-active agents – determination of cloud point
ASTM D1218-92	1998	Refractive index and refractive dispersion of hydrocarbon liquids
DIN 1342-2	1986	Viscosity; Newtonian fluids
ASTM D 1364-95	1983	Water in volatile solvents (Karl Fischer reagent titration method)
ISO 1516	1981	Paints, varnishes, petroleum, and related products – flash/no flash test – closed-cup equilibrium method
ASTM D 1544	1998	Colour of transparent liquids (Gardner colour scale)
ASTM D 1545	1989	Viscosity of transparent liquids by bubble-time method
ISO 2555	1989	Plastics – resins in the liquid state or as emulsions or dispersions – determination of apparent viscosity by the Brookfield test method
DIN/ISO 2592	1973	Petroleum products – determination of flash- and fire points – Cleveland open-cup method
ISO 2811-1	1997	Paint and varnishes – determination of density – part 1: Pycnometer method
ISO 2811-2	1997	Paint and varnishes – determination of density – part 2: immersed body (plummet method)
ISO 2811-3	1997	Paint and varnishes – determination of density – part 3: oscillation method
ISO 2811-4	1997	Paint and varnishes – determination of density – part 4: pressure-cup method

**Table 10-1.** (continued)

Standard	Edition	Explanation
ISO 2884/ASTM D4287	1974	High-shear viscosity with the ICI cone/plate viscometer
ISO 3251	1993	Paint and varnishes – determination of non-volatile components of paints and varnishes and binders in paints and varnishes
ISO 3682	1996	Binders for paints and varnishes – determination of acid value – titrimetric method
ASTM D 4287	1974	High-shear viscosity using the ICI cone/plate viscometer
ISO 4316	1977	Surface-active agents – determination of pH of aqueous solutions – potentiometric method
ISO 4630	1997	Binders for paints and varnishes – Estimation of colour of clear liquids by the Gardner colour scale
DIN/ISO 6271	1997	Clear liquids – estimation of colour by the platinum–cobalt scale
DIN 53015	1978	Viscometry: measurement of viscosity with the Hoesppler falling-ball viscometer

## References

- [10-1] Crosby, P. B., Illusions about Quality, *Across the Board* (1996), no. 6, 38
- [10-2] Lückert, O., *Prüftechnik bei Lackherstellung und Lackverarbeitung*, Vol. 2, Vincenz Verlag, 1992, p. 167

## Subject Index

- acid catalysis 249
- acids 315
  - biocides 315
- acrylic thickeners 31, 33
- additives 1, 3 ff., 7, 360
  - applications 8
  - basics 5
  - chemical composition 7
  - classification 2
  - definition 2
  - dosage 8
  - economic significance 4
  - effectiveness 7
  - interactions 5
  - introduction 1
  - quality control 360
  - quantities used 3
  - relative amounts 3
- adhesion (cross-cut test) 289 f.
- adhesion phenomena 112 f.
  - interpretation 113
- adhesion promoters 112, 115, 126
  - amides/imides 126
  - application fields 127
  - chlorinated polyolefins 122
  - definition 112
  - naphthenates 126
  - organophosphorus enamines 126
  - phosphates 124
  - platelet-shaped fillers 126
  - polyesters 123
  - polyethylenimine 124
  - rosin esters 123
  - silanes 115
  - silicone-modified polymers 125
  - sucrose derivatives 124
  - titanates, zirconates 119
- adhesive strength 114
- aerodynamic force 26
- agglomerates 67, 73
  - definition 67
- aggregates 67
  - definition 67
- alcohols 318
  - biocides 318
- ALFA values 165
- algae 307
- alkaline catalysis 249
- alkyd gloss paint 222
  - waterborne 222
- alkyl phenol ethoxylates (APE) 354
  - endocrine effects 354
- aluminium silicate 19
- amino resins 229
- amorphous silica 153
  - manufacturing process 154
- anchoring groups 84
- anodic inhibition 297
- anticorrosive pigments 295
- anti-foaming, see defoaming
- anti-foaming, see foam inhibitor
- antioxidants 260 f.
  - application 262
  - examples 261
  - mode of action 261
- anti-skinning 260, 263, 266 f.
  - antioxidants 260
  - MEKO 263
  - moisturizing agent 267
  - retention agents 266
  - solvents 266
- anti-skinning agents 258 ff.
  - definition 258
- aqueous paint 101
  - foam formation 101
- Arrhenius equation 228
- associative cellulose 45 f.
  - thickening action 46
- associative cellulose ether (HMHEC) 46
  - thickening mechanism 46
- associative thickener 32 f., 45, 50, 52
  - acrylic 33

- operating mechanism 32
- PUR 50
- thickening mechanism 52
- autooxidation 207, 209
- bacteria 307
- barium 212
- barrier coatings 295
- basic driers 204
- Benard cells 92
- bentonite 17
- binder 66
  - surface tension 66
- Bingham systems 13
- biocides 306 ff.
  - acids 315
  - alcohols 318
  - carbonic acid amides 316
  - definitions 307
  - formaldehyde 313
  - formaldehyde-releasing compounds 313
  - glutaraldehyde 314
  - in-can preservatives 312
  - isothiazolinone derivatives 316
  - phenol derivatives 314
  - quaternary ammonium compounds 316
- bismuth 213
- blocking agents 262
- Brownian movement 68
- bubble coalescence 104
- burning behaviour 326
- calcium 212
- calcium sulphonate 61
  - basic 61
- carbonic acid amides 316
  - biocides 316
- Casson relation 13
- catalysts 202, 227
  - accelerating effect 228
  - blocked 1K-PUR systems 242
  - DABCO 247
  - DBTDL 240, 242, 245, 247
  - dinonylnaphthalene sulfonic acid 231
  - driers 202
  - epoxy resins 248
  - epoxy/amine systems 249
  - epoxy/carboxy systems 251
  - epoxy/phenol/formaldehyde resin 253
  - melamine cross-linking 229
  - melamine systems 234
  - moisture-curing 1K-PUR systems 246
  - non-ionic blocked 232
  - polyurethane systems 236
  - *p*-toluenesulfonic acid 231
  - PUR powder coatings 245
  - salicylic acid 251
  - sulfonic acid 234
- catalytic effectiveness 221
  - influence of complexation 221
- catalytically active additives 3, 201
  - definition 3
- cathodic inhibition 297
- cell number 311
- cellulose 36 f.
  - characterizing 37
  - modification 36
  - structure 36
- cellulose acetobutyrate 173
- cellulose derivatives 31, 35 f.
  - cellulose ethers 35
    - chemistry 36
- cellulose ether 34, 37 f., 41, 44 f., 47 f.
  - addition 38
  - associative 34, 45
  - choice of substituent 41
  - commercial 47
  - degree of substitution (DS) 37
  - disposal 49
  - hydration time 38
  - hydroxyethyl cellulose 38
  - influence of glyoxal 39
  - influence of molecular weight 43
  - liquid 48
  - paint properties 39
  - resistance to enzymes 42
  - rheology 42
  - spatter resistance 42
  - storage stability 42
  - suspension 38
  - thickening mechanism 46
  - to paints 38
  - toxicology 49
  - water retention 39
- cerium 211
- char formation 329
- char-forming flame retardants 334

- chemical stability 5, 7
- chlorinated polyolefins 122, 127
- clays 17
- coalescing agents 2, 180, 183, 185, 187, 189, 192 f.
  - classification 187
  - definition 2, 180
  - ecology 196
  - evaporation rate 189
  - HPE 188
  - influence on dispersion viscosity 192
  - influence on pigment binding 193
  - MFT reduction 185
  - *minimum film-forming temperature* 183
  - mode of action 183
  - *N*-methylpyrrolidone 190
  - performance 191
  - three-phase model 184, 187
  - toxicology 196
  - TPiB 185, 188
- coating damage 270
- coatings 207
  - air-drying alkyd paints 207
- cobalt 210
- colloids 69
- colour change  $\Delta E$  289
- colour development 43
- colour impression 147
- combination drier 214, 218
  - lead-free 218
- combustible mass 328
- contact angle 71 f.
- contact-angle method 130
- copolymers 90
- corrosion cell 293
- corrosion inhibitors 291 ff.
  - basics 291 ff.
  - characteristics 300
  - classes/characteristics 299
  - definition 296
  - flash rust 300
  - formulation guidelines 303
  - long-term protection 301
  - mechanisms 296
  - permeability 298
  - products 300
  - toxicology 305
- corrosion protection 295
  - organic coatings 295
- co-solvents 190
- coupling agents 190
- cracking 289
- crosslinker 246
  - internally blocked 246
- curing agents 247
  - aldimines 247
  - ketimines 247
  - oxazolidines 247
- curing speeds 346
- defoamer 106
  - composition 106
- defoamer, *see* foam suppressant
- defoaming 100, 103
  - drainage effect 103
  - stability-reducing parameters 103
- deformation 15
- degree of dispersion 95
- degree of flocculation 96
- dermatology 353
- diatomaceous earth 152
- dielectric constant 79
- dilatancy 14
- dilatant flow behaviour 14
- direct-metal-reaction (DMR) 207
- dispersant demand 93
- dispersibility 68
- dispersing agents 67 ff., 86, 89
  - chemical composition 86
  - definition 68
  - polymeric 89
  - viscosity-demand curve 95
- dispersion 94 f.
  - degree of 95
  - determining 94
  - efficiency 94
- dispersion process 68 ff., 95
  - stabilization 70, 75
- dispersion stability 77
- DLVO theory 77 f.
- DOI, distinctness of reflected image 165, 289
- drier anions 205
- driers 201 f.
  - active 210
  - autooxidation process 207
  - auxiliary 212
  - BK drying recorder 223
  - cobalt-catalysed reactions 208

- combinations 214
- composition 203
- coordination effect 220
- dosages 214
- high-solids 222
- lead-containing 217
- lead-free 216
- loss of drying 215
- manufacturing 206
- mechanism 208
- metals 210
- naphthenates 203, 205
- octanoates 205
- precomplexed 221
- recommended formulations 215
- risk- and safety classifications 225
- synthetic 205
- toxicology 224
- waterborne coatings 218
- wrinkling 224
- drying ability 215
- drying acids 210
- drying performance 241
  - improvement 241
- drying promoters 202
- drying time 264
  - influence of MEKO 264
- dynamic surface tension 130
- dynamic viscosity 15
  
- elasticity 15
- electrochemical corrosion process 293
- electrophilically-active substances 312
- electrostatic repulsion 77, 82
- electrostatic stabilization 78
- emulsion paint 50, 186
  - characteristic viscosity 50
  - drying 186
- endocrine effects 354
- endothermic decomposition 328
- enthalpy 82
- entropy 82
- environmental management 353 ff.
- enzymes 311
- epoxy resins 248
  - catalysts 248
  - cross-linking reaction 248
- epoxy/amine systems 249
- epoxy/carboxy systems 251
- epoxy/phenol/formaldehyde system 253
  
- Epstein 104
- Epstein and Plesset 104
  
- fault-free coatings 102
- film formation 181
  - polymer dispersions 181
- film mechanics 194
- film preservation 318
  - see also biocides
- film preservatives 308, 321
  - benzimidazols 321
  - carbamates and dithiocarbamates 322
  - diuron 323
  - *N*-haloalkylthio compounds 322
  - zinc pyrithione 323
  - 2-*n*-octyl-4-isothiazolin-3-one 323
- film-forming aids 191
- flame retardants 325 ff.
  - char forming 329
  - char-forming 334
  - combustion process 326
  - consumption 336
  - halogen-containing 331
  - intumescent systems 334
  - mechanism 328
  - modes of action 328
  - phosphorusbased 329, 333
  - radical-scavenger 330
  - testing methods 325
- flammability classification 325
- flash-rust inhibitors 300 f., 303
- floating 91
- flocculates 68
- flocculation 93, 96
  - degree of 96
- flooding 97
- florida exposure 284, 286
- flow 10, 28
  - formula 28
  - laminar flow 10
  - turbulent flow 10
- flow behaviour 11
  - dilatant 14
  - Newtonian 11 f.
  - pseudoplastic 12
  - thixotropic 13
- flow curve 15
- flow resistance 26
- fluoro compounds 130
- fluorosurfactants 170, 175

- foam 101 f., 104 ff.
  - composition 106
  - formation 101
  - inhibitors 106 f.
  - macrofoam 100
  - microfoam 102
  - stability 104
  - stabilization 100, 102, 105
  - suppressants 106
- foam inhibitors 106
  - composition 106
- foam suppressants 106 ff.
  - agitation test 110
  - composition 106
  - craters 111
  - dosage 111
  - efficiency 110
  - formulation 108
  - mechanism 107
  - mineral oil 109
  - polyether siloxanes 109
  - siloxanes 109
  - test methods 110
- foam, see also defoaming
- foam-suppression-active substances 106
- formaldehyde-releasing compounds 313
  - biocides 313
- fungi 309
  
- germs 310
- Gibbs 104
- gloss 147
- graft polymers 90
- gravitational force 26
- grinding, see dispersion
  
- halogenated flame retardants 332
- halogen-containing flame retardants 331
- HALS 278, 283
  - side reaction 283
  - structures 278
- hardness 233
  - influence of catalyst type 233
- HASE 33
- hectorite 17, 19
- Hegman gauge 95
- hemiformals 313
- HEUR 33
  - thickening mechanism 54
- high-shear PUR thickeners 54
- high-solids coatings 222 f.
  - drying 223
  - drying characteristics 222
- hindered-amine light stabilizers (HALS) 277
  - mechanism 277
- HLB system 89
- HMEHEC 47
  - hydrophobically modified ethyl-hydroxyethyl cellulose 47
- HMHEC 47
  - hydrophobically modified hydroxyethyl cellulose 47
- homopolymers 90
  - gel time 252
- hybrid powder coating 252
- hydrogenated castor-oil 58
- hydrophilic groups 87
- hydrophobic groups 87
- hydrophobically modified ethoxylated urethanes (HEUR) 33
- hygiene 310, 356, 360
- hygiene management 353
  
- in-can preservatives 308
  - see also biocides
- inorganic flame retardants 330
- interfacial tensor 65
- intumescent systems 334
- iron 211
- isoelectric point 69
- isothiazolinone derivatives 316
  - biocides 316
- ISO-9001 360
  
- kinematic viscosity 15
- Kubelka-Munk 97
  
- Lambert-Beer 273
- laminar flow 15
- lattice constants 293
- lead 212
- lead drier 217
  - substitution 217
- levelling 28, 164 ff.
  - definition 164
  - improvement 168
  - measurement 165
  - physical factors 166
  - rheology 166

- surface flow 167
- surface tension 167
- levelling additives 164, 168, 172 f.
  - application 173, 177
  - benzoic acid 177
  - cellulose acetobutyrate 169
  - crotonic acid 177
  - fluorosurfactants 170
  - mode of action 168
  - polyacrylates 169
  - polymers 168, 173
  - properties 172
  - silicones 170
  - toxicology 178
  - waste disposal 178
- levelling agents 2, 171
  - definition 2
  - solvents 171
- light stabilizers 269 ff.
  - automotive coatings 279
  - classification 272
  - clear coatings/colour coatings 283
  - compatibility 280
  - guidelines for the use 288
  - one-coat solid shades 285
  - powder coatings 286
  - properties 279
  - recommendations for use 290
  - solubility 280
  - UV absorbers 273
  - UV-curable clear coatings 287
  - volatility 280
  - wood coatings 288
- lithium 213
- long-term corrosion protection 302
- long-term protection 303
  
- magnesium silicate 19
- manganese 211
- mar resistance 140
- mat lacquer 158
  - application 158
- mat paint surface 146
- matting 146, 149
  - mechanism 149
  - physical principles 146
  - surfaces roughness 147
- matting agents 151 f., 155 f.
  - amorphous silica 153
  - application 156
  - economical importance 151
  - in high-solids 160
  - in powder coatings 160
  - in radiation-curing systems 160
  - in solventborne systems 159
  - in waterborne systems 159
  - organic 155
- matting effect 158
- MEKO 258, 263
  - applications 264
  - methyl ethyl ketoxime 258
  - mode of action 265
  - production 263
  - toxicological properties 268
  - typical properties 264
- melamine resin 229 ff.
  - self-condensation 231
- membrane-active substances 312
- metal soaps 204
  - driers 204
- metallic soaps 202
- methyl ethyl ketoxime, see MEKO
- microbes 308
- microbicidal substances 308
- microbistatic substances 308
- micro-organisms 311
- milling process 69
- milling, see dispersion
- montmorillonite 18 f.
  
- naphthenates 205
- natural silica 155
- natural silicas 152
- Newtonian flow behaviour 11 f.
- non-ionics 88
  
- octanoates 205
- oncogenicity study 354
- organic thickener 31 ff., 58
  - solvent-borne coating 58
  - water-borne paints 31
- organoclay 17, 20 f., 24 f., 29
  - bentonite 17
  - coating properties 25
  - dispersal 24
  - easily dispersable 29
  - hydrogen bondings 25
  - incorporation 29
  - ion exchange 20
  - IR spectrum 22

- lectorite 17
- mechanism of thickening 24
- paste method 29
- powder method 29
- production 20
- production scheme 21
- rheology 21
- x-ray diffraction spectroscopy 21
- organofunctional silanes 115 f., 118 f.
  - examples 119
  - mode of action 116
  - properties 118
- oxidative drying 201
- oximes 262
  
- packaging 356
- paint properties 41
  - cellulose ether substituent 41
- paint raw materials 4
- particle-size distribution 108
- pendulum hardness 186
- penetration 74
- penetration process 73
- peroxide decomposers 272
- phenol derivatives 314
  - biocides 314
- phosphate esters 88
- phosphates 124, 127
- phosphorus-containing flame retardants 333
- photocuring 339
- photoinitiators 338
  - clear coatings 345
  - monomolecular 341
  - pigmented coatings 347
  - use 344
  - UV-curable coatings 338, 340
- photooxidation 270
- phyllosilicate 17
- physical drying 201
- pigment binding 193
- pigment particle 79
  - zeta potential 79
- pigment wetting 70
- plasticity 12
- plasticizer 180
- platelet-shaped fillers 126
- Plesset 104
- polyacrylate salts 90
- polyacrylates 169, 173
- polyamide thickeners 60
- polyamides 60
- polycarboxylates 88
- polydimethylsiloxanes 131
- polyelectrolyte 83
- polyesters 123
- polyether siloxanes 109
  - foam suppressants 109
- polyethylenimine 124, 127
- polyisocyanates 239
  - reactivities 239
- polymer dispersions 181 f.
  - film-forming 182
- polymer solutions 43
  - loss of viscosity 43
- polymeric dispersing agents 85
- polymers 98, 271
  - biological properties 98
  - degradation 271
  - toxicological properties 98
- polymethylalkylsiloxanes 131
- polyolefins 61
- polyphosphates 91
- polysaccharide 36
- polysiloxanes 129, 132 f., 142
  - organically modified 132
  - polyester-modified 133
- polyurethanes 236
  - catalysts 236
- potassium 213
- powder clearcoat 287
- precomplexation 221
- preservation 309
- preservative acids 315
- preservatives, see biocides
- primary particles 69
  - definition 69
- product stewardship 353
- pseudoplastic flow behaviour 12
- pseudoplasticity 12
- PUR catalysts 238
  - mechanism 238
- PUR resins 237
- PUR thickener 50, 54 ff.
  - applications 55
  - coating properties 57
  - composition 51
  - delivery form 51
  - flow curve 55
  - formulation of coating materials 56

- higher-shear thickening 53
- high-shear 54
- interactions 56
- mid-shear 54
- properties 53
- thickening mechanism 52
  
- quality assurance 361 ff.
- quality control 360
- quality standard ISO 9001 360
- quaternary ammonium compounds 316
  - biocides 316
- quenchers 272
  
- radical photocuring 342
  - mechanism 342
  - reaction kinetics 343
- radical scavengers 272, 330
- rare earth 211
- rate of penetration 73
- reactive diluents 341
- reactive resins 341
- repulsion 82
  - electrostatic 82
  - steric 82
- resins 227
- responsible care 353
- retention agents 267
- rheological expressions 15
- rheology 9, 21, 166
  - definition 9
  - levelling 166
  - organoclay 21
- rosin esters 123, 127
- RTIR spectroscopy 343
- rub-out number 97
- rub-out test 97
  
- safety data 355
- sag resistance 44
- sag-control 61
- sagging 27 f.
  - formula 27
  - volume 28
- scratch resistance 140 f.
- scrub resistance 43
- sedimentation 26 f.
- sedimentation velocity 26 f.
  
- seeding 60
- shear rate 10 f., 25
  - application of coatings 25
  - different processes 11
  - production of coatings 25
- shear strain rate 11
- shear stress 10
- sheen 147
- shrinking paint 149
- siccatives, see driers
- silane adhesion promoters 118
  - selection 118
- silanes 115, 117, 127
  - organofunctional 115
  - surface activity of materials 117
- silicate 17, 24
  - gelation process 24
- silicone additives 130, 134, 142
  - incorporation and testing 135
  - side effects 135
  - usage 134
- silicone surfactants 134
  - aqueous coatings 134
- silicones 125, 127, 170, 174
- siloxanes 109
- skinning 258 f.
  - avoiding 259
  - consequences 259
- slip resistance 140
- slip, see surface slip
- smectites 17 f.
  - layers 18
  - octahedral layers 18
  - structure 17
- solid shades 286
  - UV absorbers 286
- solubility 6
- solubility parameter 5
- solvated alkyd paint 50
  - characteristic viscosity 50
- solvent 66, 171, 176
  - boiling point 171
  - evaporation index 171
  - improving 176
  - levelling 176
  - organic thickener 58
  - surface tension 66
- solvent-borne coating 58
- spatter resistance 44
- spatter-free paints 45

- special-effect additives 3
  - definition 3
- stabilization 76 f., 80, 82 ff., 100
  - electrostatic 76 f.
  - nonpolar media 84
  - of foam 100
  - polar media 82
  - steric 76, 80, 84
- stabilization effects 76
- starch derivatives 31
- static surface tension 130
- steric repulsion 82
- steric stabilization 80 f., 84
  - energetic effects 81
- sterically stabilized particles 81
  - interaction 81
- Stokes' law 93
- stove-paint 235
  - storage stability 235
- strontium 213
- structural viscosity 15
- structured paints 15
- substrate 66
  - surface tension 66
- substrate wetting 128
  - polysiloxanes 131
  - surface tension 128
- sucrose 124
- sucrose acetoisobutyrate (SAIB) 124
- sucrose derivatives 127
- sulphates 87
- sulphonates 61, 87
  - overbased 61
- surface 66
  - substrates 66
- surface activity 5 f.
- surface curing 345
- surface modification 139
- surface modifiers 2
  - definition 2
- surface potential 79
- surface reflection 147
- surface slip 140, 142, 144
  - measurement 144
  - practical importance 140
  - silicone additives 142
  - waxes 143
- surface structure 147
- surface tension 66, 128 ff., 166
  - binder 66
  - influence on levelling 167
  - levelling 166
  - measurement 130
  - solvent 66
  - substrate wetting 129
- surface-active agents 2, 65
  - definition 2
- surface-active compounds 86
- surface-charge measurement 94
- surfaces 147, 320
  - characterization 147
  - restoration 320
- surfactants 65 ff., 69, 86, 88 f.
  - amphoteric 86, 89
  - anionic 86
  - biological 98
  - cationic 86, 88
  - definition 69
  - non-ionic 86, 88
  - toxicological properties 98
- synthetic driers 205
- talc 127
- terpolymers 90
- test-method standards 361
- thickener properties 59
- thickeners 9, 17, 34 f.
  - for solvent-based paints 34
  - function 34
  - inorganic 17
- thickening agents 2
  - definition 2
- thickening effects 53
- thixotropic flow behaviour 13
- thixotropy 13
- through-curing 345
- titanate 119
- titanates, zirconates 127
- toxicology 354
- triglycerides 59
- turbulence 16
- two-layer topcoats 284
  - stabilization 284
- UV absorber classes 273 f.
- UV absorbers 272, 275 f., 281
  - interaction 281
  - mode of action 275
  - permanence 281
  - structures 276

- UV-curable systems 342
- UV-curing 339 ff.
- UV-curing technique 343
  
- van der Waals forces 81
- vanadium 211
- vapour pressure 5 f.
- viscoelasticity 16
- viscosity 9, 14, 16
  - measurement 14
- viscosity curves 11, 16
- viscosity quotient 11
  
- wall paint 40
  - interior 40
  - solvent-free 40
- Washburn equation 73
- waste disposal 356
- water absorbency 57
- waterborne coatings 218 f.
  - air-drying 219
  - drying 218
- water-phase thickeners 31
- water-retention agents 266
- water-retention capacity 43
- water-softening efficiency 91
- waviness 165
- waxes 143, 152, 155
  - micronized 155
  
- wet adhesion 299
- wetting 71 f., 113
  - angle 113
  - contact 113
  - theory 71
- wetting agents 67, 69
  - definition 69
- wetting process 72
- work of adhesion 73
- work of dispersion 73
- work of immersion 73
- work of spreading 73
  
- yellowness index, YI 289
- yield value 15
- Young 71
  - contact angle 71
  
- zeta potential 79
- zinc 213
- zinc-rich coatings 295
- zirconate 119
- zirconium 213
- zirconium aluminates 121, 127
- 2-butanone oxime 258
  - MEKO 258
- 2K-PUR systems 238, 242
  - application methods 242