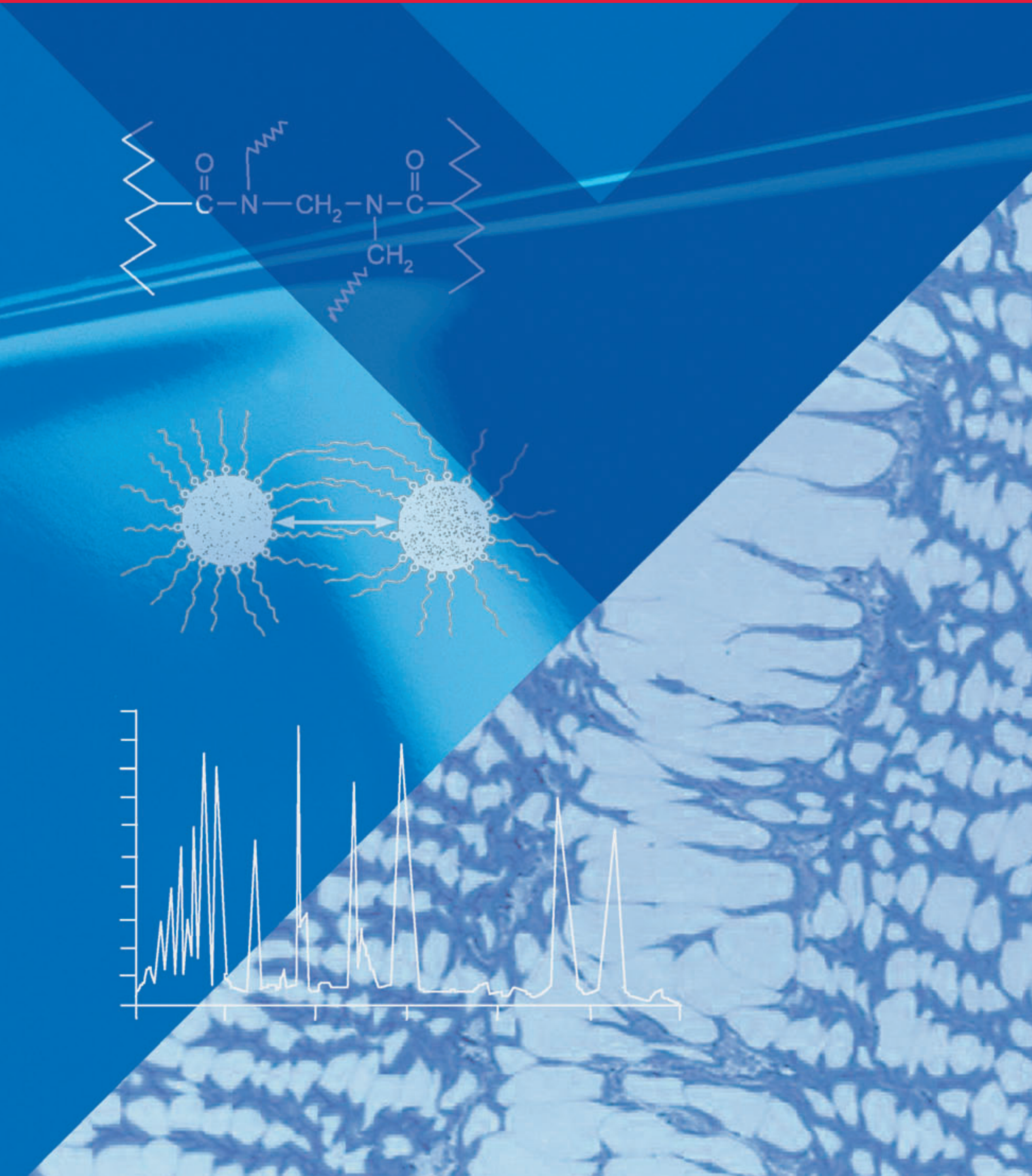
European Coatings Tech Files

VINCENTZ

Bodo Müller | Ulrich Poth

Coatings Formulation

2nd Revised Edition



Cover: Dr. Iwona Löhrke

Bibliographische Information der Deutschen Bibliothek
Die Deutsche Bibliothek verzeichnet diese Publikation in der Deutschen Nationalbibliografie; detaillierte bibliografische Daten sind im Internet über http://dnb.ddb.de abrufbar.

Bodo Müller, Ulrich Poth
Coatings Formulation: An International Textbook, 2nd Revised Edition
Hanover: Vincentz Network, 2011
EUROPEAN COATINGS TECH FILES
ISBN
ISBN 978-3-86630-891-6

Vincentz Network, P.O. Box 6247, 30062 Hanover, Germany

The information on formulations is based on testing performed to the best of our knowledge.
The appearance of commercial names, product designations and trade names in this book should not be taken as an indication that these can be used at will by anybody. They are often registered names which can only be used under certain conditions.

Please ask for our book catalogue
Vincentz Network, Plathnerstr. 4c, 30175 Hanover, Germany
T +49 511 9910-033, F +49 511 9910-029
books@european-coatings.com, www.european-coatings.com

Layout: Vincentz Network, Hanover, Germany
Printed by Quensen Druck + Verlag GmbH &Co. KG, Hildesheim, Germany

ISBN
ISBN 978-3-86630-891-6

European Coatings Tech Files

Bodo Müller | Ulrich Poth

Coatings Formulation

An international textbook

2nd revised edition

Bodo Müller, Ulrich Poth: Coatings Formulation

ISBN: 978-3-86630-891-6

Preface

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 To this end, they have replaced outdated guide formulations, eliminated errors and added several new figures.

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

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

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

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

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

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

Esslingen and Münster, Germany in February 2011

Bodo Müller		Ulrich Poth

bodo.mueller@hs-esslingen.de		ulr.poth@t-online.de

Bodo Müller, Ulrich Poth: Coatings Formulation

ISBN: 978-3-86630-891-6

Exclusion of liability

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

Contents

Part I Basics

Bodo Müller, Ulrich Poth: Coatings Formulation

ISBN: 978-3-86630-891-6

Part II Solvent-borne paints

Part III Water-borne paints

Part IV Solvent-free coatings

Part I Basics

Bodo Müller, Ulrich Poth: Coatings Formulation

ISBN: 978-3-86630-891-6

- intentionally left blank -

Part I Basics

1 Introduction

1.1 Preliminary remarks

Paints are semifinished products (intermediates); the end products are the coated objects. Paints are used in a wide variety of applications (Figure I-1.1).

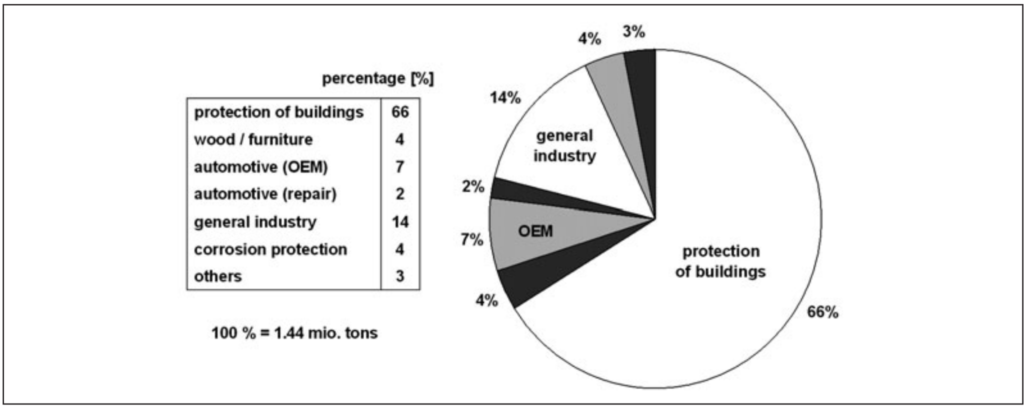


Figure I-1.1: Analysis of paint consumption in Germany in 2009 *Source: www.lackindustrie.de*

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

1.2 Comments on environmental protection

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

Bodo Müller, Ulrich Poth: Coatings Formulation

ISBN: 978-3-86630-891-6

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

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

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

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

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

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

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

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

paint type	nonvolatile matter [wt.%]
low-solids	< 30
normal-solids	30 to 60
medium-solids	60 to 70
high-solids	> 70 (sometimes > 80)

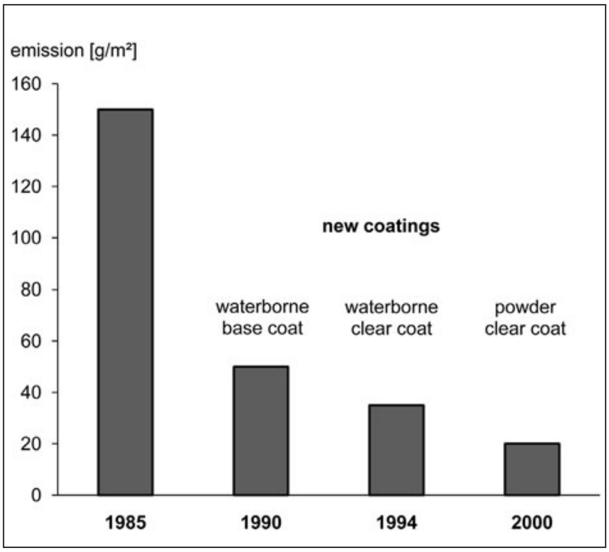


Figure I-1.2: Total emissions (g) of organic solvents during painting of vehicles (OEM), expressed in terms of surface area (m^2) of the vehicle bodies (average values; years may vary with vehicle producer)

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

Corrosion protection as a means of protecting the environment

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

Thermodynamically, the atmospheric corrosion of iron or unalloyed steel (formation of rust: $Fe_2O_3 \cdot H_2O$) is the opposite of its production. The production of iron (in a blast furnace) uses iron ore (e.g. Fe_2O_3) and coal or coke (C) and generates the greenhouse gas, carbon dioxide (CO_2; Figure I-1.3). Corrosion protection extends the working life of corrodible metallic materials (e.g. steel). This means that raw materials and energy are conserved and there is less of a burden placed on the environment. Besides preserving value, any corrosion protection measure, e.g. coating, therefore also serves to protect the environment. For example, only 15 to 25 kg paint is required for coating a 1,000 kg vehicle; but this coating greatly extends the working life.

Integrated view of paints and coatings

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

Any assessment of the ecological impact of a paint system must consider all the production steps shown in Figure I-1.4.

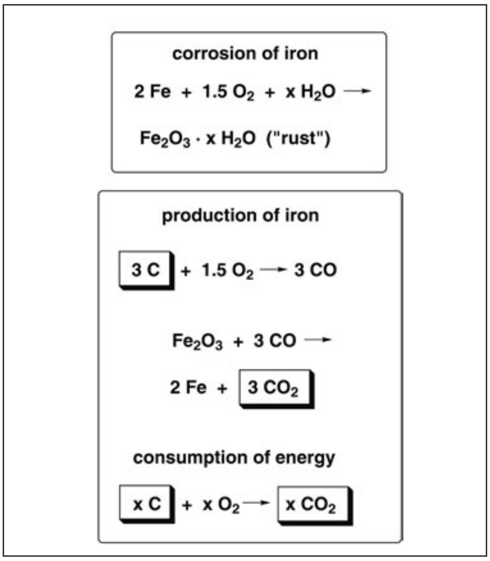


Figure I-1.3: Corrosion protection as a means of protecting the environment (highly simplified equations)

1.3 Paints and coatings as high-tech products

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

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

In addition, nanostructures have generated further innovative ideas in coatings technol-

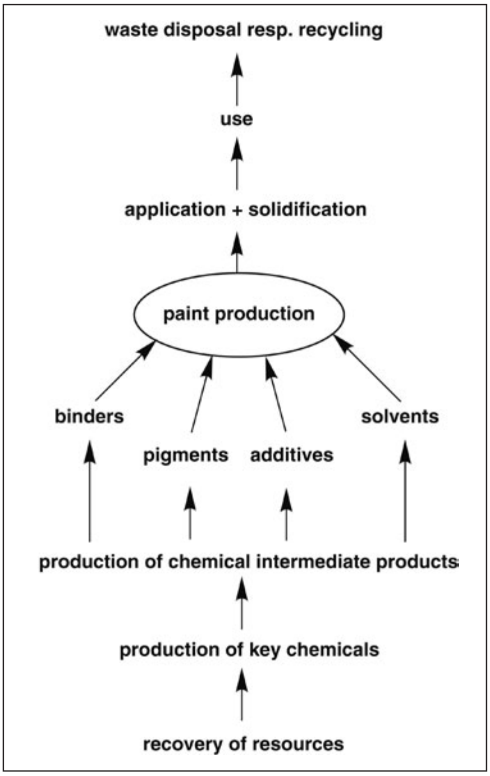


Figure I-1.4: Integrated view of paints and coatings. By recovery of resources is meant, e.g., oil recovery. Key chemicals are, e.g., ethylene, propylene. Examples of chemical intermediates are acrylic acid, epichlorohydrin.

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

1.4 Definitions

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

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

Coating materials can be subdivided as follows:

- Paints
- Coating materials for plasters
- Knifing fillers
- Special coating materials (e.g. for floors)

The paints or coating materials described in this book can be further subdivided as follows:

- Dilutability (solvent-borne or water-borne, solvent-free)
- Position in multi-coat systems (e.g. primer or topcoat)
- Application (e.g. for industrial products or buildings)
- Properties (e.g. anticorrosion or effect coating, clear coat)

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

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

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

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

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

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

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

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

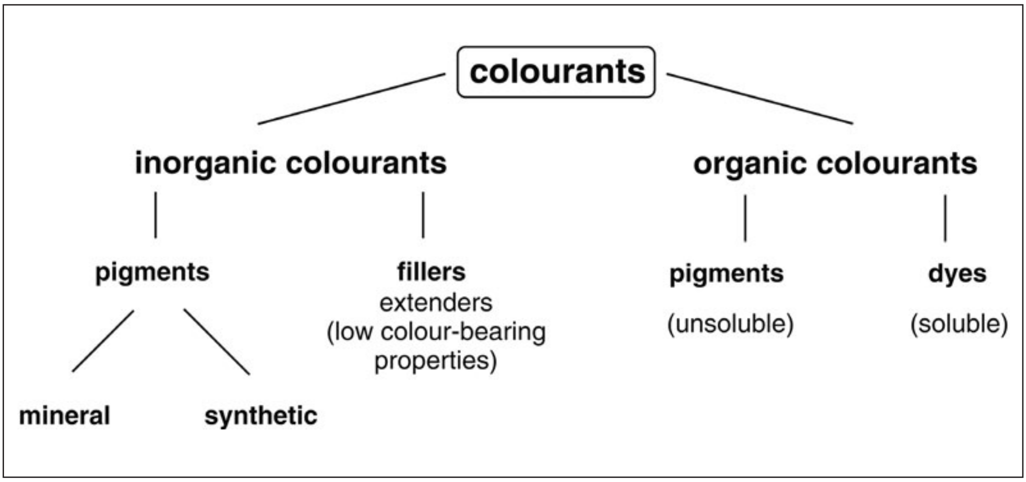


Figure I-1.5: Colourants

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

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

1.5 Coatings

1.5.1 Solidification of paints

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

Physical drying

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

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

Table I-1.2: Abbreviations for some binders

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

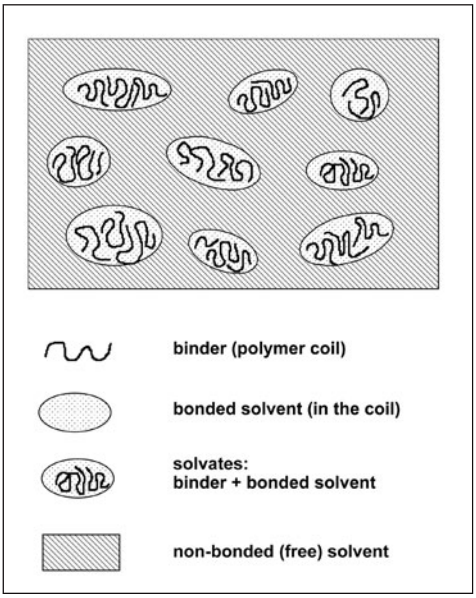


Figure I-1.6: Simplified diagram of a diluted binder solution

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

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

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

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

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

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

Chemical curing

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

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

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

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

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

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

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

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

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

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

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

Organic binders as polymeric materials

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

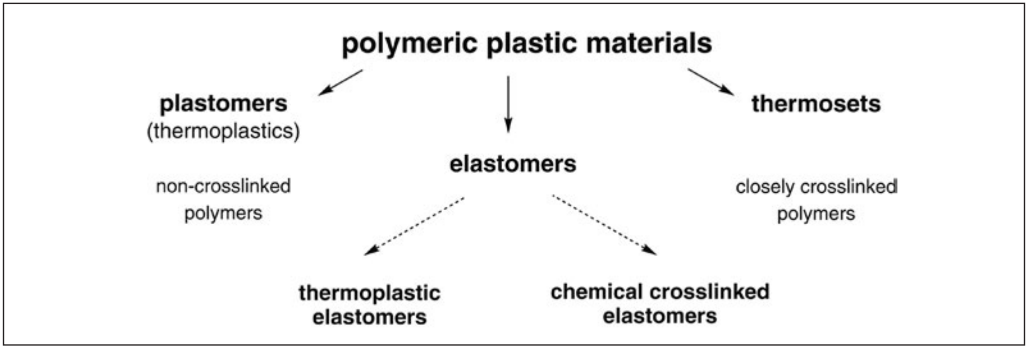


Figure I-1.7: Classification of polymeric plastic materials

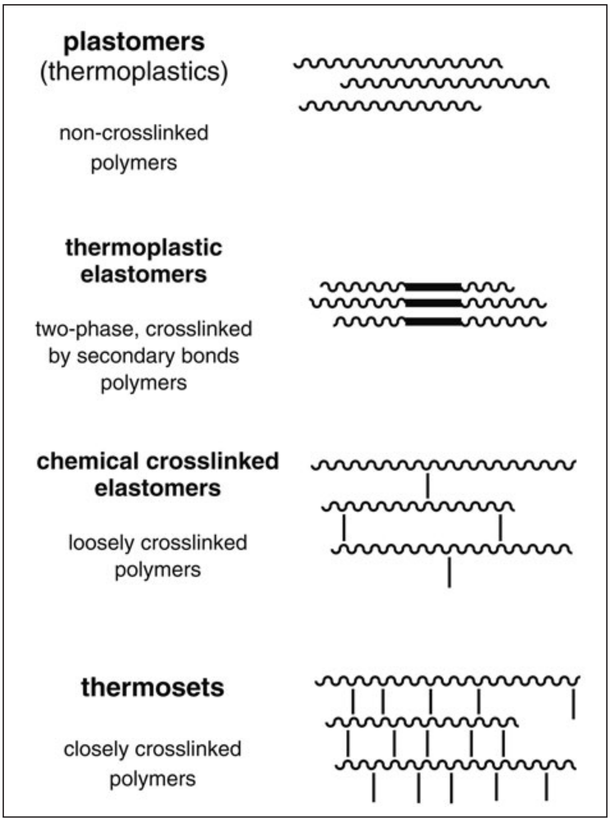


Figure I-1.8: Schematic diagram of polymeric plastic materials

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

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

1.5.2 Phase boundaries in coatings

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

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

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

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

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

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

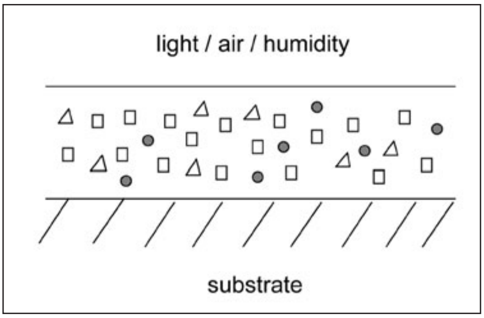


Figure I-1.9: Simplified diagram of coating below the critical pigment volume concentration on a substrate (cross-section)

1.6 Adhesion

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

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

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

1.6.1 Wetting of substrates

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

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

Surface and interfacial tension

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

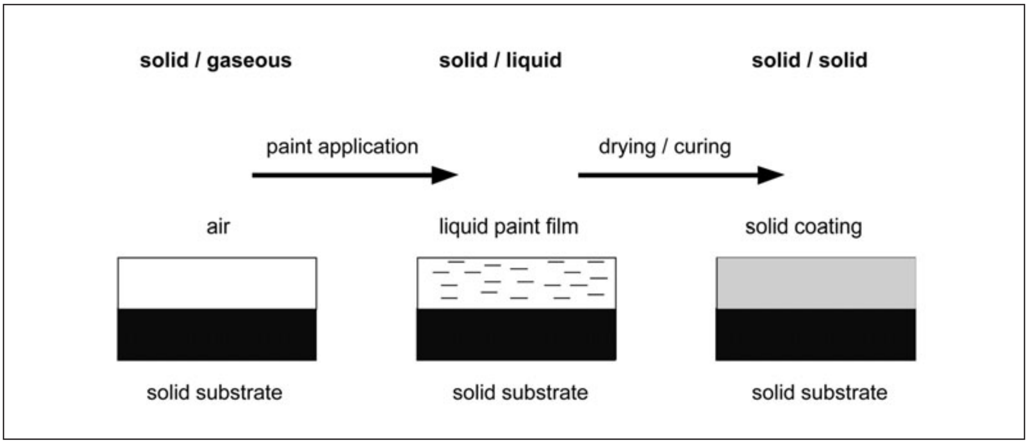


Figure I-1.10: Interfaces on solid substrates (diagram not true to scale)

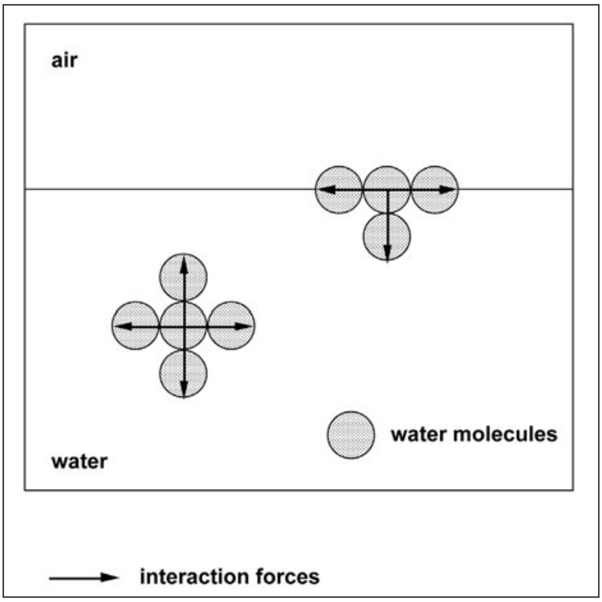


Figure I-1.11: Force diagram to explain surface tension

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

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

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

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

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

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

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

Wetting

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

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

Wetting is mathematically described by Young's equation:

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

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

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

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

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

Metal surfaces

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

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

liquid	surface tension [mN/m]	remark
mercury	500	liquid metal
water	73	
epoxy resins	45 to 60	
melamine resins	42 to 58	
alkyd resins	33 to 60	
acrylic resins	32 to 40	
butyl glycol	32	
xylene	29 to 30	
white spirit	26 to 27	
butyl acetate	25	
butanol	23	
white spirit	18 to 22	free of aromatic hydrocarbons
hexane	18	

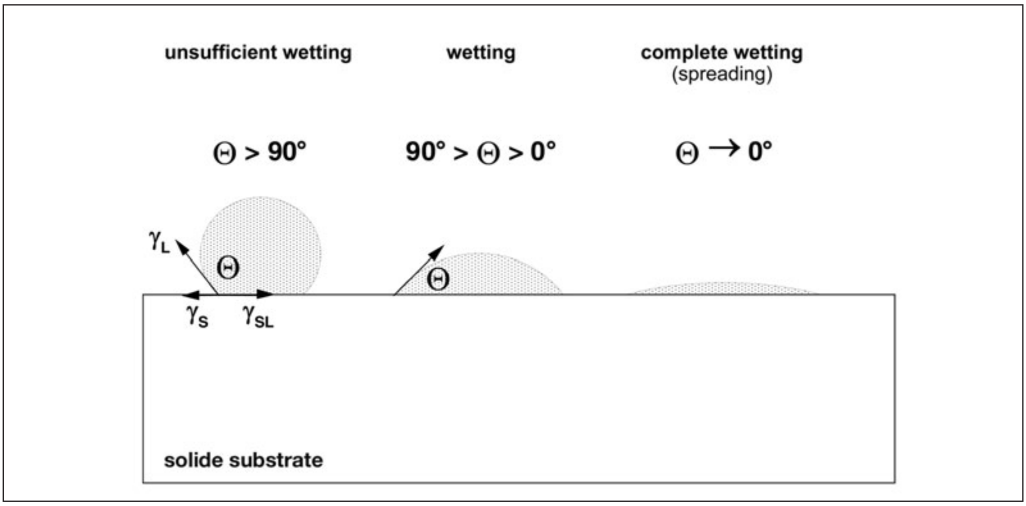


Figure I-1.12: Wetting of a solid substrate by a liquid.
γ_S Surface tension of the solid substrate *γ_L Surface tension of the liquid*
γ_{SL} Interfacial tension between solid substrate and liquid *Θ Contact angle of the liquid on the substrate*

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

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

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

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

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

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

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

Surfaces of plastics

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

Composition of plastics

Many plastics contain low-molecular components, such as additives

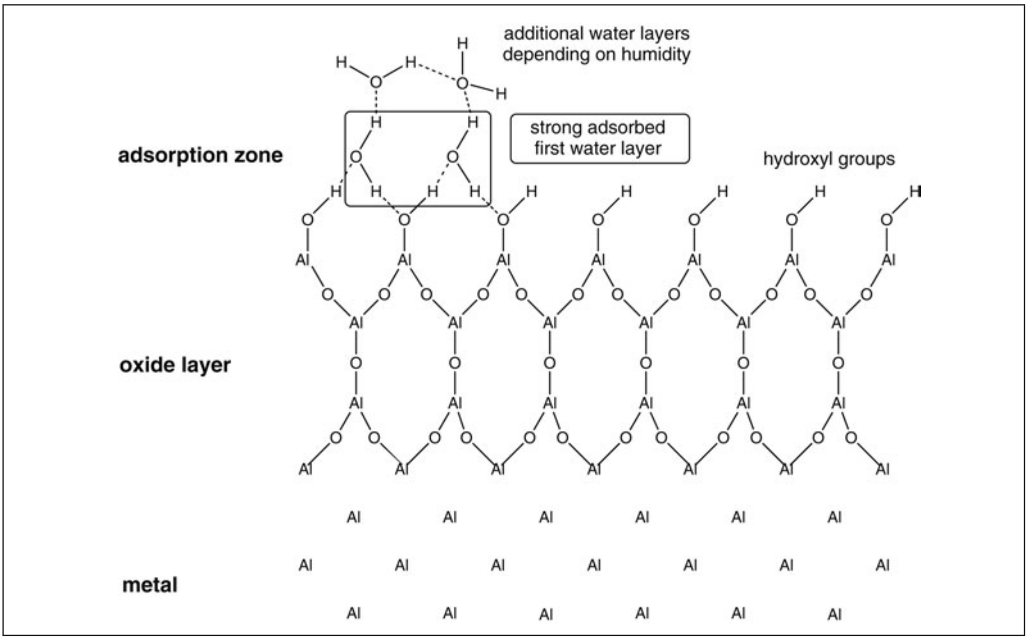


Figure I-1.13: Hydrated aluminium (oxide) surface (very simplified model). Similar considerations apply to the Fe/Fe_2O_3 system (e.g. stabilizers), residues of solvents and sometimes plasticizers. All these components can impair adhesion if they are on the surface. Many low-molecular components tend to migrate to the surface and accumulate there. Thus, there may be an anti-adhesive layer on the surface of plastics (Figure I-1.14).

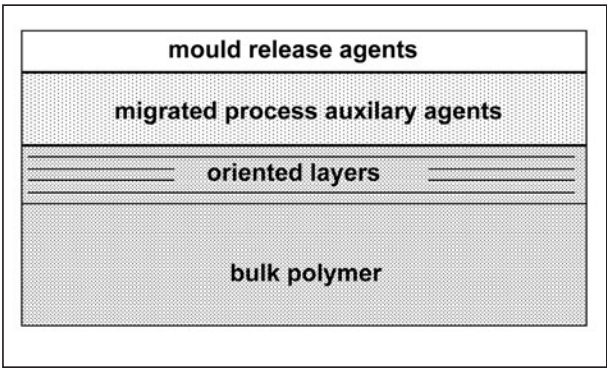


Figure I-1.14: Surface of engineering plastics

Production and processing conditions of plastics

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

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

Improvements in wetting

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

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

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

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

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

1.6.2 Adhesion forces and mechanisms

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

Adhesion/cohesion

Adhesion is defined as the effect of forces of attraction at the interface of two different solid phases. Adhesion is expressed in units of energy/area (compare surface tension). In contrast, the units of adhesive strength are force/area: N/mm^2 (MPa).

The counterpart to adhesion is cohesion. Cohesion is the effect of forces of attraction within the same phase (e.g. in the solid coating). Cohesion is the state in which particles (molecules) of a single substance are held together; it is a special instance of adhesion in which only molecules of the same kind adhere to each other.

Adhesive failure

Loss of adhesion by coatings can lead to the following fracture patterns, which vary with the level of adhesion and cohesion.

Adhesive failure:	Adhesion < cohesion	
Cohesive failure:	Adhesion > cohesion	(desired)
Both types of fractures:	Adhesion ≈ cohesion	
Fracture of the substrate:	Adhesion or cohesion > strength of the substrate (rare)	

It should be pointed out that adhesive failure is often cohesive failure in a weak layer of the coating close to the interface ("weak boundary layer") that goes unrecognized. The chemical composition of the coating or the arrangement of the polymer molecules in the boundary layer often differs from that in the bulk coating. For example, a zone of reduced strength can be formed between the chemisorbed polymer on the substrate (monolayer) and the bulk polymer. For simplicity, this unwanted fracture pattern is usually called adhesive failure too.

Theories of adhesion

In general, a distinction is made between **specific adhesion** (inter-action of interfaces independent of the geometrical shape of the surface) and **mechanical adhesion** (Figure I-1.15). Mechanical adhesion (Figure I-1.16) takes place when liquid paint enters into cavities (voids, roughness) of the substrate and the cured coating is anchored mechanically therein.

Rough or even porous substrates are frequently encountered, e.g. crystalline and therefore rough, phosphated metal surfaces (see Figure I-3.11 later) and porous wood surfaces; Figure I-1.17 clearly shows the pores in beech wood.

Prerequisites for efficient mechanical adhesion are adequate wetting of the substrate by the paint and a low paint viscosity.

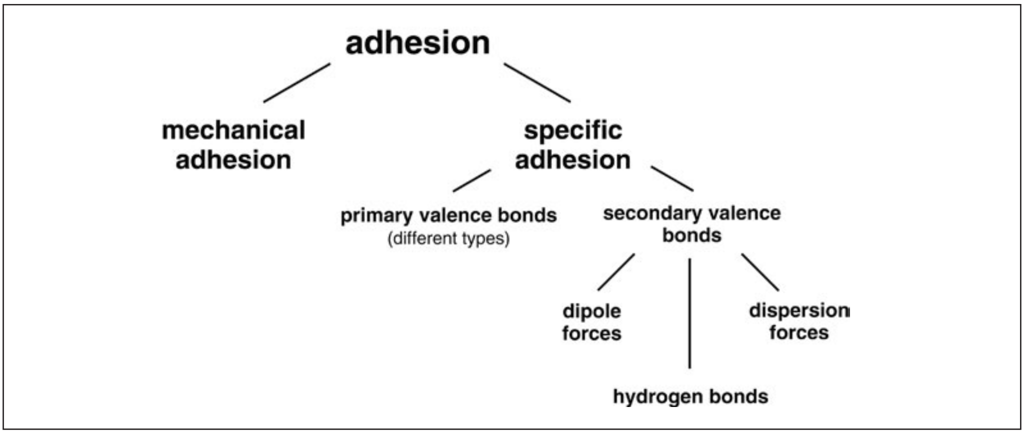


Figure I-1.15: Mechanisms of adhesion

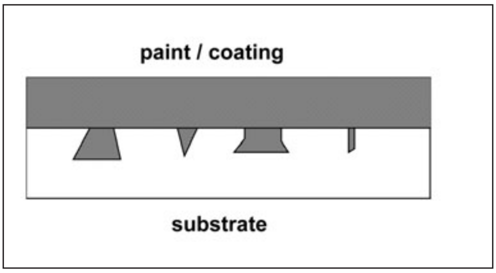


Figure I-1.16: Mechanical adhesion

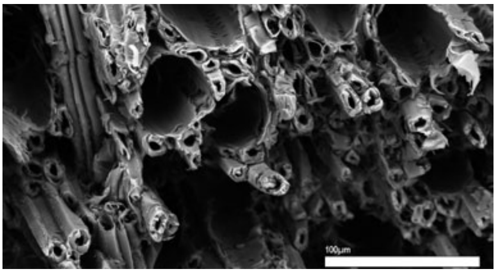


Figure I-1.17: Scanning electron micrograph of beech wood (scale bar: 100 µm = 0.1 mm)

A consequence of Table I-1.6 is that primary valence bonds between coating and substrate lead to optimal adhesion. Thus, primary valence bonds will be discussed first.

Ionic bonds

Ionic bonds (e.g. salt formation) are formed especially on mineral substrates, such as metal oxide layers, phosphated metal surfaces and so on (Figures I-1.18).

Table I-1.6: Types of chemical bonds and bond energies [13]

type of chemical bond	bond energy [kJ/mol]
primary valence bonds	
ionic linkage (salt links)	600 to 1000
covalent bonds	60 to 700
secondary valence bonds	
permanent dipoles (Keesom)	< 20
induced dipoles (London)	< 2
dispersion forces (London)	< 40
hydrogen bonds	< 50

In different references one may find a slight variation of these values.

Figure I-1.18 shows an acid-base reaction between a hydroxyl group at the surface and a carboxyl group from a binder and a metal salt or complex. The disadvantage of ionic bonds is that permeating water can break them and that can lead to loss of adhesion under wet conditions.

Chelate complexes on surfaces

Chelate complexes on metal (oxide) surfaces should be largely stable

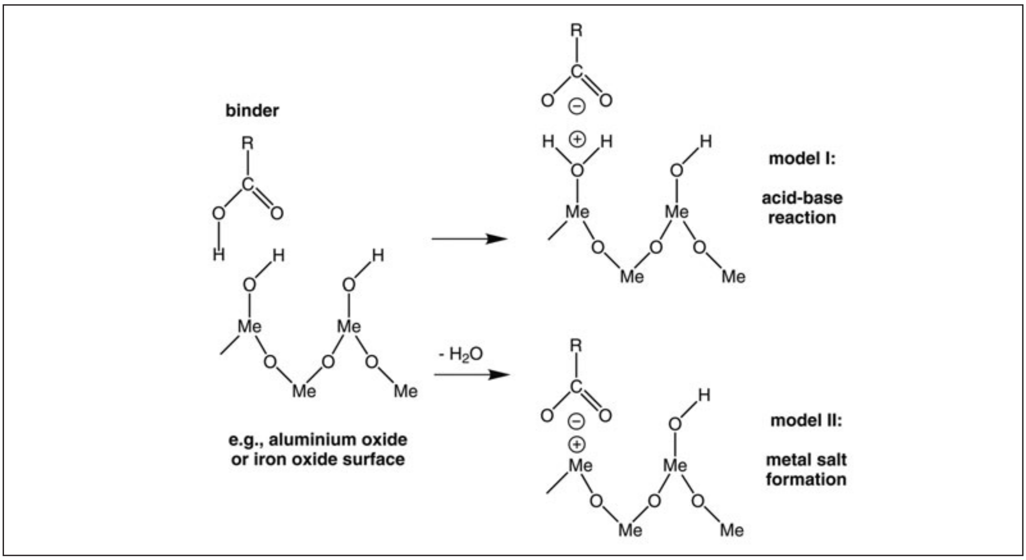


Figure I-1.18: Salt formation on metal oxide surfaces

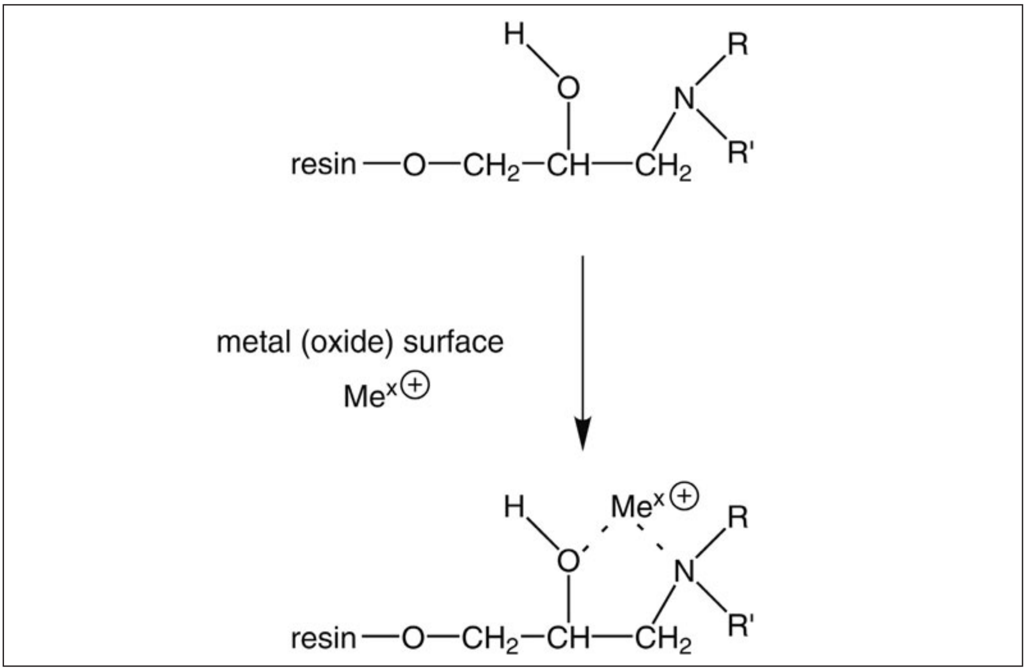


Figure I-1.19: Adhesion of 2-components epoxy coatings by the formation of chelate complexes (model)

to hydrolysis and lead to improved adhesion in wet conditions. Experience shows that epoxy resins cured with amines and curing phenolic resins (resols) exhibit very good adhesion on metals, even in wet conditions; both observations can be explained by assuming that chelate complexes are formed (Figure I-1.19 and I-1.20) [14, 15].

Chelates forming 6-member rings are known to be stable (Figure I-1.20) [15]. Recent molecular calculations [16] suggest that a second resol-metal chelate (8-member-ring chelate in Figure I-1.20) is formed. As a rule, chelates forming 8-member rings are less stable than their 6-member counterparts but should also be considered in this special case.

Covalent bonds

A further possibility is the formation of covalent bonds on polymer substrates, such as primers and plastics, by chemical reaction between the binder and suitable functional groups on the polymer substrate. There is a rule in the coating of curing primers with topcoats that the primers should not be completely cured before the application of the topcoat because otherwise the binder of the primer will not have any reactive functional groups left for reaction with the topcoat. In contrast, oxidation of plastic surfaces (e.g. flame treatment, Chapter I-1.7.1) generates reactive functional groups (e.g. -OH, -COOH) that may react chemically with the binder of a coating.

Secondary valence bonds

The less effective secondary valence bonds (Table I-1.6) are the more common type of specific adhesion. A prerequisite for this is close contact between coating and substrate because secondary valence bonds have only a limited radius of action. The following types of secondary valence bonds exist:

- Dipole forces (dipole-dipole interaction)
- Prerequisite: Polar groups (permanent dipoles) on the surface of the substrate and in the coating.

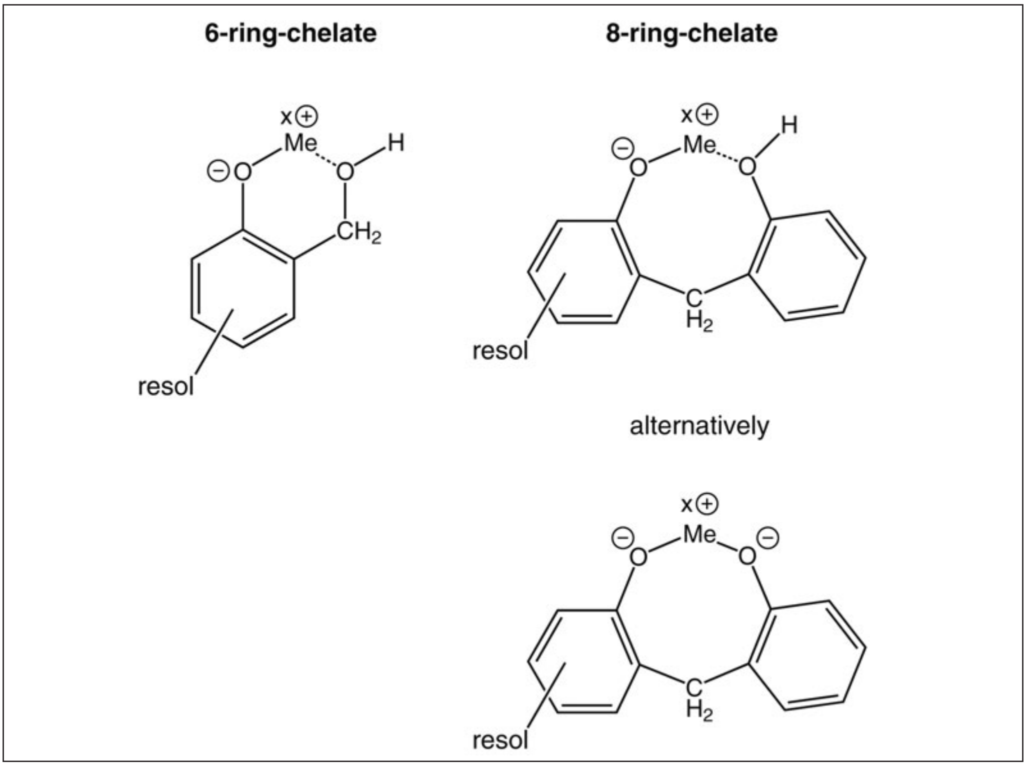


Figure I-1.20: Adhesion of resols by the formation of chelate complexes (model)

- Hydrogen bonds
- A disadvantage of hydrogen bonds (Figure I-1.21) is that they can be broken by water and that may decrease the level of adhesion in wet conditions.
- Dispersion forces
- Dispersion forces are of universal importance, but not very specific. Dispersion forces increase with increase in molar mass. In nonpolar materials (e.g. polyethylene), dispersion forces are virtually the only forces present.

Further adhesion theories

Adhesion by means of covalent bonds could alternatively be called chemisorption (adsorbate and substrate react chemically) while adhesion by secondary valence bonds could be termed physisorption (neither adsorbate nor substrate is chemically involved) – this is the so-called adsorption theory.

Other adhesion theories exist:

Diffusion theory

This theory applies to polymer substrates such as plastics or primers. The coating adheres by diffusion of oligomer chains of the binder into the surface layer of the polymer substrate; this leads to a mechanical linkage. Diffusion takes place especially above the glass temperature T_g of polymers. Swelling of the polymer substrate by organic solvents also improves diffusion because T_g is lowered (plasticization).

For example, the adhesion of water-borne paints on plastics can be improved by adding a slowly evaporating co-solvent, such as N-methylpyrrolidone (NMP; see Chapter III-1.4.3), or by rubbing the plastic with a suitable organic solvent. Both actions cause swelling of the polymer substrate.

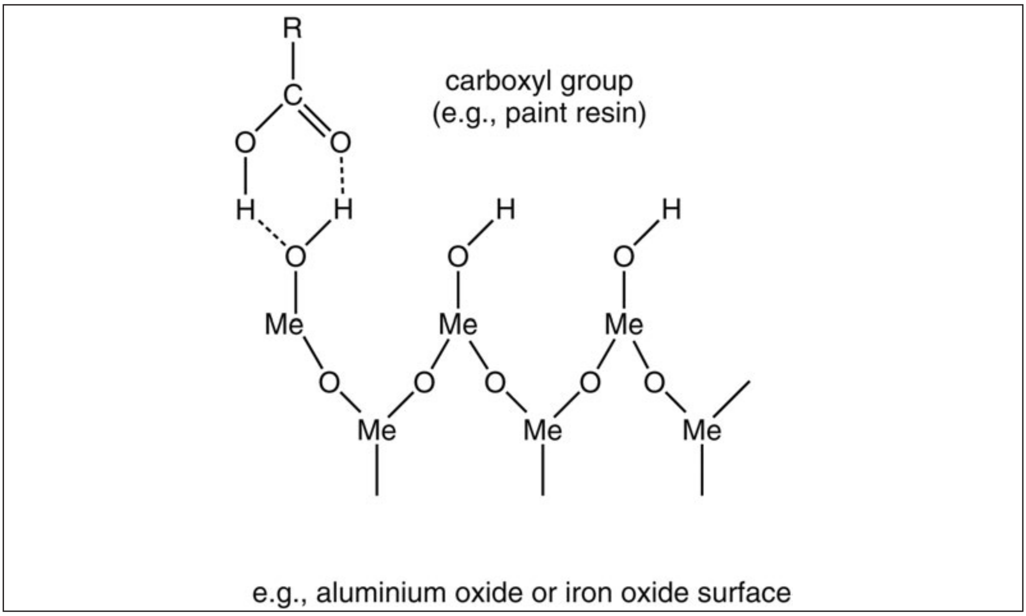


Figure I-1.21: Hydrogen bonds on metal (oxide) surfaces (model)

Electrostatic adhesion

This effect is not very important in coatings technology. Electrostatic adhesion occurs by close contact of two different polymers or a polymer (e.g. binder) and a metal. Because of different electronic emission energies, electron transfer can occur between the two materials. Electron transfer creates an electrical double layer that induces electrostatic attraction.

1.6.3 Adhesion promoters/adhesion-promoting layers

1.6.3.1 Silane adhesion promoters

Silane adhesion promoters are well established in adhesives technology [11, 17, 27]. They can also be called functional trialkoxysilanes (Figure I-1.22).

Function of silane adhesion promoters

Hydrolysis of alkoxy groups by atmospheric moisture yields reactive silanol groups (Figure I-1.23). Silanol groups can react by condensation with the hydroxyl groups on the surfaces of metals (Me-OH), glass (Si-OH), mineral fillers and construction materials (e.g. Si-OH, Ti-OH, Al-OH) and with each other (Si-OH). The reaction with hydroxyl groups on surfaces effects a change in the functionality of the inorganic surface (Figure I-1.23). Functional group X, with a corresponding functionality of the binder, can react with the binder to produce a covalent bond between the binder and the inorganic surface. Figure I-1.24 shows an example of this type of covalent bonding produced by the reaction of aminosilane with epoxy resin.

Silane adhesion promoters are also called coupling agents (Figure I-1.25) [18]. The effectiveness of silane adhesion promoters strongly depends on the substrate (Figure I-1.26) [11].

Applications of silane adhesion promoters

a) Coupling of adhesives and sealants (significant) [11]
Adhesive bonding and sealing of glass, metals and mineral construction materials.

b) Coupling of binders and mineral fillers
   Inorganic fillers such as talc may be surface-treated with silane adhesion promoters. Choosing an appropriate silane for the respective binder can improve the bond between the (cured) binder and filler. Thus, water-vapour diffusion through the coating can be decreased and corrosion protection improved [20].
c) Coupling of coatings (so far of minor significance); aimed especially at improving adhesion in wet conditions [19].
   It should be noted that silane adhesion promoters in paints may react with traces of water in solvent-borne paints or with atmospheric moisture (Figure I-1.27). These side-reactions (hydrolysis + condensation, Figure I-1.27) produce polysiloxanes which may cause cratering. Before silane adhesion promoters are added, traces of water should be removed with the appropriate additives (e.g. molecular sieves); overly high humidity should be avoided if possible.

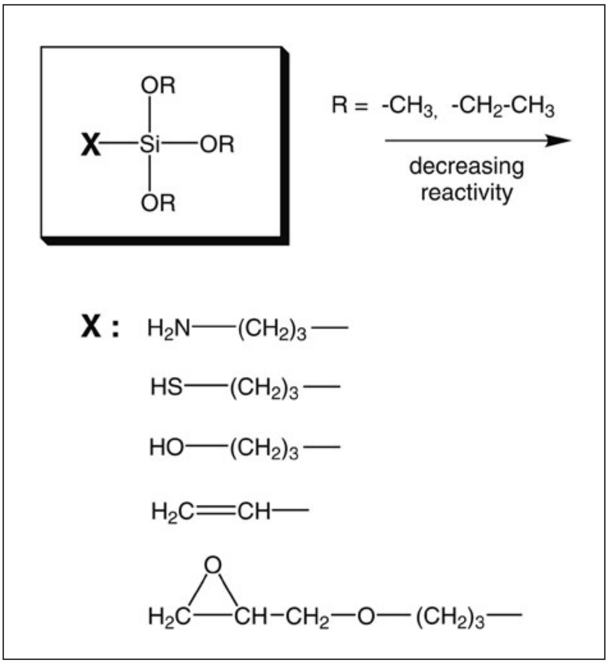


Figure I-1.22: Typical silane adhesion promoters

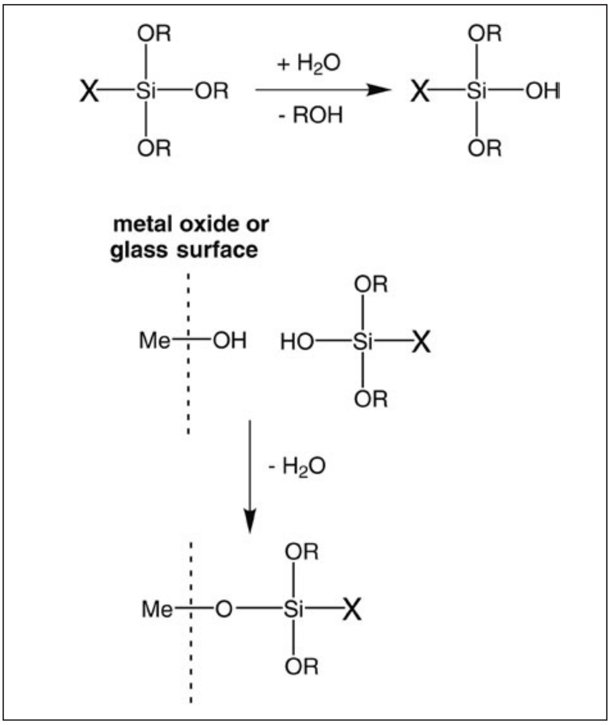


Figure I-1.23: Reaction of silane adhesion promoters

1.6.3.2 Thin polymeric adhesive layers

Thin layers of poly(meth)acrylic acids can improve adhesion of cured coatings (e.g. AK/MF or two-components PUR) on steel in wet conditions [21]. These layers are produced by dipping steel sheets into dilute (about 1 wt.%) aqueous solutions of poly(meth)acrylic acids (for 1 to 2 min); pH about 3. Iron is converted into iron(II) to yield an organic conversion coating.

The thickness of these layers is 20 to 30 nm. For polyacrylic acid, the optimum efficiency was established to be a molar mass of about 100,000 [21]. A rough chemical composition of

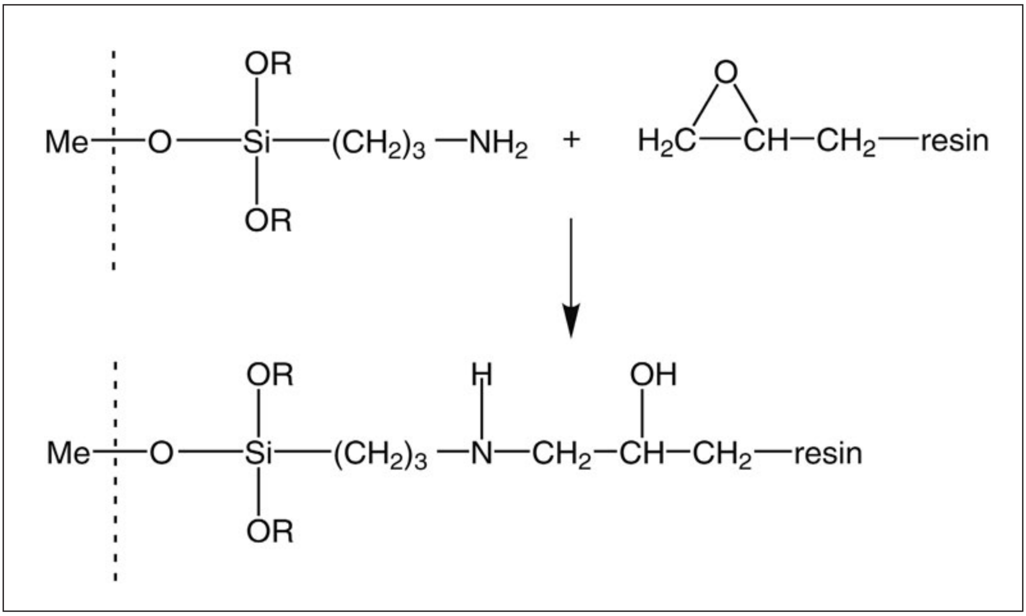


Figure I-1.24: Reaction between silane adhesion promoter and epoxy resin

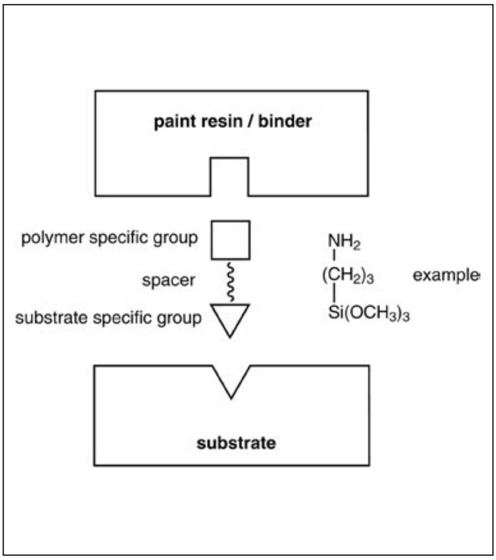


Figure I-1.25: Silane adhesion promoters as coupling agents

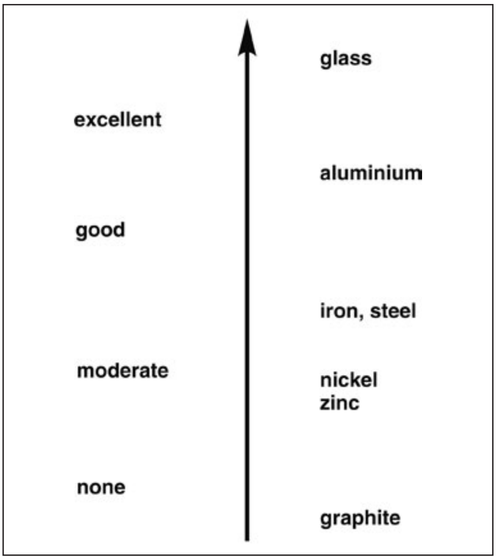


Figure I-1.26: Effectiveness of silane adhesion promoters for various substrates

such adhesive layers is presented in Figure I-1.28. Phenolic resins (resols) and epoxy resins may also generate thin adhesive layers [13].

1.6.4 Corrosion inhibitors, anticorrosive pigments, corrosion protection additives

Adhesion of a coating is a necessary but on its own insufficient requirement for corrosion protection. Additional protective measures should be considered. Thus, corrosion inhibitors, anticorrosive pigments, corrosion protective additives will be discussed briefly in this chapter.

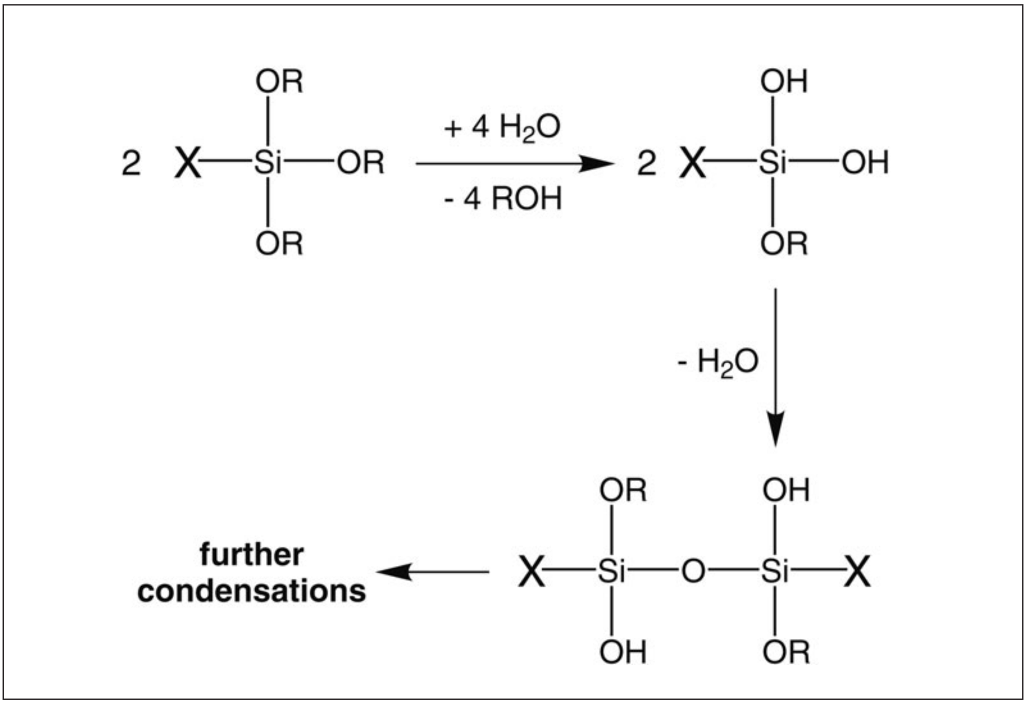


Figure I-1.27: Side-reactions of silane adhesion promoters

Anticorrosive pigments can be classified as follows:

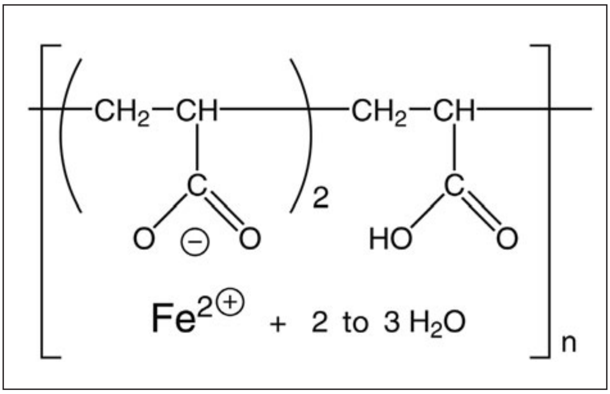


Figure I-1.28: Composition of an adhesive layer of polyacrylic acid on steel

a) **Chemically active anticorrosive pigments** (e.g. zinc oxide) bind corrosion stimulators such as chloride or sulphate by forming insoluble compounds and/or stabilizing the pH value of a coating in contact with the corrosion medium. Therefore, slight solubility in the corrosion medium is necessary.

b) **Electrochemically active anticorrosive pigments** (e.g. zinc chromate, zinc phosphate) passivate metal surfaces by forming thin layers, such as chromate or phosphate layers. Again, slight solubility in the corrosion medium is necessary. The distinction from chemically active pigments a) is sometimes unclear because anticorrosive pigments exist which can act in both ways (e.g. zinc phosphate).

c) **Active, cathodic protective anticorrosion pigments** (e.g. zinc dust) act as sacrificial anodes and protect the metal substrate (see Chapter II-1.2.6). They are “classic” pigments and insoluble.

d) **Passive anticorrosive pigments**, barrier pigments (e.g. micaceous iron oxide, se Figure I-3-8) lengthen the diffusion pathways for corrosion stimulators and therefore improve the corrosion protection of a coating (see Chapter I-3.2). Again, they are “classic” pigments, and insoluble.

Anticorrosive pigments can be classified with respect to their solubility in corrosion media as slightly soluble (a, b) and completely insoluble (c, d).

Some highly active anticorrosive pigments (e.g. the carcinogenic zinc chromates) should not be used anymore on account of ecological and toxicological reasons. But relatively ecologically safe active anticorrosive pigments (e.g. phosphates) are comparatively less efficient. Thus, where possible, non-toxic organic additives are needed to improve the corrosion protection afforded by coatings. Such additives are commonly termed ***corrosion inhibitors*** [22, 23]; a more correct term is ***corrosion protection additives*** [24]. The difference between the two terms is explained below.

Corrosion inhibitors in particular are substances dissolved in a liquid medium that concentrate at the metal (oxide)/medium interface; i.e., a protective layer at the interface is generated by adsorption. This layer prevents or decreases corrosion (see electrochemically active anticorrosive pigments). This definition characterizes the primary property of corrosion inhibitors used in the water of heating and cooling circuits.

For application in anticorrosive paints, corrosion inhibitors have to meet additional requirements such as:

- Adequate solubility in the liquid paint
- Compatibility with the binder(s)
- Low water solubility in the dried or cured coating
- No negative side effects, such as discolouration or increased hydrophilicity of the coating

These demands have led to the development of corrosion inhibitors that possess secondary properties specifically for coatings [22], namely corrosion protection additives. Corrosion protection additives are a thus subset of corrosion inhibitors (Figure I-1.29). In other words, a corrosion protection additive is a corrosion inhibitor but the converse is not true.

Figure I-1.29 tries to visualize with the aid of set theory the differences between corrosion inhibitors, corrosion protection additives and the four different types of anticorrosive pigments (a - d, see above).

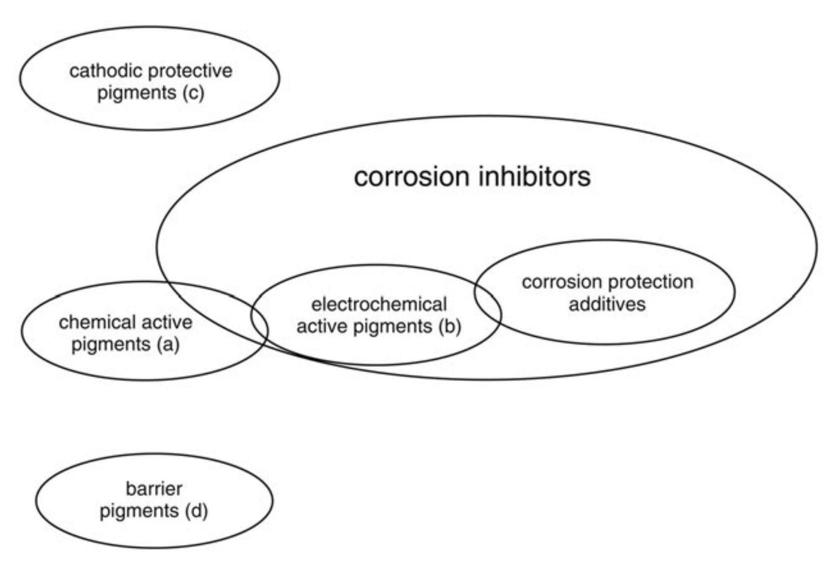


Figure I-1.29: Sets of corrosion inhibitors, corrosion protection additives and different anticorrosive pigments (simplified diagram)

1.7 References

[1] A. Goldschmidt, H.-J. Streitberger, BASF Handbook on Basics of Coatings Technology, Vincentz Network (2003) and Perizonius, I-Lack 62 (1994) p. 82 ff
[2] M. Harsch, Lacktechnologien ganzheitlich optimieren, Lack im Gespräch, Informationsdienst Deutsches Lackinstitut, No. 62, März 2000
[3] A. Rössler, G. Skillas, S. E. Pratsinis, Chemie in unserer Zeit 35 (2001) No. 1, p. 32-41
[4] C. Göbbert, M. Schichtel, R. Nonninger, Farbe & Lack, 108 (2002) No. 7, p. 20-24
[5] T. Adebahr, Europ. Coat. Journ. No. 4, p. 144-149 (2001)
[6] A. J. Vreugdenhil, V. N. Balbyshev, M. S. Donley, Journ. Coat. Technol. 73 (2001) No. 915, p. 35-43
[7] A. C. Pierre, Introduction to Sol-Gel Processing, Kluwer Academic Publishers, 2. ed. (2002)
[8] DIN-Term, Beschichtungsstoffe, Vincentz Verlag, Hannover, 1st ed., 2001
[9] Römpp Lexikon, Lacke und Druckfarben, Hrsg. U. Zorll, Thieme Verlag, 1998
[10] W. Funke, U. Zorll, defazet, 29 (1975) p. 146 ff
[11] E. M. Petrie, Handbook of Adhesives and Sealants, McGraw-Hill, New York (2000), Chapter 6, 7 and 16 as well as appendix D-2.
[12] W. Brockmann, S. Emrich, Adhäsion, 44 (2000) No. 9, p. 40-44
[13] J. Gähde, Farbe & Lack 101 (1995) p. 689 ff
[14] H. Kollek, C. Matz, Adhäsion 12/1989, p. 27 ff
[15] B. Müller, kleben & dichten, Adhäsion, 46 (2002) No. 6, p. 34 - 38 and Surface Coat. Int. Chapter B, 85 (2002) p. 111-114
[16] V. Strehmel, B. Strehmel, Modification of Phenol-Methanal Network Polymers, in Polymer Modification – Principles, Techniques and Applications, Marcel Dekker New York - Basel, p. 575 - 705 (2000) especially p. 599
[17] E. P. Plueddemann, Silane Coupling Agents, Plenum Press, New York (1982) und U. Deschler et al., Angew. Chem. 98 (1986) p. 237-253
[18] B. Meyer-Roscher, S. Wellman, H. Brockmann, kleben & dichten, Adhäsion, 39 (1995) No. 4, p. 34-37
[19] W.-D. Kaiser, A. Rudolf, S. Pietsch, Farbe & Lack 103, No. 7 (1997) p. 80-88
[20] N. Wamser, E. Urbino, Farbe & Lack 95 (1989) p. 109 ff
[21] Z. Gao, H. Yamabe, B. Marold, W. Funke, Farbe & Lack, 98 (1992) p. 917 ff
[22] A. Braig, Corrosion Inhibitors, in Additives for Coatings (editor J. Bielemann), Wiley-VCH (2000), p. 291-305
[23] G. Schulte, W. Greß, R. Höfer, Welt der Farben (1995) No. 2, p. 17-22
[24] B. Müller, Farbe & Lack, 106 (2000) No. 11, p. 156
[25] R. Fernando, JCT CoatingsTech, Vol. 1, May 2004, p. 32-38
[26] G. Meichsner, T. Mezger, J. Schröder, Lackeigenschaften messen und steuern, Vincentz Network (2003) Chapter 5.5.3
[27] B. Müller, W. Rath, Formulating Adhesives and Sealants, Vincentz Network (2010)

2 Pigment dispersions

As the dispersion of pigments and fillers (extenders) is the most important step in paint manufacturing, some fundamentals of disperse systems are presented below. These are essential for an understanding of dispersing agents and polymer dispersions (see Chapter III-1.3.1).

2.1 Fundamentals of disperse systems

Pigmented paints are disperse systems with very large phase boundaries. This chapter deals only with coatings technology and presents a simplified view of the most important facts needed for an understanding of the manufacturing and properties of paints.

Phase boundaries

What is a phase boundary? A phase boundary separates two immiscible phases. For example, a paint may consist of two phases, the binder solution (liquid) and the pigment (solid) dispersed therein; the two are separated by the phase boundary. If one phase is gaseous (e.g. air), this boundary is called a surface. For example, non-dispersed pigment powders have a large surface (area) in contact with air.

Disperse systems

Next, we need to define what a disperse system is. A disperse system (dispersion) consists of a (finely divided) disperse phase (discontinuous or inner phase) and a dispersion medium (continuous phase). Between the disperse phase and the dispersion medium exists a phase boundary which can be very extensive and which largely determines the properties of the disperse system. Disperse systems may be classified physically according to disperse phase and dispersion medium (Table I-2.1).

Table I-2.1: Classification of disperse systems

disperse phase	dispersion medium	examples
solid	solid	gold ruby glass; solidified coatings**; powder coatings**
liquid	solid	minerals with liquid inclusions, e.g. opal
gaseous	solid	minerals with gaseous inclusions, e.g. pumice stone, foamed polymers
solid	liquid	liquid paints**, polmer dispersions
liquid	liquid	emulsions, e.g. milk, silicone resin emulsions
gaseous	liquid	foames
solid	gaseous	solid aerosols, e.g. smoke, sprayed powder coatings
liquid	gaseous	liquid aerosols, e.g. fog, sprayed liquid paints
gaseous	gaseous	not possible because gases mix up homogeneously

*** an exeption are nearly all paints without pigments (clear coats)*

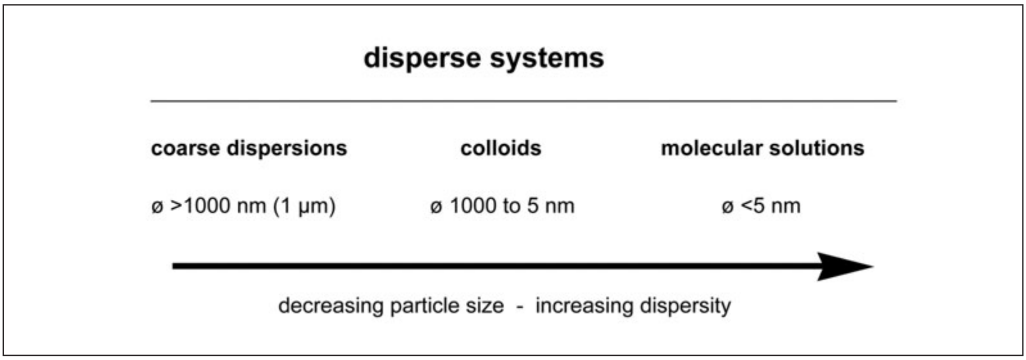


Figure I-2.1: Classification of disperse systems by reference to the size of the disperse phase. By molecular solutions is meant more or less low-molecular substances.

Colloids

Another characteristic feature of disperse systems is the particle size of the disperse phase (Figure I-2.1). Dispersions whose particle diameters range from 5 to 1,000 nm* are called colloids or colloidal dispersions (Figure I-2.1) because the inner phase boundaries in these cases significantly determine the properties of the disperse system.

Industrial pigments and filler dispersions:

Disperse phase:	Pigment or filler particles (primary particle size: 10 to 1000 nm; fillers may be larger in some cases)
Dispersion medium:	Solvent, solvent-free liquid binder, binder solution (homogeneous) or binder dispersion (additional phase boundary!)

Industrial polymer dispersions:

Disperse phase:	Polymer particles (particle diameter: 50 to 5000 nm)
Dispersion medium:	Mostly water

In other words, pigments and polymer dispersions used in coatings technology are mostly colloids.

The relationship between the surface area and the particle size of the disperse phase was calculated long ago on the basis of the following model [1, 2] (Table I-2.2). The calculation envisages a cube with an edge length of 1 cm and a surface area of 6 cm². This cube is divided 10 times in all three dimensions to yield 10 · 10 · 10 = 1,000 cubes with an edge length of 1 mm and a total surface area of 60 cm². This operation is then repeated endlessly (Table I-2.2).

Table I-2.2: Increase in the surface area of a cube with increasing decimal division (model calculation)

edge length of a single cube	number of cubes	surface area (total)
1 cm	1	6 cm²
1 mm	10^3	60 cm²
0.1 mm	10^6	600 cm²
0.01 mm (10 µm)	10^9	6000 cm²
1 µm (1000 nm)	10^{12}	6 m²
0.1 µm (100 nm)	10^{15}	60 m²
0.01 µm (10 nm)	10^{18}	600 m²
1 nm	10^{21}	6000 m²

The increase in surface area that occurs as the particles become smaller is important because

---

* *Slightly varying figures may be found in the literature on account of uncertainty.*

atoms or molecules on the surface of a particle have a higher energy content than those inside it. A particle (of a low-molecular substance) with a diameter of 10nm has about 25% of its molecules in the phase boundary [3]. Therefore, the term colloid characterizes a state of matter which has a large surface or interface area and a high energy content.

Pigments and fillers

The correlations between particle size and surface area calculated in Table I-2.2 are transferable to pigments and fillers (Table I-2.3). Industrial pigments and fillers have a more or less pronounced particle size distribution.

Table I-2.3 leads to two conclusions:

- As expected, the specific surface area decreases with increasing particle size.

Table I-2.3: Average primary particle diameter and specific surface area (BET) of various pigments and fillers (extenders)

pigment or filler	primary particle diameter [nm]	specific surface area [m^2/g]
isometric particles		
carbon black		
gas black	13	460
furnace black	95	20
silica		
grinded quartz sand	16,000	0.9
pyrogenic silica	7	390
phthalocyanine blue		
phthalocyanine blue 1	50	72
phthalocyanine blue 2	100	36
calcium carbonate		
precipitated calcium carbonate	80	20
grinded marble	2500	3.4
titanium dioxide (rutile)		
ultrafine, transparent	10 to 20	45 to110
opaque, not surface treated	250 to 300	about 6
iron oxide red		
transparent	20	100
opaque	300	6
anisometric particles		
lamellar pigments (1 µm = 1000 nm)	[µm]	
aluminium flakes		
fine	16 · 0.3	5
coarse	49 · 0.3	1.6
pearlescent pigments		
fine	16 · 0.8	11
coarse	20 · 0.8	10

All examples in this table are actual commercial products; the first has a very fine and the second example a very coarse particle diameter.Particles with diameters of 100 nm or less are nowadays called nanoparticles (see chapter I-1.3).

- For geometrical reasons, anisometric particles have a larger specific surface area than isometric particles.

Properties of disperse systems

Figure I-2.2 shows how the properties of disperse systems change with increase in dispersity [1]. Turbidity, filterability, diffusion and dialysis increase or decrease with increasing dispersity. In contrast, colouring power and opalescence are a maximum in the colloidal state. Table I-2.4 shows that this maximum in the colloidal state is also observed for industrial pigments.

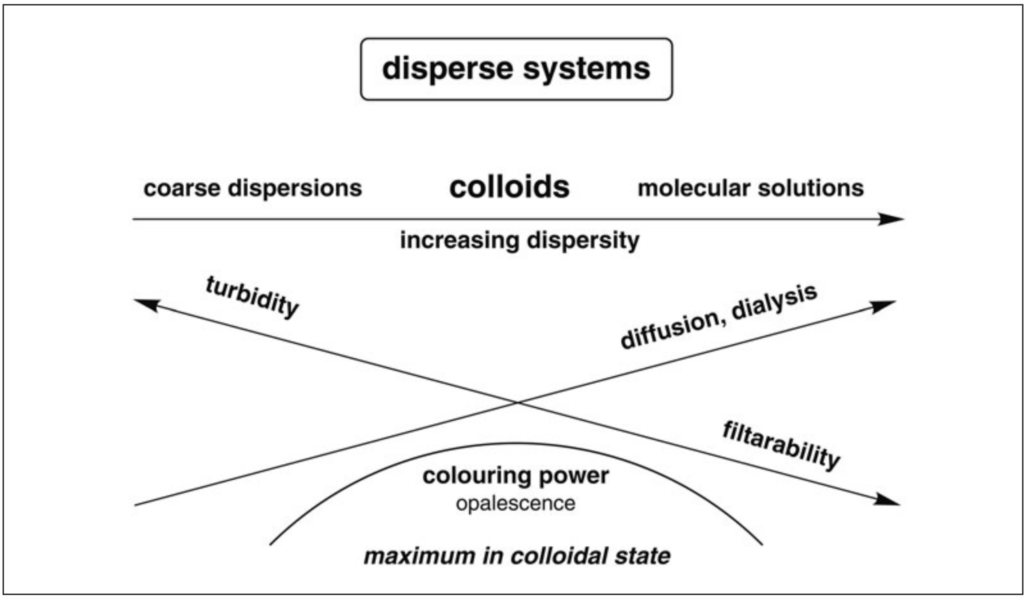


Figure I-2.2: Properties of disperse systems

Table I-2.4: Properties of spherical iron oxide red pigments [4]

particle size [nm]	100	150	170	250	300	350	450	800	900	1000
spec. surface area	decreasing →									
oil adsorption value	decreasing →									
colour shade	increasing bluish →									
tinting strength	← decreasing						decreasing →			
hiding power	← decreasing						decreasing →			

Tinting strength and hiding power show a maximum by particle sizes of about 300 nm (compare Figure I-2.2).

2.2 Stabilization of dispersions

Flocculation is the association of dispersed pigment particles in the liquid paint medium. Flocculation reduces the size of the phase boundary between the pigment and the dispersion medium. Most disperse systems are thermodynamically unstable with regard to flocculation. The question now arises as to why such disperse systems are thermodynamically unstable. To answer it, let us calculate the increase in surface area that occurs when a droplet of emulsion is subdivided (Figure I-2.3). As expected, the total surface area of the emulsion droplets increases.

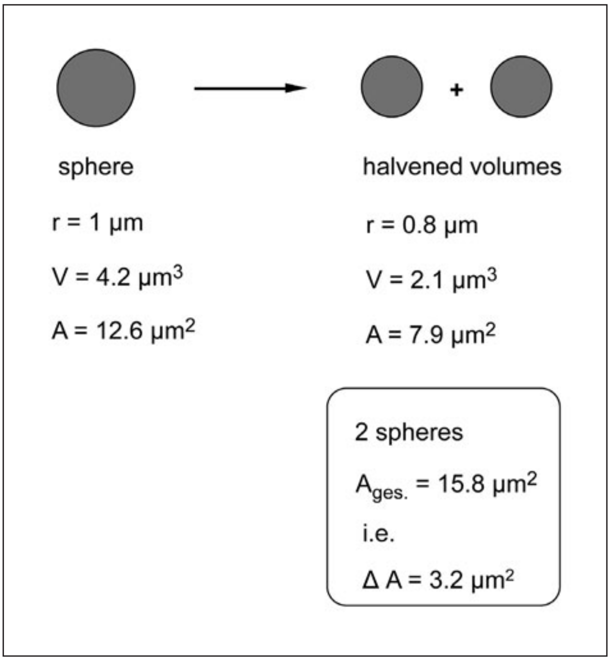


Figure I-2.3: Subdivision of an emulsion droplet (increase in surface area)

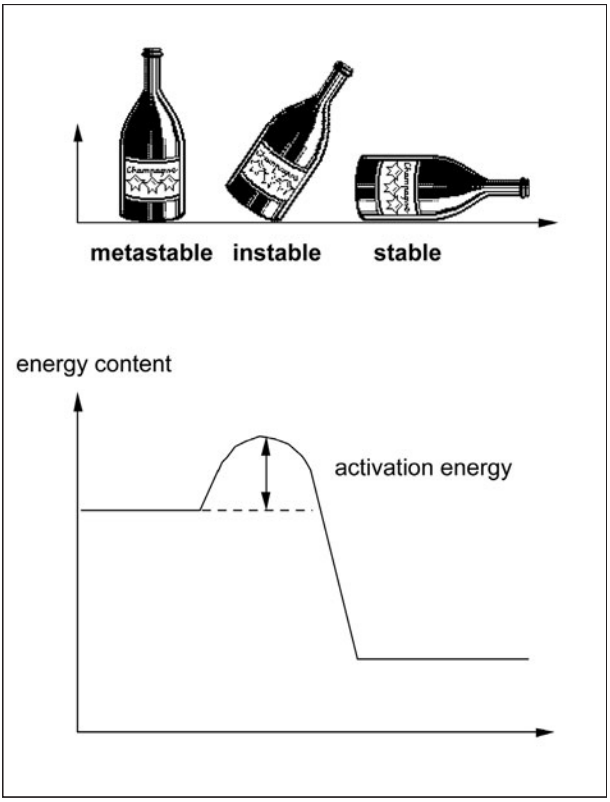


Figure I-2.4: Metastability, instability, stability (x-axis: tilting angle of the bottle and reaction coordinate)

For the surface area of a liquid to increase, molecules have to be taken from the bulk of the liquid to the surface; i.e., cohesion forces have to be overcome. Work (energy) therefore has to be performed.

Consequently, both divided droplets have a higher energy content than the single (undivided) droplet. The work needed (energy consumption) can be calculated as follows.

$$W = \gamma \cdot \Delta A$$

W	work [energy]
γ	surface tension [force/length = energy/area]; see Chapter I-1.5.1
ΔA	increase in phase boundary [area]

The work W is proportional to the increase in the phase boundary area ΔA and to the surface tension γ. This means that the larger the phase boundary and the higher the surface tension, the higher is the energy content of the disperse system and the less thermodynamically stable it is.

Pigment and polymer dispersions are generally stable for years on end because they are metastable. The term metastability is illustrated in Figure I-2.4 [3].

The energy content of the bottle (Figure I-2.4) should equal the potential energy ($m \cdot g \cdot \Delta h$) at the centre of gravity. A bottle lying on its side has the lowest centre of gravity and, therefore, the lowest potential energy (it is stable). The centre of gravity is at its highest in a bottle tilted on its edge. This state has the highest potential energy (i.e. is unstable) and the tiniest current of air would knock the bottle over. The centre of gravity in an upright bottle (metastable) is higher than in the lying bottle, but lower than in the bottle standing on its edge.

Everybody knows that it takes energy to upset an upright bottle (to effect a transition to the stable state). This expenditure of energy is called the activation energy; the bottle standing on its edge is said to be in a transition state (Figure I-2.4). The heavier the bottle and the larger the area of its base, the more firmly the bottle stands; i.e., the higher the activation energy needed to tip it over (transition to the stable state) and the more stable the metastable state is.

So why do pigment dispersions have a long shelf life, i.e., why are they metastable? Because they can be prevented from flocculating by electrostatic or steric stabilization. These terms are explained in detail below. The combination of both these stabilization mechanisms is called electrosteric stabilization.

Stabilization is a kinetic effect. Transition to the thermodynamically stable state by flocculation is prevented or retarded by a high activation energy.

2.2.1 Electrostatic stabilization

Inorganic pigments and fillers dispersed especially in water (which has a high dielectric constant) are mostly charged. Since the overall disperse system is uncharged, the liquid phase must contain an equal number of counter ions in close proximity to the particles (Figure I-2.5). An electric double layer (ion cloud) exists and flocculation is prevented because of the electrostatic repulsion of like charges (this is known as electrostatic stabilization).

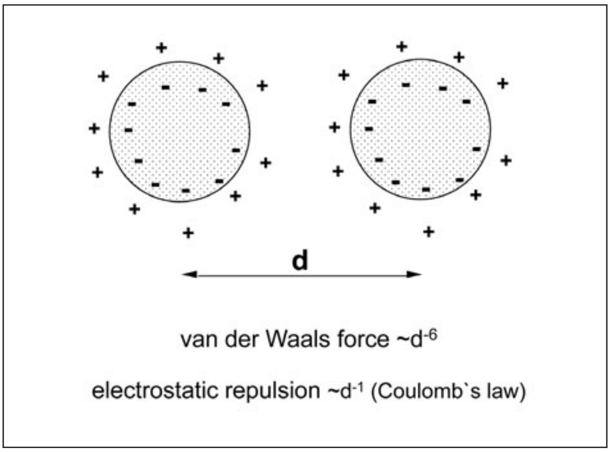


Figure I-2.5: Simplified diagram of the electric double layer of two pigment particles

It is important for the forces of repulsion (Coulomb's law) to have a larger sphere of action in the dispersion medium than do the forces of attraction (van der Waals forces; Figure I-2.5). If there are opposite charges (e.g. in the case of different pigments), co-flocculation occurs because of electrostatic attraction.

Adding electrolytes (salts) causes contraction of the electric double layer (ion cloud) and may lead to flocculation (Table I-2.5) [3].

The Schulze-Hardy rule describes how the ionic charge of added salts influences their flocculating power:

- In negatively charged dispersions (the commonest), the flocculating power of cations increases with increase in cationic charge: $Na^+ < Ca^{2+} < Al^{3+}/Fe^{3+}$
- In positively charged dispersions (rare, e.g. cathodic electrodeposition primers), the flocculating power of anions increases with increase in anionic charge: $Cl^- < SO_4^{2-} < PO_4^{3-}$

Table I-2.5: Influence of the sodium chloride concentration on the sphere of action of electrostatic forces

NaCl in water [mol/l]:	10^{-1}	10^{-3}	10^{-5}
range of action of electrostatic forces [nm]	1	10	100

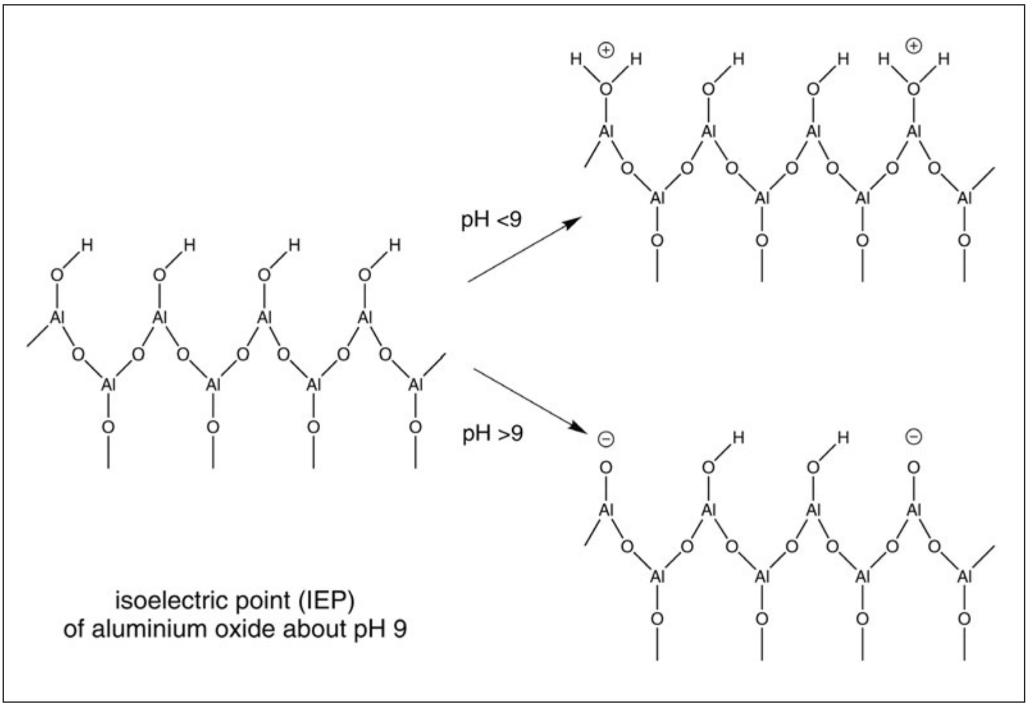


Figure I-2.6: Very simplified diagram of an aluminium oxide surface at different pH values

From a practical point of view, it is important to avoid any electrolytes (salts) in water-borne paints.

There are various mechanisms by which surfaces of pigment or filler particles can acquire a charge:

- Dissociation of functional groups on particle surfaces
- Adsorption of ions (mostly polyanions); see dispersing agents (Chapter I-2.3.1)

Dissociation of functional groups on particle surfaces

Oxides have hydroxyl groups on their surfaces (see aluminium oxide surface in Chapter I-1.6.1) that may react as acids or bases depending on the oxide concerned. The pH value at which the surface charge is zero (point of zero charge) is called the isoelectric point (IEP) [5]. Above the IEP, the oxide surface is negatively charged by deprotonation while, below it, the surface is positively charged by protonation (Figure I-2.6). The density of electric charges increases with increase in the difference between the pH of the dispersion medium and the IEP.

Table I-2.6: Isoelectric points (IEPs) of certain oxides [5]

oxide	IEP (pH value)
MgO	12.5
Al_2O_3	9
ZnO	9
Cr_2O_3	7
Fe_3O_4	6.5
Fe_2O_3	6.7
TiO_2	4.5 to 6.5
SiO_2	2

These data (Table I-2.6) apply to chemically pure oxides. There may be significant deviations from these IEP values in the case of industrial pigments or fillers where surfaces may have been after-treated (e.g. titanium dioxide). Also, various crystalline structures may influence the IEP.

Electrostatic stabilization is especially important in water-borne paints or latex paints because of the high dielectric constant of water. Studies have shown that the electric charge on pigment surfaces is also important in solvent-borne paints [6]; the same pigment dispersed in different paint resins may show no charge at all or opposite charges.

2.2.2 Steric stabilization

It has been known for more than 100 years that aqueous dispersions (colloids) can be readily stabilized against flocculation by adding water-soluble polymers (so-called protective colloids), such as gelatine, casein, and polyvinyl alcohol. In contrast to electrostatic stabilization, stabilization with polymers is insensitive to the addition of electrolytes (salts).

As a rule, the addition of suitable polymers is the only way to stabilize dispersions in organic solvents. The polymers (oligomeric dispersing agents or paint resins) must be adsorbed on the surface of the dispersed particles; i.e., the polymers must displace adsorbed solvent and/or surfactant molecules (competition).

As pigment particles approach each other, the polymer segments become restricted in their mobility and this causes a loss of freedom of movement and a decrease in entropy; the outcome is a repulsive force (Figure I-2.7). For this reason, steric stabilization is also referred to as entropic repulsion or deflocculation.

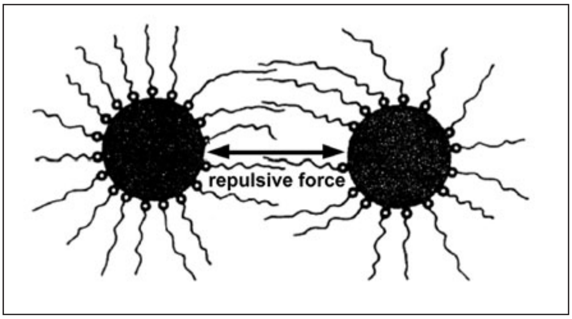


Figure I-2.7: Steric stabilization (simplified diagram; <u>not</u> to scale)

Studies [7, 8] have shown that, for steric stabilization of dispersed particles of up to 10 µm (10,000 nm) in diameter, a steric barrier of just 10 nm is sufficient (Figure I-2.8); the figure is also quoted to 5 to 20 nm.

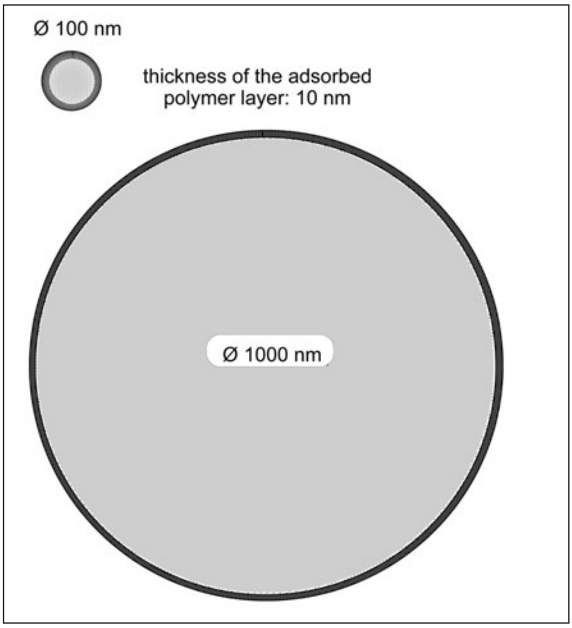


Figure I-2.8: Size relationships required for steric stabilization; the black rim around the particles shows the 10-nm-thick steric barrier (diagram roughly to scale)

The diagram in Figure I-2.7 suggests that surfactants (wetting agents) may be also able to act as steric stabilizers (especially if it is not realized that Figure I-2.7 is not to scale). Low-molecular surfactants (wetting agents) do <u>not</u> act as steric stabilizers since these mole-cules are much too small (see Chapter I-2.3.2). Only oligomers or polymers have the necessary molecular size.

Requirements for steric stabilization

a) The polymers must be strongly adsorbed on the pigment surface by appropriate functional groups (anchoring groups).
b) The polymers must have sufficiently long macromolecular chains which dissolve in the dispersion medium (organic solvents or water), a pro-

cess that leads to extension of the polymer chains (barrier groups). The addition of poor solvents can cause these polymer chains to coil and that may lead to flocculation (see Dispersing agents in Chapter I-2.3.1). The molecular masses of these solvated polymer chains should be 1,000 to 15,000.

c) Polymers (oligomers) of medium molecular mass are optimal:

- If the molecular mass is too low, the chain is not long enough.
- If the molecular mass is too high, bridging flocculation may occur (see Dispersing agents in Chapter I-2.3.1). Moreover, if the molecular mass is too high, incompatibility may occur or the viscosity may increase.

d) A minimum polymer concentration is necessary; if the concentration is too low, flocculation may occur, especially in the case of high molar masses (see c).

2.3 Wetting and dispersing agents

Wetting and dispersing agents are paint additives. Generally additives are added to paint formulations in small amounts to improve the properties of the solid coating or the application of the liquid paint.

Unfortunately, manufacturers offer hardly any information about their chemical composition and so an explanation of their effectiveness is complicated. They often employ the terms wetting agents and dispersing agents together because there is no definite distinction between them.

In this book, we distinguish them by molar mass:

- Wetting agents (surfactants) are low-molecular amphiphilic substances.
- Dispersing agents are oligomers or polymers which stabilize dispersions of pigments and fillers against flocculation.

The following chapter on stabilization of dispersions deals with dispersing agents first.

2.3.1 Dispersing agents

Polyanionic dispersing agents for electrostatic stabilization

Polyanions serving as dispersing agents or dispersing additives are adsorbed primarily on inorganic pigment and filler surfaces, which they charge by means of their own electric charges.

Such polyanionic dispersing agents should increase the repulsive potential and, therefore, improve electrostatic stabilization; they achieve this by:

- Increase in like charges
- Charge reversal of oppositely charged pigments (prevention of coflocculation)
- Complexation of multivalent cations (e.g. Ca^{2+}; thereby increasing the sphere of action of electrostatic forces)

Examples of polyanionic dispersing agents:

a) Polycarboxylates (mostly salts of polyacrylic acids; Figure I-2.9)

Figure I-2.10 is a schematic diagram of the adsorption of a polyacrylic acid salt on zinc oxide (IEP pH 9).

Advantages of polycarboxylates:

- Hydrolytic resistance
- Similarity to paint resins (compatibility, film quality).

Disadvantages of polycarboxylates:

- Higher cost (in comparison to polyphosphates)
- Sensitivity to multivalent cations
- Relatively high addition level.

b) Polyphosphates

- Linear polyphosphates: $Na_{n+2}P_nO_{3n+1}$ (“Calgon”)
- n = 2: pyrophosphate $Na_4P_2O_7$
- n = 4: tetraphosphate $Na_6P_4O_{13}$
- Cyclic metaphosphates: $(NaPO_3)_n$
- Charge and, therefore, dispersing efficiency increases with increase in n.

Advantages of polyphosphates:

+ Lower cost (in comparison to polycarboxylates)
+ Complexation of multivalent cations (e.g. Ca^{2+})
+ Relatively low addition level (0.2 to 0.5 wt.%)

Disadvantages of polyphosphates:

- Slow hydrolysis to (mono-)phosphate
- Soluble phosphate salts may lead to dilution and crystallization on the coating

In latex paints, a combination of polyacrylate and polyphosphate is often used.

Polymeric dispersing agents for steric stabilization

From Chapter I-2.2.2 “Steric stabilization”, it follows that block and graft copolymers (Figure I-2.11) are better suited to stabilization than random copolymers or homopolymers.

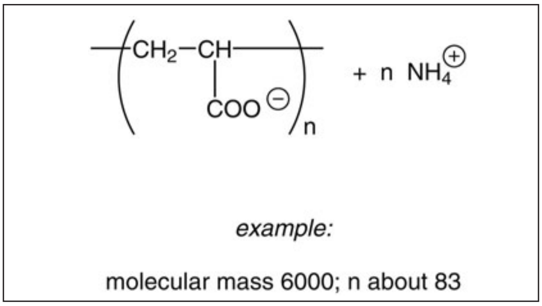


Figure I-2.9: Salt of a polyacrylic acid as dispersing agent for water-borne paints

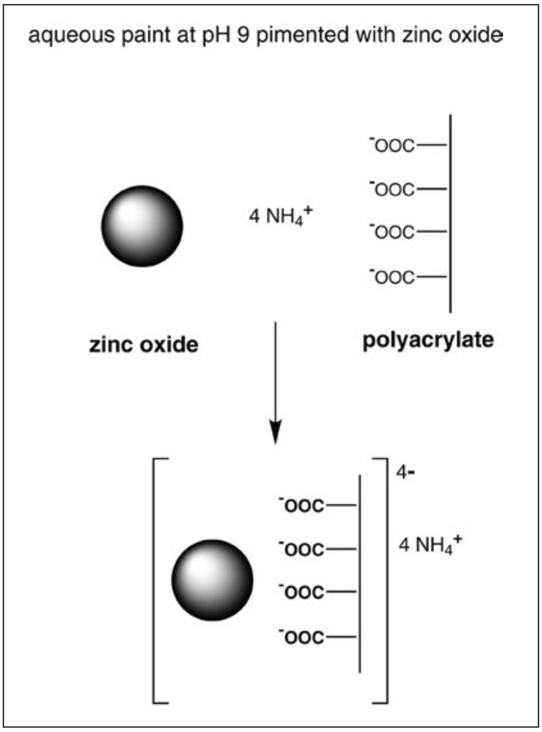


Figure I-2.10: Charging of zinc oxide pigment by a polyacrylic acid salt (simplified diagram, not to scale)

If there is a significant difference in polarity between blocks A and B (Figure I-2.11), AB block copolymers may have amphiphilic properties (see Polymeric surfactants); in such cases, the term “wetting and dispersing agent” often used by the manufacturers is correct.

A concrete description of the chemical composition of polymeric dispersing agents is rarely found in the literature.

Steric stabilization of titanium dioxide dispersions in methyl ethyl ketone by AB block copolymers of 2-vinylpyridine and methacrylic acid methyl ester (Figure I-2.12) is described in ref. [9]. Even a 2-vinylpyridine content of just 18 mol% in the block copolymer is sufficient to effectively stabilize titanium dioxide dispersions (rutile) against flocculation. The degree of polymerization of 2-vinylpyridine in the block copolymer containing 18 mol% of 2-vinylpyridine computes to $n \approx 27$ while the corresponding figure for methacrylic acid methyl ester is $m \approx 122$ (Figure I-2.12).

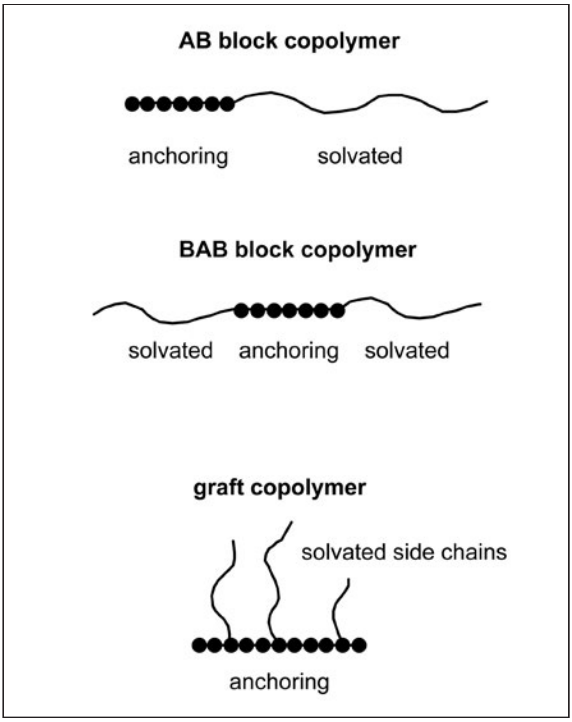


Figure I-2.11: Block and graft copolymers as dispersing agents (multiblock copolymers or branched copolymers could also be used)

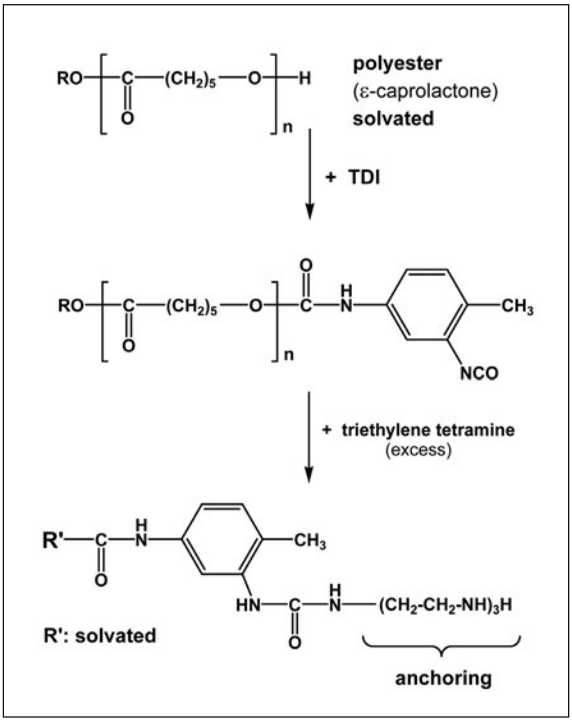


Figure I-2.13: AB block copolymer as dispersing agent

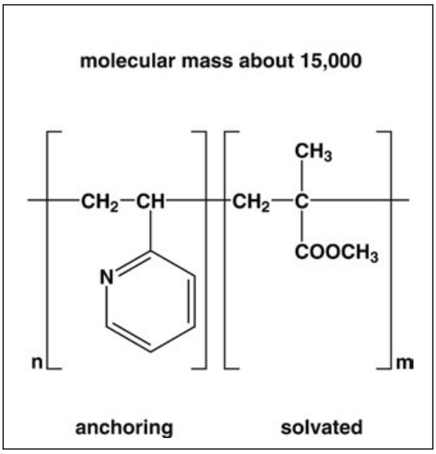


Figure I-2.12: AB block copolymer as dispersing agent for titanium dioxide in an organic solvent

A second example of a polymeric dispersing agent employed for steric stabilization is shown in Figure I-2.13. Polyurethane chemistry can be used to build up these AB block copolymers in steps.

The nitrogen atoms in both AB block copolymers (Figures I-2.12 and I-2.13) are Lewis bases capable of interacting with metal ions (Lewis acids). They act as anchoring groups, especially for inorganic pigments and fillers.

Dilution of sterically stabilized pigment dispersions with unsuitable solvents may cause coiling of the solvated polymer chains of the dispersing agent and, therefore, flocculation (Figure I-2.14).

Especially when the polymer concentration is too low and the molecular mass are very high, bridging flocculation may occur (Figure I-2.15a). The use of certain dispersing agents to effect deliberate but reversible bridging flocculation is called controlled flocculation (see below and Figure I-2.15b).

At this stage, a short discussion about the properties of mixtures of different pigments is needed. Since paints generally contain more than one pigment, the various pigments may separate on

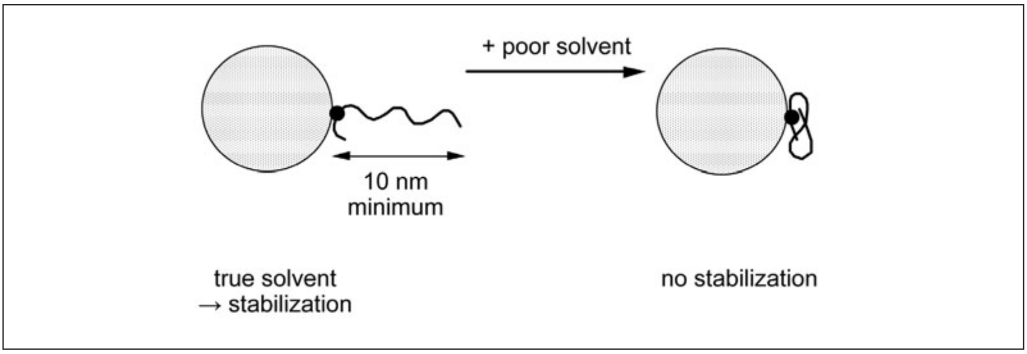


Figure I-2.14: Effect of solvents on steric stabilization (diagram not to scale)

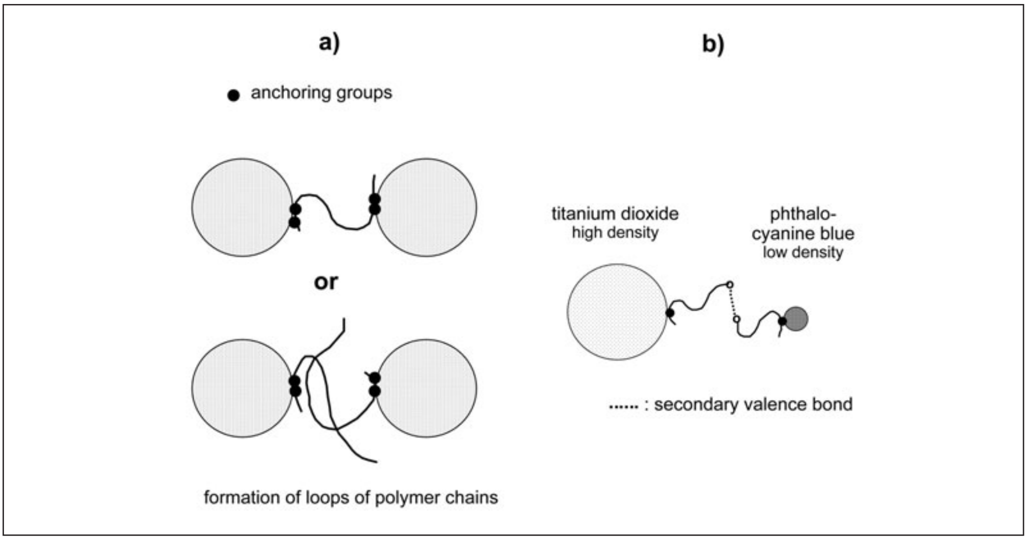


Figure I-2.15: Bridging flocculation (diagrams not to scale).
a) Principle behind bridging flocculation, b) Controlled flocculation

account of their different mobilities (due to different sizes and/or densities). This separation occurs when different pigments in the fresh and still flowable paint film are no longer distributed uniformly. There are two different types of pigment separation:

- Vertical pigment separation (floating): Local differences in concentration on the paint surface is called vertical pigment separation, and often leads to Bénard cells (Figure I-2.16) or to streaking. The surface of the coating has no uniform colour, but instead looks speckled or streaky.
- Horizontal pigment separation (flooding): If the differences in concentration occur not on the paint surface but perpendicularly to it, this is called horizontal pigment separation. In this case, the coating has a uniform colour. This paint defect only becomes apparent when, e.g., the rub-out test is carried out or a refinishing paint is applied.
- Both types of pigment separation may be prevented or reduced by controlled flocculation or – better – controlled coflocculation (Figure I-2.15b).

Advantages of controlled flocculation

- No separation of pigments of different density

→ Little or no pigment separation
→ Little or no occurrence of Bénard cells or streaking.

- Rheological action: Increase in non-Newtonian flow (reversible three-dimensional network)
  → Improved application properties (e.g. less sagging)
  → Less settling of pigments.
- No direct contact between the pigments in the flocs
  → Easily redispersible (mostly by stirring)
  → "Soft" sediment.

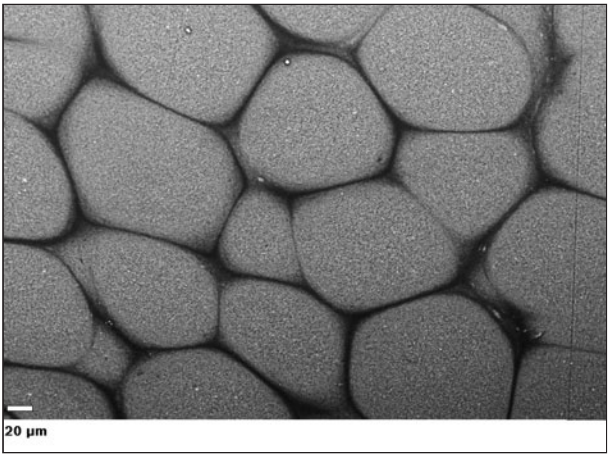


Figure I-2.16: Bénard cells (scanning electron micrograph of a coating with titanium dioxide and pigment red 3 [16])

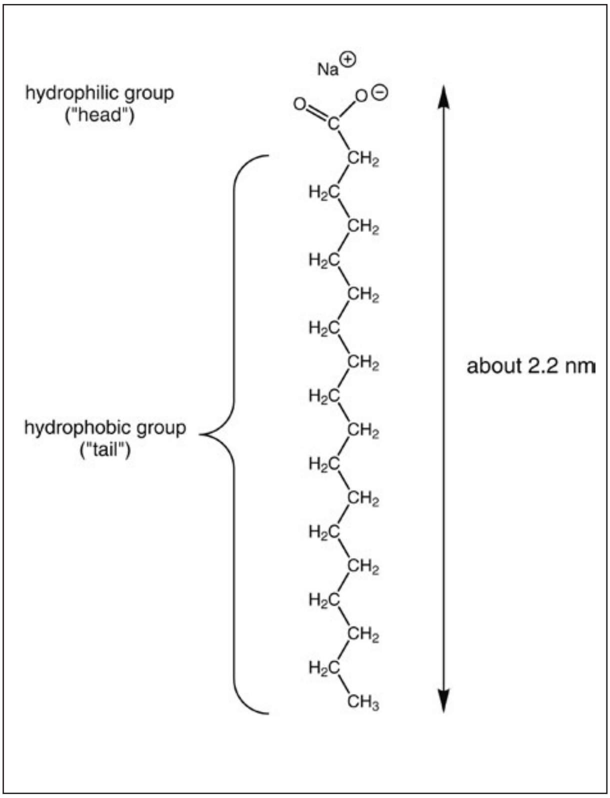


Figure I-2.17: Sodium stearate

Finally, it should be stated that paint resins (oligomers) are able to stabilize pigment dispersion sterically in many cases.

2.3.2 Wetting agents (surfactants)

This chapter covers the "classic" low-molecular wetting agents. Wetting agents are also called surfactants, surface-active or amphiphilic compounds and are substances which decrease surface or interfacial tension at phase boundaries. They therefore improve wetting (see Chapter I-1.5.1). The terms wetting agent and surfactant are used synonymously in this book.

The first wetting agents to be employed were salts of fatty acids (soaps); a typical example is sodium stearate (salt of stearic acid, Figure I-2.17). Sodium stearate has a hydrophilic group (carboxylate group) and a hydrophobic group (long-chain alkyl group). Each molecule therefore has hydrophilic as well as hydrophobic properties ("head-tail structure") and is said to be amphiphilic.

The maximum length of the stearic acid molecule is about 2.2 nm (Figure I-2.17). Sodium stearate is therefore unable to stabilize pigment dispersions sterically because that would require a chain length of at least 5 nm (Chapter I-2.2.2) [7, 8, 15].

Wetting agents align themselves at phase boundaries, where they lower the interfacial tension and improve wetting. Figure I-2.18 shows the self-alignment of wetting agents at the water-air phase boundary. The hydrophilic groups align themselves with the water, and the hydrophobic groups, with the air. The water surface now no longer consists of water molecules (high surface tension) but of hydrocarbon chains of lower surface tension.

Usually, wetting agents are classified according to the charge on the hydrophilic group. There are anionic, cationic, amphoteric and nonionic types (Figure I-2.19).

Wetting agents can then be further classified on the basis of the chemical composition of the hydrophobic group, namely as hydrocarbon, silicone and fluorinated surfactants. The greater the hydrophobicity of the "tail", the more the surface tension of water decreases when wetting agents are added to it; i.e., the more efficient the wetting agent becomes (Table I-2.7). A typical hydrocarbon surfactant is the sodium stearate already mentioned (Figure I-2.17). Examples of silicone and fluorinated surfactants are presented in Figure I-2.20.

The influence of the hydrophilic group on surfactant activity (surface tension) of nonylphenol ethoxylates (Figure I-2.21) is shown in Table I-2.8. The longer the hydrophilic polyether chain, the more hydrophilic these nonionic surfactants become. At the same time, the surface tension of the aqueous surfactant solution increases. In other words, as the "head" becomes more hydrophilic, the less efficient the surfactant becomes.

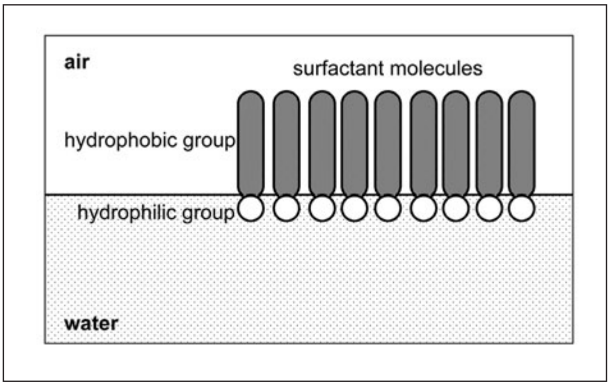


Figure I-2.18: Self-alignment of wetting agents at the water/air phase boundary

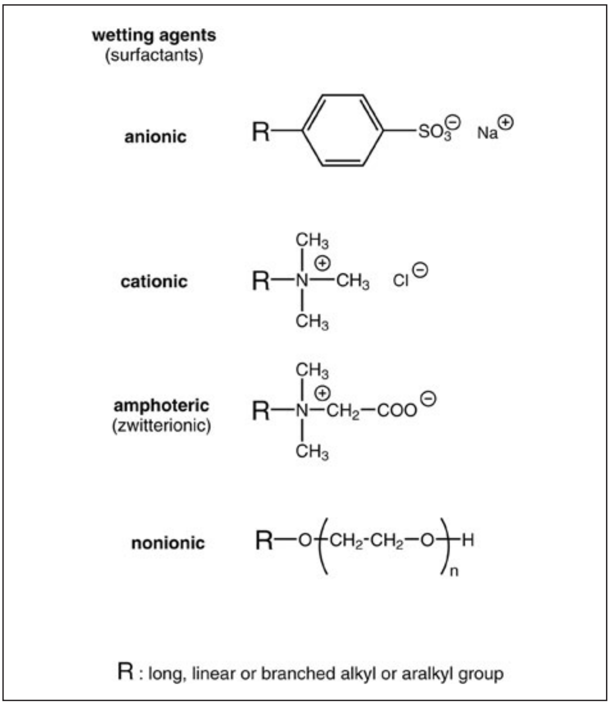


Figure I-2.19: Classification of wetting agents according to the charge on the hydrophilic group

Table I-2.7: Influence of the hydrophobic group on surface activity in water (surface tension)

	surface tension [mN/m]
water	73
+ hydrocarbon surfactants	40 to 25
+ silicone surfactants	30 to 20
+ fluorinated surfactants	25 to 15

Table I-2.8 shows the influence exerted by the surfactant concentration. As expected, increasing the concentration causes the surface tension of the aqueous solution to decrease;

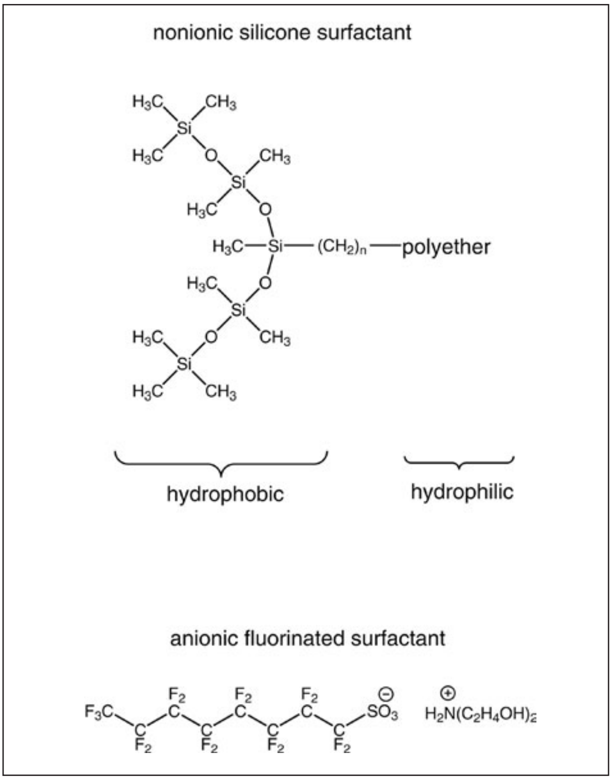


Figure I-2.20: Examples of silicone and fluorinated surfactants

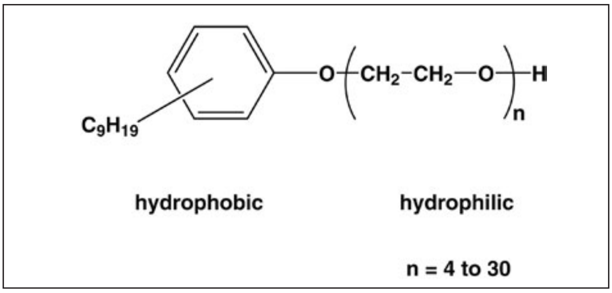


Figure I-2.21: Nonylphenol ethoxylates (nonionic hydrocarbon surfactants)

Table I-2.8: Influence of the hydrophilic group on surface activity (surface tension) for different nonylphenol ethoxylates (see Figure I-2.21)

	surface tension [mN/m]		
water	73		
+ surfactant	0.01 g/l	0.1 g/l	1 g/l
n = 6	38	30	29
n = 10	45	31	30
n = 30	54	40	36

It should be noted, that recently nonylphenol ethoxylates showed disadvantages with respect to toxicity

i.e., the effectiveness of the added surfactant increases. But Table I-2.8 also shows clearly that 0.1 g/l is the optimal level of surfactant addition; increasing it further up to 1 g/l does not help much more.

Secondary effects

Wetting agents (like all paint additives) have an optimal addition level which should not be exceeded because wetting agents (again, like all paint additives) can have unwanted side-reactions. For example, wetting agents increase the hydrophilicity of coatings. An additional unwanted side-reaction of surface-active compounds, such as wetting agents, is foaming in water, with the foam lamellas (which have large surface areas) being stabilized by the wetting agent. One remedy to this is to add a defoamer.

To sum up so far, the more hydrophobic the “tail” and the less hydrophilic the “head”, the more effective is the wetting agent. However, solubility acts as a limiting condition in water. If the “head” is not hydrophilic enough, the surfactant will not dissolve. For example, in the case of the nonylphenol ethoxylates (Figure I-2.21), the surfactant having n = 4 is not completely soluble in water.

Orientation at phase boundaries

Wetting agents align themselves at phase boundaries and are able to alter the polarity (and the wettability) of solid surfaces. For example, a cationic surfactant is able to hydrophobize a hydrophilic, negatively charged metal oxide surface (pigment or filler; Figure I-2.22).

In water-borne paints, wetting of hydrophobic organic pigments may be improved by appropriate surfactants (Figure I-2.23), but surfactants are also often employed in solvent-borne paints. Furthermore, Figure I-2.23 shows that adsorption of an anionic surfactant causes the surface of an organic pigment to become negatively charged, and that leads to electrostatic stabilization of the pigment. Pigment wetting is a requirement for successful pigment dispersion (see Chapter I-2.3). Paint properties, such as gloss and tinting strength, can be improved by wetting agents and, as a result, the time necessary for dispersing can be reduced.

In 2003 12 million tons of surfactants were produced world wide; 2.7% (324,000 tons) thereof was used for paints and coatings.

Examples of wetting agents that are important in coatings technology

Three important wetting agents for paints are described in detail below. The first one is the amphoteric (zwitterionic) lecithin, a renewable non-toxic raw material

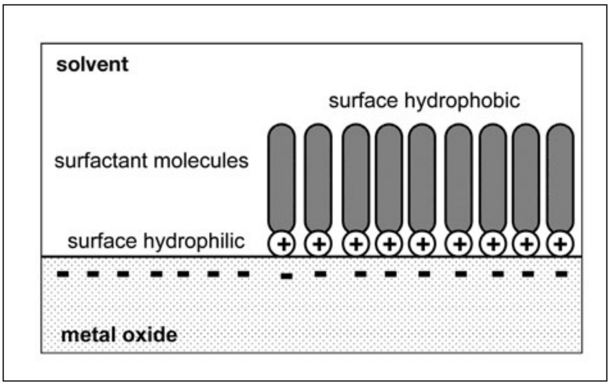


Figure I-2.22: Adsorption of a cationic surfactant on a negatively charged metal oxide surface (highly simplified; not to scale)

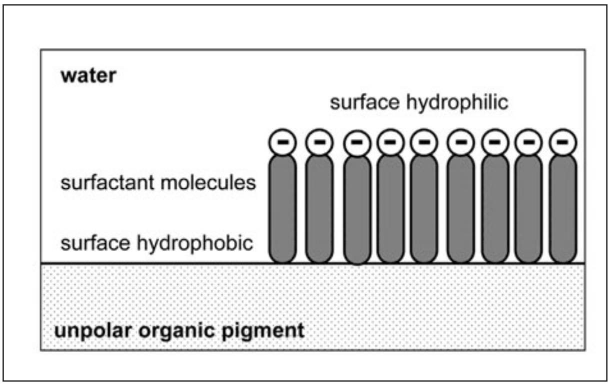


Figure I-2.23: Adsorption of an anionic surfactant on a nonpolar organic pigment surface (highly simplified, not to scale)

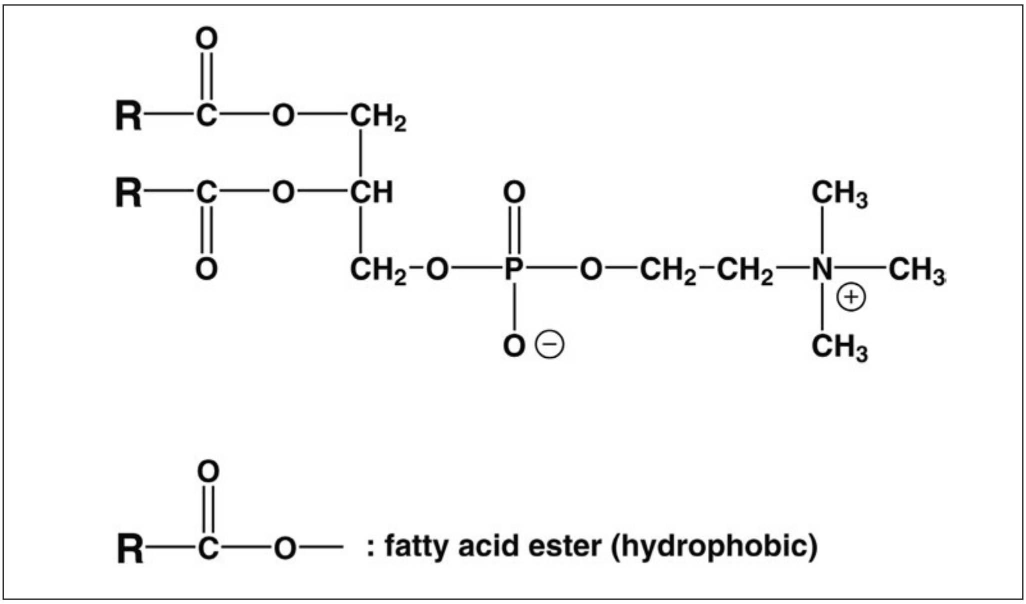


Figure I-2.24: Lecithin as an amphoteric surfactant

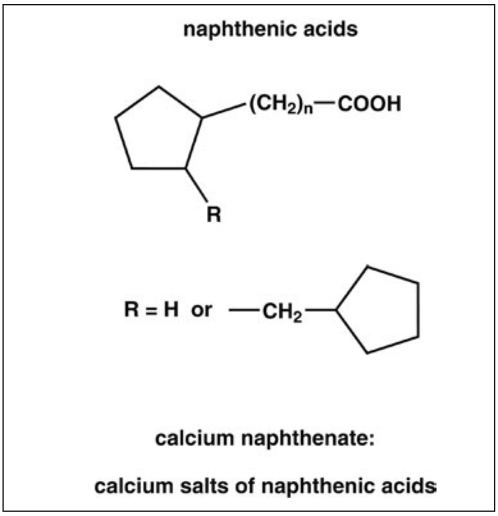


Figure I-2.25: Naphthenates

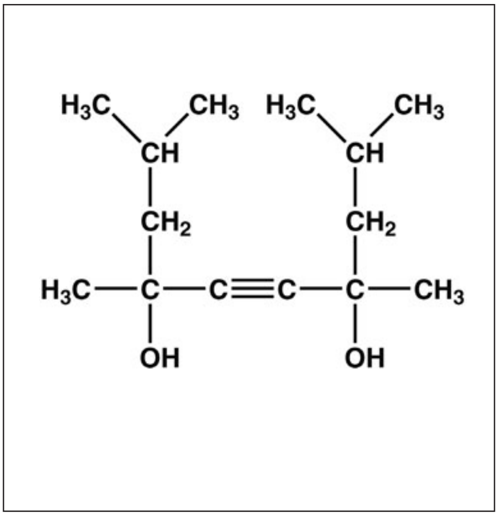


Figure I-2.26: Nonionic surfactant based on butynediol

shown in Figure I-2.24. Note that there are two hydrophobic groups. Lecithin is produced from soybean oil (soybean lecithin) and is chiefly used in solvent-borne paints. Soybean fatty acids occur as a natural mixture (C16:0 10%, C18:0 4%, C18:1 21%, C18:2 56%, C18:3 8% and others, variable). Such mixtures are used often as raw materials for paints because they have little tendency to crystallize.

Naphthenates (e.g. calcium salts of naphthenic acids) are an industrial mixture of substances obtained from mineral oil and are added to solvent-borne paints as wetting agents and driers (see Chapter II-1.2.3; Figure I-2.25). Additives often have dual functions and users should be aware of this.

Nonionic surfactants based on butynediol (Figure I-2.26) are recommended as low-foaming wetting agents for water-borne paints. Moreover, it is claimed that they improve levelling (dual function). The two hydrophobic groups have relatively short chains; the hydrophilic group (butynediol group) has a strong affinity for pigment surfaces.

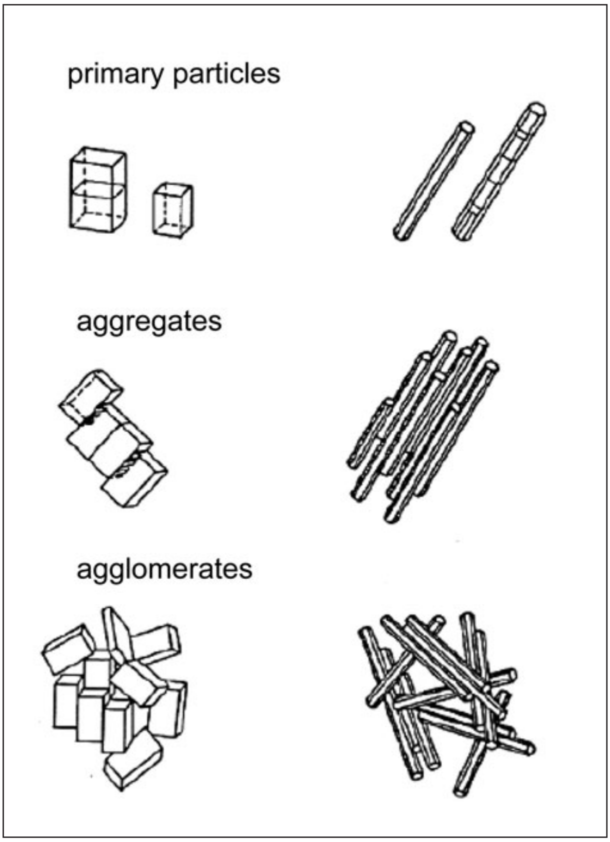


Figure I-2.27: Simplified diagram of primary particles, aggregates and agglomerates

2.4 Wetting of pigments

Aside from the wetting of pigments, this chapter will briefly describe the dispersion process. Industrial dispersion equipment (e.g. the various types of mill) is not discussed in this chapter because very good descriptions are to be found in the literature [10, 11]. Sample mill-base formulations will be presented in parts II to IV of this book.

Dispersion of powdery pigments or fillers (extenders) in liquid media is the most important step in paint manufacturing. Before we discuss it, we need some definitions of pigment particles (Figure I-2.27) [15]. **Primary particles** are single (or double) crystals and are the smallest particles obtained during pigment synthesis. **Aggregates** are rigid clusters of primary particles joined by crystal faces; dispersion does not cause aggregates to separate into primary particles. **Agglomerates** are clusters of primary particles or aggregates that are loosely joined by crystal edges (Figure I-2.27).

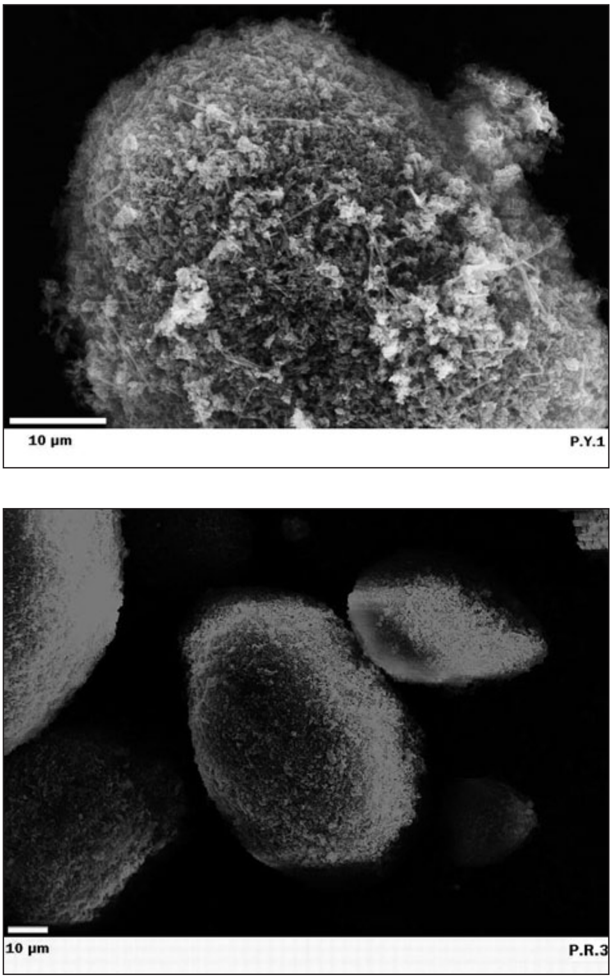


Figure I-2.28: Scanning electron micrographs of agglomerates of pigment yellow 1 and pigment red 3

Figure I-2.28 shows scanning electron micrographs of agglomerates of organic pigments [16].

Dispersion process

The goal of dispersion is to divide agglomerates into primary particles and aggregates. In practice, large agglomerates usually end up being divided into smaller agglomerates.

There are three steps in the dispersion process:

- **Wetting** of pigment agglomerates
- **Mechanical size-reduction** of pigment agglomerates (industrial dispersion equipment see [10, 11])
- **Stabilization** of the dispersion against flocculation (see Chapter I-2.2)

Wetting

There are two steps in the wetting of pigment agglomerates by the liquid phase. The first is wetting of the surfaces of pigment agglomerates and the second is penetration of the liquid phase into the pores or cavities of the agglomerates (to displace the air there).

The thermodynamic requirement for wetting is a contact angle $\Theta < 90°$ (optimal $\Theta = 0°$, i.e., spreading). Thermodynamics say nothing about the time needed for wetting. But, in practice, this time is very important. The height to which liquids rise in capillary tubes as a function of time has been approximated by Washburn [12]:

$$h = \sqrt{\frac{t \cdot r_P \cdot \gamma_L \cdot \cos\Theta}{2\eta}}$$ *Equation I-2.1*

t	Time
γ_L	Surface tension of the liquid phase
Θ	Contact angle (of the liquid phase on the pigment surface)
r_p	Radius of the pores (of the pigment agglomerates)
η	Dynamic viscosity of the liquid phase

The relationship between the height rise h and time t describes a parabola (Equation I-2.1); i.e., the height rise slows down as more and more time elapses. Other books (e.g. [13]) present a different form of the Washburn equation (based on volume), but the conclusions are the same.

Conclusions from the Washburn equation (Equation I-2.1):

1. The wetting rate increases with increase in radius of the capillary pores; i.e., coarse pigments are wetted much faster than fine pigments.
2. The lower the viscosity of the liquid phase (e.g. solution of paint resin), the faster is the wetting. It should be noted that viscosity decreases with increase in temperature.
3. The longer the pores (i.e., the larger the agglomerates), the more slowly wetting occurs.
4. The higher the surface tension γ_L of the liquid phase and the smaller the contact angle Θ, the more rapidly wetting occurs.

Ad 2.) This fact is corroborated by the empirical Daniel's rule: "Disperse in poor solvents and let down with good solvents". Since the resin oligomers are more coiled in poor solvents, resin solutions have a lower viscosity (and that improves wetting).

Radius r_p and length h of the pores vary with the type of pigment employed. The viscosity of the liquid phase can be lowered only to the limits of the dispersion equipment employed [10, 11]. Thus, there are only two variables of the dispersion process remaining, namely the surface tension of the liquid phase γ_L and the contact angle Θ; both variables can be influenced by wetting agents.

Wetting agents (and some dispersing agents) lower the surface tension of the liquid phase γ_L but this (negative) effect is compensated by the reduction in the contact angle Θ. This is because, as may be seen in Equation I-2.1, the contact angle is $\cos\Theta$ and a $\Theta > 90°$ produces a negative wetting rate (i.e., no wetting at all).

Equation I-2.2 describes the maximum height rise $h_{max.}$ of liquids in cylindrical capillary tubes. Equation I-2.2 can serve as an approximate description of the wetting of pigment and filler agglomerates [14]. When $h_{max.}$ is reached, capillary force and gravity are in equilibrium (Equation I-2.2).

$$h_{max.} = \frac{2 \cdot \gamma_L \cdot \cos\Theta}{\rho \cdot r_P \cdot g}$$ *Equation I-2.2*

ρ	Density of the liquid phase
g	Gravitational acceleration

The dependence of the maximum height rise $h_{max.}$ on the contact angle Θ and surface tension γ_L (and hence on the influence of wetting agents) is analogous to the Washburn equation (Eq. I-2.1). But the dependence of maximum height rise $h_{max.}$ on the radius r_p is the opposite of the Washburn equation (Eq. I-2.1). The smaller the radius (of the capillary tubes), the greater is the height rise, i.e., the further the liquid phase penetrates into the inner cavities of the pigment agglomerates. In fine pigments (r_p small), penetration by the liquid phase should be greater than it is in coarse pigments (r_p larger; Eq. I-2.2).

But Equation I-2.2 ($h_{max.}$) fails to say anything about the time or rate; only Washburn describes the time dependence (Equation I-2.1).

It may be concluded from Equations I-2.1 and I-2.2 that the liquid phase penetrates further but more slowly in agglomerates of fine pigments. In contrast, it penetrates less, but more rapidly in agglomerates of coarse pigments. Wetting agents influence this penetration positively by lowering the contact angle Θ.

In practice, full penetration of the resin solution into the cavities of pigment agglomerates is facilitated by allowing the mill base to stand over night.

2.5 References

[1] Wo. Ostwald, Die Welt der vernachlässigten Dimensionen, 12. ed., Verlag Th. Steinkopff 1944
[2] Booklet “Colloids” (Topics in Chemistry), BASF AG 1995
[3] D. H. Everett, Basic Principles of Colloid Science, RSC Paperbacks 1988
[4] Technical information about iron oxide red pigments, Bayer AG
[5] K. Köhler, C. W. Schläpfer, Chemie in unserer Zeit, 27 (1993) No. 5, p. 248-255
[6] M. Knospe, W. Scholz, Farbe & Lack 96 (1990) p. 120 ff
[7] R Jérôme, Farbe & Lack 98 (1992) p. 325-329
[8] A. Bouvy, Europ. Coat. Journ. 11/1996, p. 822-826
[9] J. M. Reck, L. Dulog, Farbe & Lack 99 (1993) p. 95 ff
[10] Th. Brock, M. Groteklaes, P. Mischke, European Coatings Handbook, Vincentz Network 2000
[11] Lehrbuch der Lacke und Beschichtungen - Volume 8: Herstellung von Lacken und Beschichtungsstoffen, Arbeitssicherheit, Umweltschutz, 2nd ed., editors H. W. Ritter, W. Zöllner, S. Hirzel Verlag 2004
[12] U. Demlehner, Farbe & Lack 95 (1989) No. 10, p. 708-714
[13] J. M. Oyarzún, Pigment-Processing – Physico-chemical Principles, Vincentz Network 2000
[14] B. Müller, Farbe & Lack 105 (1999) No. 1, p. 102-107
[15] B. Müller, Understanding Additives, Vincentz Network 2010, Chapter 1
[16] S. Ljesic, Diploma Thesis, University of Applied Sciences Esslingen 2005

3 Paint formulation

Any coating material to be developed has to meet specific requirements, i.e., it must fulfil the demands of the customer (properties of the coating, substrate, application), the environment and so on. The skilled paint chemist has to accommodate all these different demands, choose the appropriate raw materials from the vast number available and, finally, develop a paint formulation. This is mostly done in paint laboratories.

One objective of this textbook is to prepare students for working in industry. Therefore, it is vital to understand the workflows that occur in an industrial paint laboratory [1]. Figure I-3.1 tries to show these workflows in simplified form. All paint development starts with the statement of the problem. The paint formulation is then devised, and a sample is made in the lab. The sample is applied to the substrate concerned and the coating is dried or cured. This coating then has to be tested.

The test results have to be compared against the specifications of the problem. Usually, they are not perfect. So, in practice, the paint formulation has to be optimized. Therefore, the cycle shown in Figure I-3.1 has to be repeated many times. The optimization steps become smaller from cycle to cycle. The "input" into this cycle of paint development is the statement of the problem while the "output" is the optimized paint formulation [1].

A calculation recipe contains all the information about the components of the paint; it is formulated to yield 100 parts by weight. The calculation recipe usually lists the raw materials in the following order: binders, pigments and fillers, additives, solvents. A production recipe is formulated for each quantity, along with additional information about the production process. The production recipe lists the raw materials in the order in which they are added. It is common industrial practice to provide additional information about the properties of the paint or coating, the test methods and permissible variations.

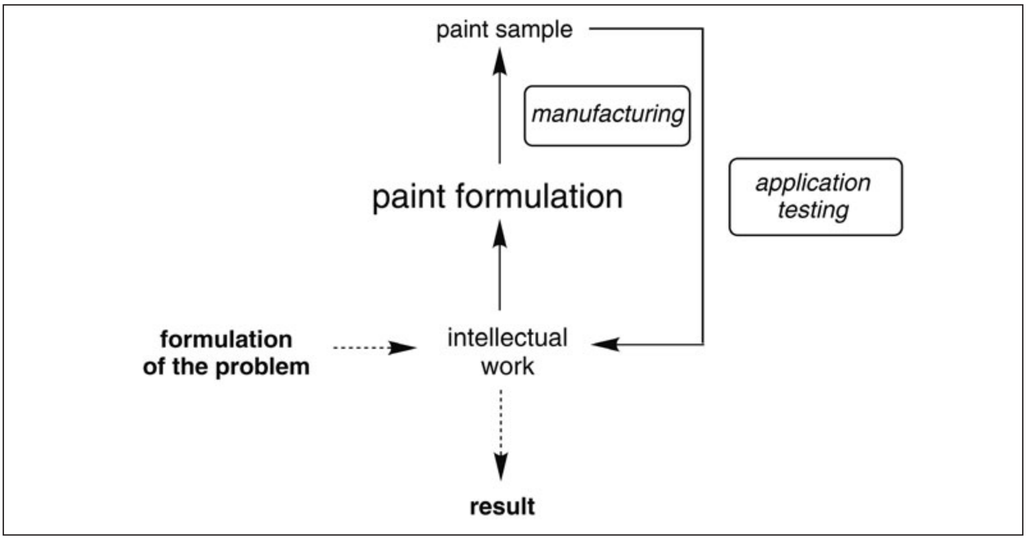


Figure I-3.1: Cycle of paint development

When the paint is being formulated, allowance is made for some fundamental physical parameters that greatly influence the technological properties of a coating:

- Pigment/binder ratio and pigment volume concentration
- Particle size and packing of pigments or fillers

Of course, the types of binders and pigments or fillers (chemical composition) are also very important. Finally, the physicochemical interactions of the binders with the surfaces of pigments and fillers (i.e., the quality of the “composite” coating) are important.

3.1 Ratio of binder to solid particles

3.1.1 Pigment/binder ratio and pigment volume concentration

Only the non-volatile content (solids) of a paint remains after the coating has solidified. Important formulation parameters, such as pigment/binder ratio (P/B), pigment volume concentration (PVC 1) and the ratio of binders, always refer to the non-volatile content (solids).

The pigment/binder ratio is the weight ratio of the sum of the pigments and fillers to the binder (solids): P/B.

The pigment volume concentration (PVC) is the ratio of the pigment volume to the total volume of the solid coating [vol.%]. The pigment volume is the sum of the pigment and filler volumes.

$$\mathrm{PVC} = \frac{V_P + V_F}{V_P + V_F + V_B} \cdot 100\%$$

V_P: Volume of the pigments
V_F: Volume of the fillers (extenders)
V_B: Volumes of the dried film of all binders (sum of film-forming agents, resins, plasticizers and additional resins)

The volumes (V) are calculated as the quotient of mass (m) and density (ρ):

$$V = \frac{m}{\rho}$$

The densities of pigments and fillers are listed in the manufacturers’ data sheets. Average densities of dried films of several binders are shown in Table I-3.1 [2]. These average densities of dried films are sufficiently accurate to allow an approximate calculation of the PVC.

It should be noted that most commercial paint resins (binders) are supplied already dissolved in solvents; therefore, the densities listed in the resin data sheets mostly refer to the resin solution and not to the density of the dried or cured film.

Table I-3.1: Average densities of dried binder films

binder (paint resin)	**average density [g/cm³]**
styrene-acrylates	1.1
SP, AK, EP, CAB, PF, AY, PUR, PVAC, CN	1.2
UF, MF	1.5
RUC	1.6

For example, glossy topcoats have PVCs of 10 to 20%. Matt coatings of latex paints have PVCs of 40 to 85%. Transparent varnishes may have PVCs below 10%.

---

1) Do not confuse with polyvinyl chloride

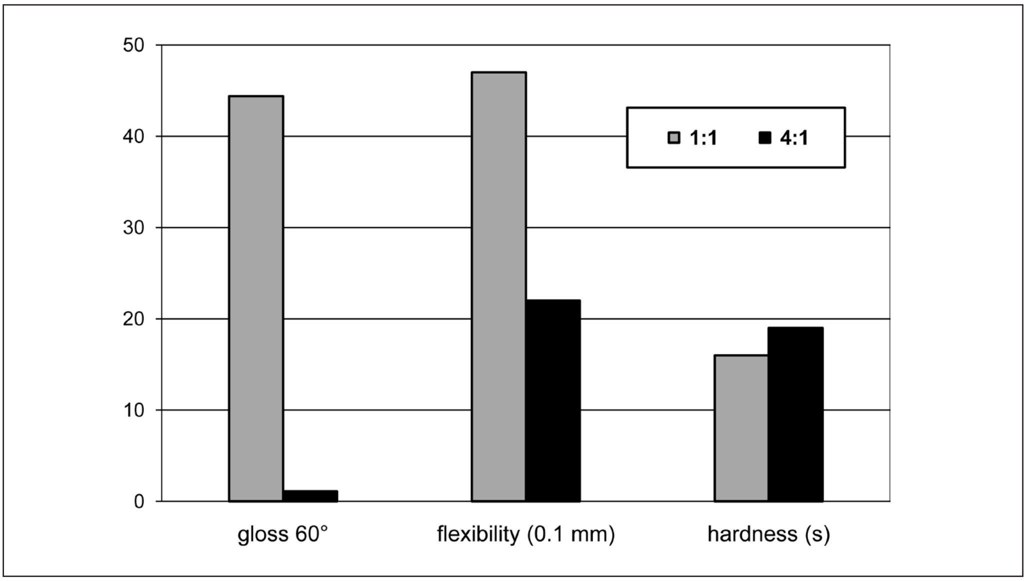


Figure I-3.2: Properties of oxidatively cured coatings as a function of pigment/binder ratio

Critical pigment volume concentration

The critical pigment volume concentration (CPVC [1]) is the PVC at which the binder concentration is just barely sufficient to completely wet pigments and fillers. Furthermore, the spaces between the particles are filled with binder. The pigments and fillers are very closely packed.

Table I-3.2: Simplified formulation for a stoving enamel

parts by weight	raw material	solids
51	SP, 60% solids	30.6
5.0	HMMM, about 100% solids	5.0
35.6	titanium dioxide rutile	35.6
8.4	solvents + additives*	–
100	sum	71.2

** for simplification, in this first example solvents and additives are not presented individually because this is not necessary for the following calculations.*
Examples for binders: “Vialkyd AN 950” (SP) and “Cymel 300” (HMMM = hexamethoxymethylmelamine)

Above the CPVC, the porosity of the coating increases rapidly. The position of the CPVC depends heavily on the particle size, the particle size distribution and the shape of the pigment and filler particles. Latex paints have a CPVC of about 60%.

The following example illustrates the influence of the PVC or pigment/binder ratio on the properties of a coating. Consider an oxidatively curing paint (long oil alkyd resin) with iron oxide red : barium sulphate (filler) = 1 : 1. The pigment/binder ratios are P/B = 1: 1 and 1 : 4. The PVCs compute to 21% and 51%. The properties of these two coatings are summarized in Figure I-3.2. As the pigment/binder ratio rises, the flexibility and, especially, the gloss decrease dramatically, whereas the hardness is barely affected at all.

The following sample calculation shows how the pigment/binder ratio and the PVC is used in practice (more calculations like this will be presented later in the book). A simplified formulation for a stoving enamel is listed in Table I-3.2. This kind of paint formulation with

---

[1] Do not confuse with polyvinyl chloride

a sum of 100 parts by weight is also called the calculation recipe. Usually, all numbers in paint formulations are specified to one decimal place. It is not usual to list parts by weight (solids) in starting formulations and so these have to be calculated.

Calculation of the pigment/binder ratio
(Sum) of pigments (+ fillers): 35.6
Sum of binders (solids): 30.6 + 5.0 = 35.6
→ Pigment/binder ratio P/B = 35.6 : 35.6 = 1 : 1

Calculation of the PVC (density of titanium dioxide rutile 4.1 g/cm^3; see Table I-3.1 for densities of the dried binder films)

$$\text{PVC} = \frac{35.6 / 4.1}{35.6 / 4.1 + 30.6 / 1.2 + 5 / 1.5} \cdot 100\% = 23\%$$

This PVC calculation is an approximation because the real density of the crosslinked binders has not been measured. But this simple type of calculation is sufficient for many applications.

3.1.2 Oil adsorption value

The oil adsorption value (OA) is determined with linseed oil (of specified quality, acid number about 2.8 mg KOH/g). The linseed oil is slowly worked with a spatula into a given amount of pigment on a glass plate. When just enough linseed oil has been added, a coherent pigment paste is formed; oil adsorption value: g linseed oil/100g pigment.

The oil adsorption value is not transferable to other binders (even when different densities are allowed for) since the specific wetting action of those binders needs to be taken into account. Empirically determined oil adsorption values can vary significantly (by up to 50%).

Table I-3.3 clearly shows that the oil adsorption value increases with increase in specific surface area (BET) – but not to the same extent.

Table I-3.3: Pigment and filler data

pigment for filler	**mean particle diameter [nm]**	**BET surface [m^2/g]**	**oil adsorption value [g linseed oil/100 g]**	**density (ρ_P) [g/cm^3]**	**CPVC (linseed oil) [vol.%]**
gas black	13	460	620	1.8	8
furnace black	95	20	280	1.8	16
phthalocyanine blue 1	50	72	50	1.6	54
phthalocyanine blue 2	100	36	45	1.6	56
precipitated calcium carbonate	80	20	40	2.8	45
grinded marble ($CaCO_3$)	2500	3.4	19	2.7	65
transparent iron oxide red	20	100	40	4.5	34
opaque iron oxide red	300	6	24	5.0	44

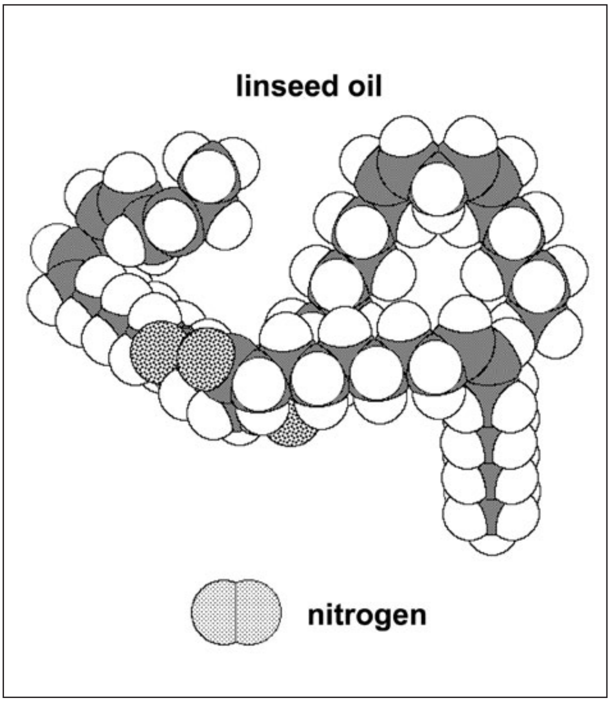


Figure I-3.3: Simplified diagram of the space-filling models of linseed oil (glycerol ester of oleic, linolic and linolenic acid) and nitrogen

Possible explanations are:

- The oil adsorption value characterizes not only the phase boundary between the pigments and the linseed oil but also the volume between the pigment particles at maximum packing density. Furthermore, there is a relationship between the oil adsorption value and the critical pigment volume concentration (CPVC; see below).
- Presumably, the linseed oil can only be adsorbed on a smaller part of the total surface area relative to nitrogen – especially in the case of fine pigments. Unlike the much larger linseed oil molecule, the small nitrogen molecule is believed to penetrate into very small pores of the pigment agglomerates; comparison of the sizes of both molecules makes this assumption plausible (Figure I-3.3).
- Adsorption of the linseed oil – in contrast to that of non-specific nitrogen adsorption – can also be influenced by the polarity (oleophilicity) of the pigment surface.

To sum up so far, the specific surface area (BET) of pigments and fillers is only an approximate value of the area of the phase boundaries in paints. For coatings technology, the oil adsorption value is more important because this value characterizes the binder demand of pigments and fillers.

The CPVC (for linseed oil) can be calculated from the oil adsorption value (OA; see Table I-3.3).

$$\text{CPVC} = 100 / (1 + \frac{\rho_P \cdot \text{OA}}{\rho_L \cdot 100})$$

ρ_P: Density of the pigment
ρ_L : Density of linseed oil (0.93 g/cm^3)

Sample calculation of the CPVC of opaque iron oxide red (ρ_P = 5.0 g/cm^3):

$$\text{CPVC} = 100 / (1 + \frac{5 \cdot 24}{0.93 \cdot 100}) = 43.7 \approx 44 \text{ [vol.-\%]}$$

Sometimes, it is assumed that the oil adsorption value characterizes only the free volume between the pigment particles (maximum packing density). If this is true, then the calculated CPVC could be transferred to other binders. However, this assumption is untenable as the specific interaction of different binders with the very large pigment surface areas is an important factor controlling paint and coating properties [3].

3.2 Influence of pigments on the properties of coatings

The influence of particle size of pigments on properties of coatings is discussed briefly below. Table I-3.4 shows that coarse pigments opacify (hide) whereas fine pigments are transparent. The smallest possible particle size is a single molecule; it forms a molecularly disperse solution and is thus a soluble dye (Figure I-3.4).

The particle sizes of pigments have other consequences, as shown in Figure I-3.4.

Light fastness is only a problem for organic pigments and dyes; inorganic pigments are unaffected by light (i.e. are photostable; Figure I-3.4). As soluble dyes are not photostable, they cannot used for exterior coatings.

Carbon blacks absorb radiation across the complete spectrum of visible light and, at higher levels of addition, exhibit adequate hiding power. Fine carbon blacks are transparent at low addition levels and can be used in transparent coatings. Moreover, carbon blacks are photostable, absorb ultraviolet light and, therefore, improve the weathering resistance of coatings. Thus, carbon blacks are exceptions among pigments.

Table I-3.4: Opaque and transparent pigment types

pigment type	mean primary particle diameter [nm]
phthalocyanine blue 1	
transparent	50
iron oxide red	
transparent	20
opaque	300
iron oxide yellow	
transparent	20
opaque	1500 · 100*
titanium dioxide (rutile)	
transparent	10 to 20
opaque	250 to 300

** needle-shaped*

Pigment particles of different size (polydisperse) have a greater packing density than particles of the same size (monodisperse). Figure I-3.5 shows that, in the case of polydisperse particle packing, the

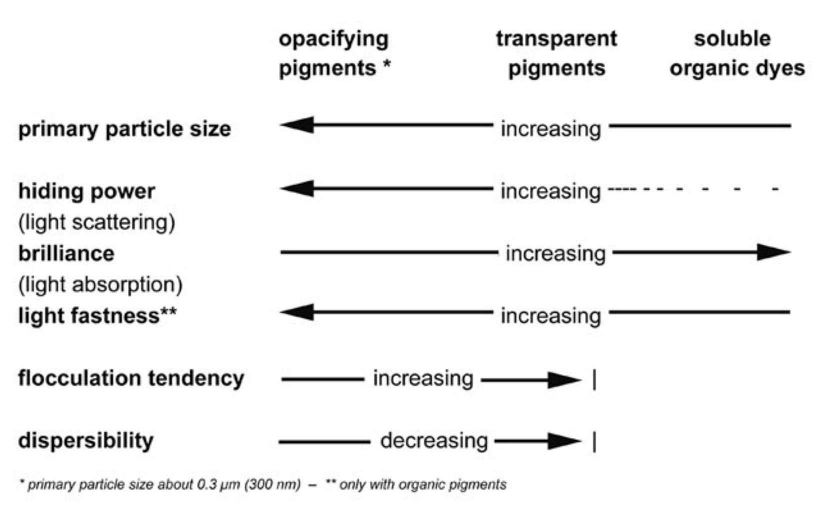


Figure I-3.4: Comparison of opacifying, transparent pigments and dyes

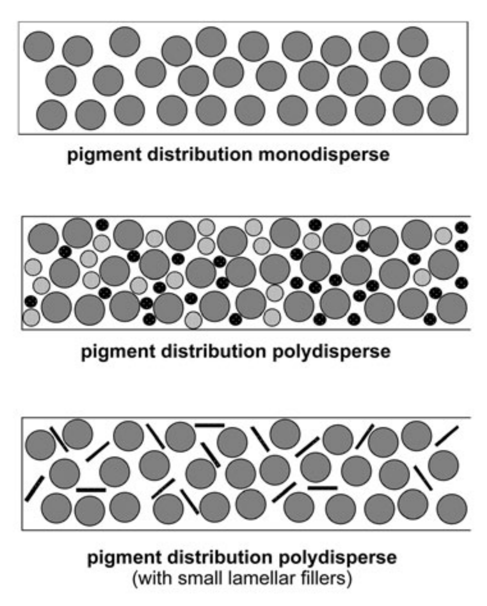


Figure I-3.5: Packing density of pigment and filler particles (not to scale)

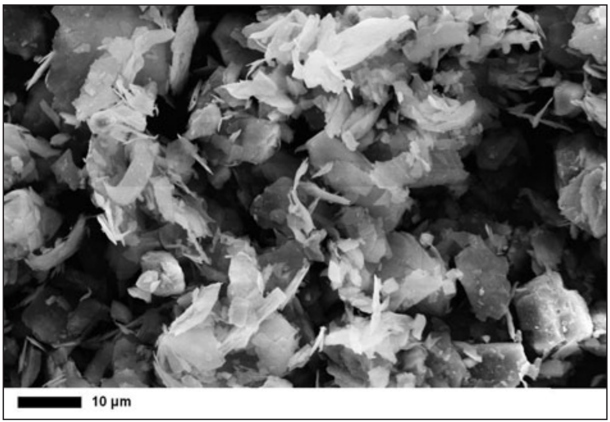


Figure I-3.6: Scanning electron micrograph of talc

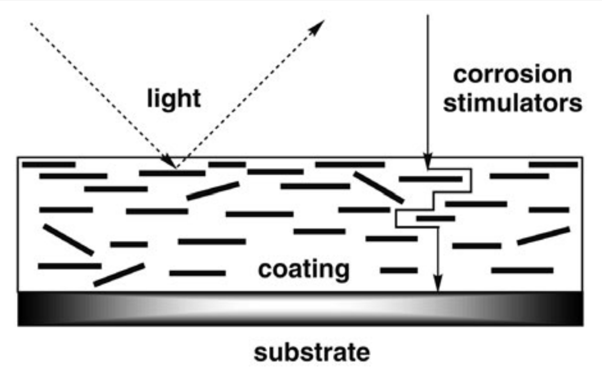


Figure I-3.7: Barrier effect of lamellar pigments (not to scale)

CPVC increases because the free volume between the large pigment particles can be filled with small ones. Also, fine lamellar fillers (e.g. talc, Figure I-3-6) can fill the free volume between the larger particles (Figure I-3.5); see below for a discussion of the barrier effect.

Lamellar pigments are used as passive anticorrosive pigments (barrier pigments) because they lengthen the diffusion pathways for corrosion stimulators (Figure I-3.7). Moreover, lamellar pigments protect the binder against light and photooxidation [4]. Suitable lamellar pigments are aluminium flakes and micaceous iron oxide (Figure I-3.8), which are mainly used in topcoats for providing corrosion protection in multi-coat systems.

3.3 Development of paint formulations

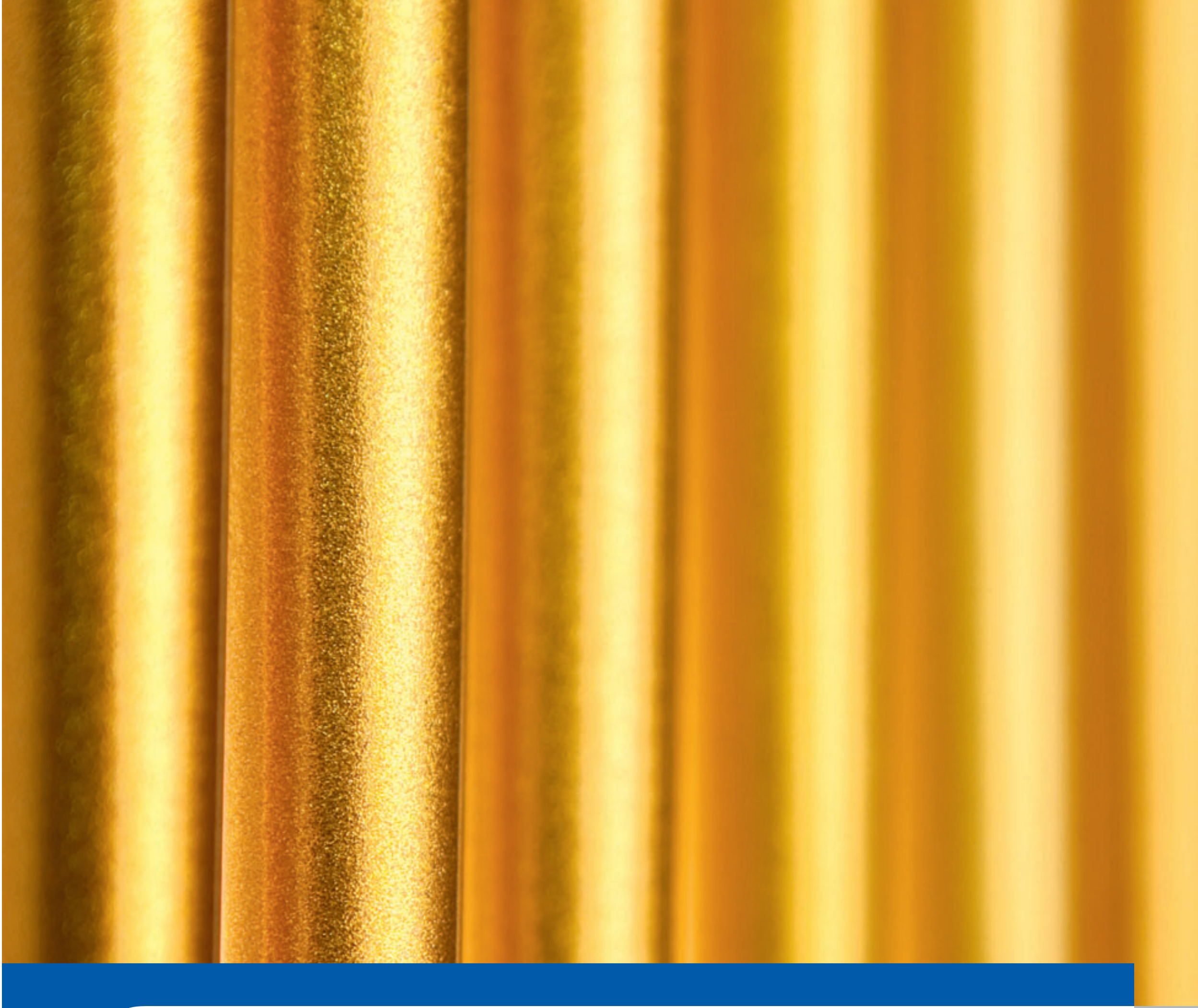
The formal procedure for developing a simple paint formulation is presented below. The problem has been stated and the goal is to develop a paint formulation (calculation recipe).

Problem:

- Stoving topcoat, white
- P/B = 0.6 : 1 (pigment/binder ratio)
- AK : MF = 7 : 3 (solids/solids)
- Non-volatiles content (solids) as delivered (about 80 s, DIN cup 4): 60 to 65%

The first step in solving this problem is shown in Figure I-3.9; the non-volatiles content is arbitrarily taken to be 63% (roughly the average of the specified value).

The next step is to choose the binders (compatibility also has to be tested).



ECKART – Effect Pigments
for Coatings and Formulations

ECKART metallic effect pigments stand for high-tech, precision and elegance: You can see it, for example, in the sophisticated shine of surfaces in the automobile industry or in weather-resistant coatings for industrial applications. You can practically smell it, for instance in environmentally friendly waterbased paint systems. Or you can feel it using heat reflecting interior wall paints. Or simply know – like our customers in the coatings and paint industry. Because to them, ECKART represents the commitment to constantly strive anew for custom-fit optical effects, top quality and excellent service.

ECKART is the world's leading manufacturer of metallic pigments for the coatings industry. Innovation, research and the constant further development of our products ensure that we remain so!

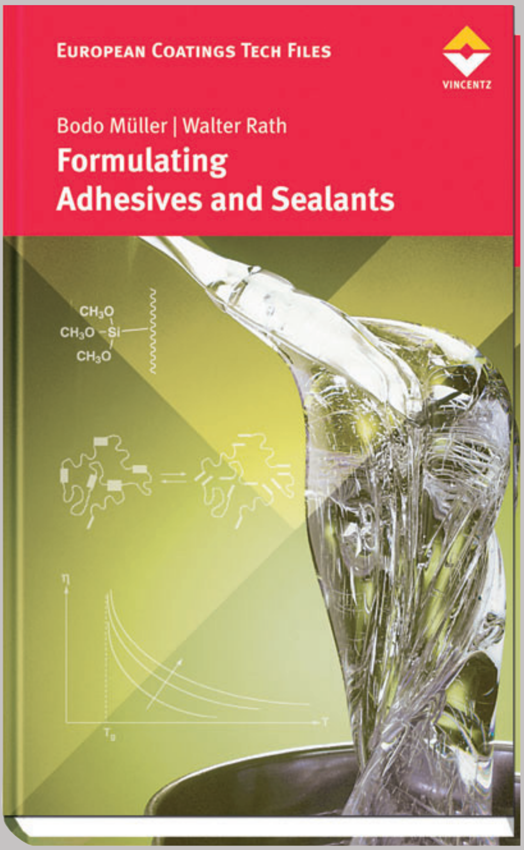
ECKART – take the brilliant way. **www.eckart.net**

ECKART GmbH · Guentersthal 4 · 91235 Hartenstein · Germany
Tel +49 9152 77-0 · Fax +49 9152 77-7008 · info.eckart@altana.com

ECKART
Effect Pigments

A member of ALTANA

This is a dedicated single-user copy of an ebook.
Copyright laws apply; it is prohibited to copy or distribute
the ebook or any part hereof. ©2012 Vincentz Network


EUROPEAN COATINGS TECH FILES
VINCENTZ
Bodo Müller | Walter Rath
Formulating Adhesives and Sealants

Alkyd resin: short-oil, non-drying, non-yellowing AK, e.g. “Worléekyd C 628” (70% in xylene)

Melamine resin: reactive melamine resin, e.g. “Maprenal MF 580” (55% in alcohols)

This yields (see Figure I-3.9):

AK (solids) 27.6 parts by weight
→ 39.4 parts by weight (70%)

AK (solids) 11.8 parts by weight
→ 21.5 parts by weight (55%)

The solvents chosen as follows: aromatics, methoxy propanol and some butyl glycol acetate (high-boiling solvent, levelling effect). For simplicity, no further additives and no tinting pigments will be used in this example. Usually, a white paint is formulated with titanium dioxide as white pigment, tinted with small amounts (e.g. 0.1%) of iron oxide yellow and/or carbon black to improve hiding power. The paint can now be formulated (Table I-3.5).

The PVC can be calculated from this formulation (approximate calculation).

Table I-3.5: Formulation (calculation recipe) for a white stoving topcoat; simplified model formulation (without sag-control agent or tinting pigments)

parts by weight	raw material	solids	volatile
39.4	Worléekyd C 628 (70%)	27.6	11.8
21.5	Maprenal MF 580 (55%)	11.8	9.7
23.6	titanium dioxide rutile	23.6	
5.0	xylene		5.0
6.5	Solvesso 100		6.5
3.0	methoxypropanol		3.0
1.0	butyl glycol acetate		1.0
100.0	sum	63.0	37.0

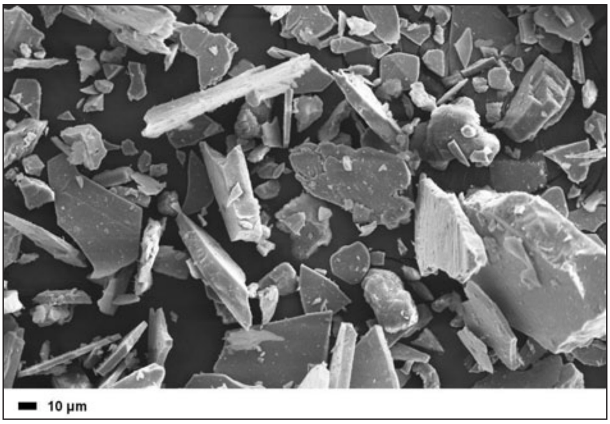


Figure I-3.8: Scanning electron micrograph of micaceous iron oxide

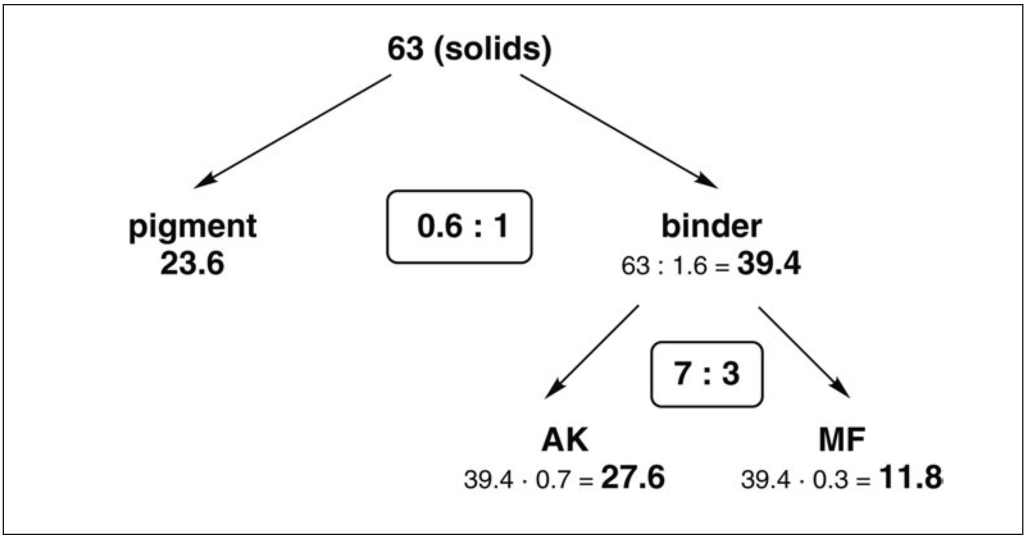


Figure I-3.9: Development of a paint formulation for a white stoving topcoat (all data refer to solids)

$$\text{PVC} = \frac{23.6 / 4.1}{23.6 / 4.1 + 27.6 / 1.2 + 11.8 / 1.5} \cdot 100\% = 15.7\%$$

The production recipe for 600g paint is presented in Table I-3.6 (numbers rounded). For simplicity, the total alkyd resin included with the pigment paste; in actual practice, the amount of alkyd resin in the pigment paste would be minimized by trials to reduce machine running time (to save energy and costs). Furthermore, the high-boiling solvents are included with the pigment paste to reduce losses by evaporation during milling.

Table I-3.6: Production recipe for 600 g of white stoving topcoat

parts by weight	raw material respectively intermediate product
237	Worléekyd C 628 (70%)
6	butyl glycol acetate
18	methoxypropanol
12	Solvesso 100
142	titanium dioxide rutile
	1. dissolver, 2. pearl mill: 5 to10 µm fineness of grain
	3. completition
129	Maprenal MF 580 (55%)
27	Solvesso 100
30	xylene (up to 80 sec DIN cup 4)
600	sum
composition of the paint	
%	
39.4	binders (solids)
23.6	pigments and fillers (solids)
37.0	solvents (total)

The quantities of solvents in the first paint formulation can only be estimated; i.e., the solvents are added in portions during the first lab production to avoid addition of excess and, therefore, to avoid over-dilution. It may be necessary to adjust the addition levels of solvents; i.e., the non-volatiles content may vary slightly. The subsequent optimization steps will yield more precise information about the addition levels for solvents.

3.4 Multi-coat systems

As a rule, the required properties of a coating cannot be met by a single coat; i.e., several coats that have been balanced with each other are necessary (multi-coat system). The various coats in a multi-coat system can be designated as follows.

1. Primer; its functions are:

- To act as the basis of the multi-coat system

- To provide adhesion between substrate and coating
- To protect the substrate against environmental influences (e.g. corrosion)
- To protect subsequent coats from the substrate (e.g. the alkalinity of concrete or migration of plasticizer from plastic substrates): barrier layer.

2. Intermediate coat (primer surfacer)

- To improve the barrier effect of the primer
- To create an optimum surface for the topcoat:
  - Covering, levelling of substrate roughness
  - Grindability.
- To absorb mechanical load (stone-chip resistance).

3. Topcoat

- To confer long-lasting protection on the multi-coat system:
  - Weatherability (e.g. UV radiation, rain or humidity) [4]
  - Chemical resistance (e.g. battery acid, bird droppings)
  - Resistance to solvents (e.g. petrol).

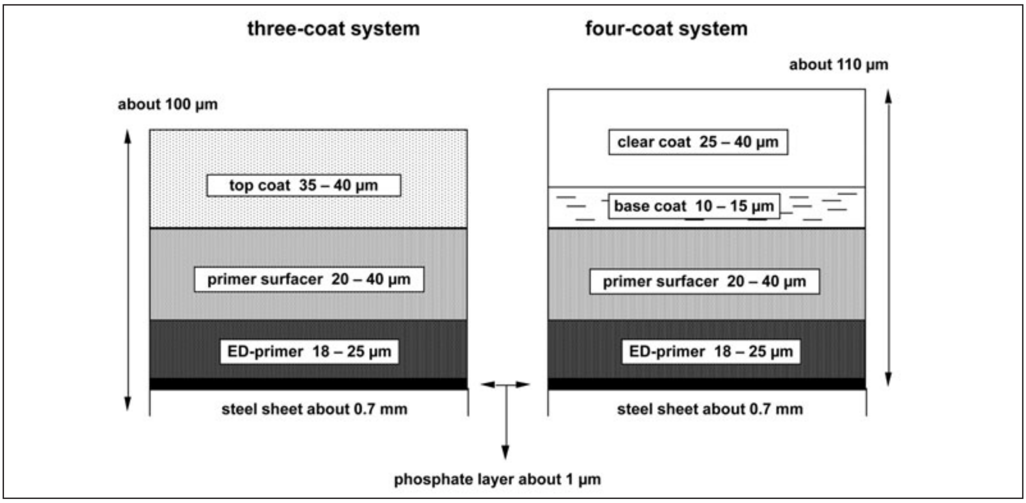


Figure I-3.10: Multi-coat systems for automotive coatings [ED = (cathodic) electrodeposition primer; basecoats: metallic 10 to 15 µm, solid colours up to 30 µm]

- To provide optical properties:
  - Colour
  - Gloss.

The individual coats need to be balanced to each other. As a rule, the primer has a greater pigment/binder ratio than the topcoat (Table I-3.7); thus, the primer is not as flexible as the topcoat. Conversely, application of a brittle topcoat over a flexible primer would create a crackle finish.

Multi-coat systems can have an overall coating thickness of up to 1,000 µm (1 mm) for anti-corrosion coatings; steel constructions in sea water and interior coatings of containers need even higher film thicknesses. Multi-coat systems for automotive coatings are presented in Figure I-3.10.

Most coatings for automotive multi-coat systems are highly crosslinked thermoset coatings. The main functions of the various balanced coats in automotive multi-coat systems (Figure I-3.8) are:

1. Phosphate coating (conversion coating, metal pretreatment)
   Adhesion promotion and corrosion protection
2. Cathodic electrodeposition primer
   Corrosion protection
3. Primer surfacer
   Covering the roughness of the metal substrate
   Stone-chip resistance
4. There are two possibilities for topcoats (Figure I-3.10).
   a) (three-coat system) see Figure I-3.12, solid colours
      Colour, gloss
      Weather stability, resistance to chemicals and solvents
   b) (four-coat system) see Figure I-3.13, metallic (effect) colours
      - Metallic (effect) basecoat
      - Clear coat
        Gloss, weatherability, resistance to chemicals and solvents, and to mechanical stresses such as scratching and abrasion.

Table I-3.7: Guide values for pigment/binder ratios of oxidatively curing paints

paint types	pigment binder ratio (P/B)
primers	(2 to 4) : 1
primer surfacers	(1.5 to 2.5) : 1
top coats	(0.1 to 1) : 1

Figure I-3.11: Scanning electron micrograph of a phosphate conversion coating on steel; scale bar: 3 µm

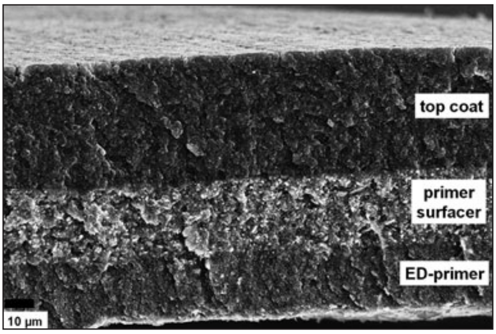


Figure I-3.12: Scanning electron micrograph of a cross-section through an automotive coating (three-coat system)

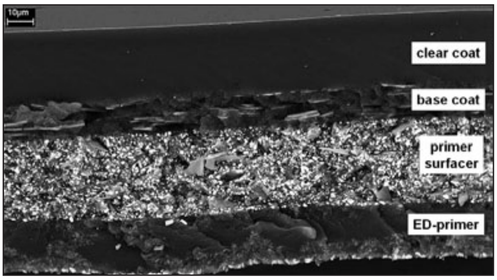


Figure I-3.13: Scanning electron micrograph of a cross-section through an automotive coating (four-coat system)

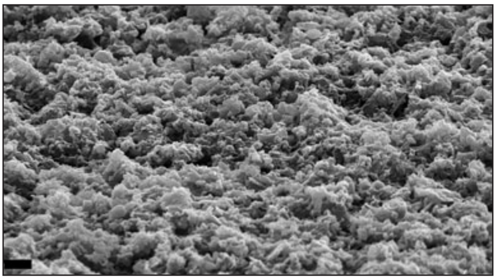


Figure I-3.14: Scanning electron micrograph of a surface of a railcar coating after long-term outdoor weathering; scale bar: 2 µm

Automotive coatings are an example of just how complex multi-coat systems are. Nowadays, there are new automotive multi-coat systems which differ from Figure I-3.10. For example, the two-coat system of the "Smart" car has a roughly 20 µm thick coat of cathodic ED primer and a 70 to 80 µm thick powder topcoat; car body areas vulnerable to stone-chipping feature a powder primer surfacer. The various types of automotive paints will be described more in detail in the corresponding chapters of this book.

Automotive coatings are an example of how complicated multicoat systems can be (Figures I-3.10 to I-3.13) [5]. Furthermore, other multicoat systems for automotives now exist, such as the two-coat system for the "Smart". Here, a cathodic electrodeposition primer (about 20 µm) and a powder topcoat (70 to 80 µm) are applied; that area of the car body which is vulnerable to stone-chipping is partly coated with a powder primer surfacer. The various automotive paints will be described in detail in the respective chapters of this book.

In connection with topcoats, the term weathering resistance has been mentioned several times. By way of illustration, Figure I-3.13 shows the damage caused to coating's surface by prolonged outdoor weathering (scanning electron micrograph). It can be clearly seen that the organic binder has been degraded by photooxidation to expose the filler and pigment particles [4].

3.5 References

[1] B. Müller, Farbe & Lack, 106, No. 3 (2000) p. 62 ff
[2] H. Saechtling, Kunststofftaschenbuch, 23rd ed., Hanser Verlag (1986) p. 527
[3] H. Kittel (editor J. Spille), Lehrbuch der Lacke und Beschichtungen - Volume 5: Pigmente, Füllstoffe und Farbmetrik, 2nd ed., S. Hirzel Verlag (2003) p. 79 ff
[4] B. Müller, Understanding Additives, Vincentz Network (2010), chapter 8
[5] C. Friedrich, student project work, University of Applied Sciences, Esslingen (2010)

Part II Solvent-borne paints

Part II Solvent-borne paints

1 Paints that form films at ambient temperature

Paints that form films at ambient temperatures or at the temperatures prevailing in buildings are often called “paints forming films at room temperature”. For these paints, film forming conditions at temperatures below 0 °C are often ruled out. This group of paints includes those which form films exclusively by physically drying – that means by evaporation of solvents only – as well as those which contain binders with reactive chemical groups that crosslink at ambient temperatures during film formation.

1.1 Physically drying paints

Solvent-borne paints that contain polymers as binders and that form films by evaporation of solvents only are called “physically drying paints“. In order that films with adequate properties may be achieved, the polymers for the most part have high molar masses. Additionally, these polymers may contain molecular structures that support evaporation of the solvents during film formation. The disadvantage of using such binders is that large amounts of solvents are needed to make the paints ready for application (i.e. to ensure they have the necessary viscosity for application). Moreover, films which are formed by a chemical crosslinking process offer much greater resistance to solvents and other agents than films which are formed by physical drying only. Nevertheless, physically drying paints still play an important role in the coatings industry. They have excellent storage stability and are easy to handle during production and application.

Binders for physically drying paints are [1 to 3]:

- Cellulose nitrate
- Other cellulose esters
- Polyvinyl halides and their copolymers
- Polyvinyl esters
- Polystyrene
- Hydrocarbon resins
- Derivatives of rubber
- Epoxy resins with high molar masses
- Polyamides
- Polycarbonates

The reason that solvents evaporate very quickly is the tendency of the molecules of the binder resins to form molecular “associates”. In particular, the molecules may form crystalline domains. This tendency may lead to negative film properties, e.g. brittleness. Therefore, plasticizers need to be added to most physically drying polymers if optimum film properties are to be achieved. Additionally, other resin components are combined with the physically drying main resins to improve gloss, levelling, and appearance (filling power) of the coating.

Certain physically drying paint systems require elevated temperatures for solidification (organosols, plastisols).

1.1.1 Paints based on cellulose nitrate

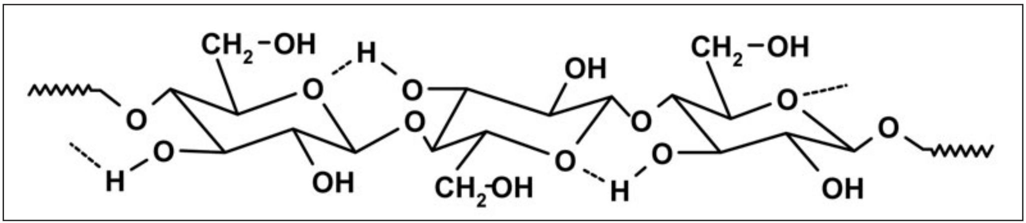


Figure II-1.1: Molecular structure of cellulose (β-1,4-glycoside)

1.1.1.1 Structure and properties of cellulose nitrate

Natural cellulose is the scaffolding material of all plants. It is a high-molecular carbohydrate consisting of glucose units connected by β-1,4-glycoside bridges [4]. These are relatively large, elongated molecules (molar mass about 10^6 g/mol), with a high degree of association, as shown in Figure II-1.1

Due to its molecular structure (very high molar mass, semi-crystallinity), cellulose is insoluble in all solvents and unable to form coatings. In the past, there have been many attempts to transform cellulose into products useful for the coatings industry. The most successful of these was cellulose nitrate (CN). Very often, cellulose nitrate is called nitrocellulose, but this is wrong. Cellulose nitrate contains esters of nitric acid, but no nitro groups.

Cellulose nitrate is produced by treating natural cellulose with a mixture of nitric acid, sulphuric acid, and water. In the past, the cellulose came from cotton linters that could not be used for textile goods. Nowadays, the cellulose is produced from coniferous wood. The acid mixture, for example, consists of 57 wt.% concentrated sulphuric acid, 25 wt.% concentrated nitric acid and 18 wt.% water. The process is an esterification performed at elevated temperature. The temperature, reaction duration, and concentration of the acids determine how many of the hydroxyl groups of the cellulose are transformed into ester groups. Additionally, the polymer molecules undergo partial decomposition by hydrolysis of the glycoside bridges. After the aqueous phase has been separated, the cellulose nitrate consists of a white solid product resembling wool fibres, and is therefore often called "nitrocotton".

Cellulose nitrate is closely related to the gunpowder product and is highly explosive. Handling of cellulose nitrate is subject to a number of regulations. The delivery form is a material which is wetted with alcohols (the most common variant consists of two parts by weight cellulose nitrate and one part 1-butanol). Another variant is a combination of cellulose nitrate with a plasticizer (most commonly phthalate esters) that comes in the form of chips.

Table II-1.1: Content of nitrogen in relation to the amount of ester groups

number of nitrate groups per structure unit	content of nitrogen (theoretical)
1	6.76%
2	11.11%
3	14.14%

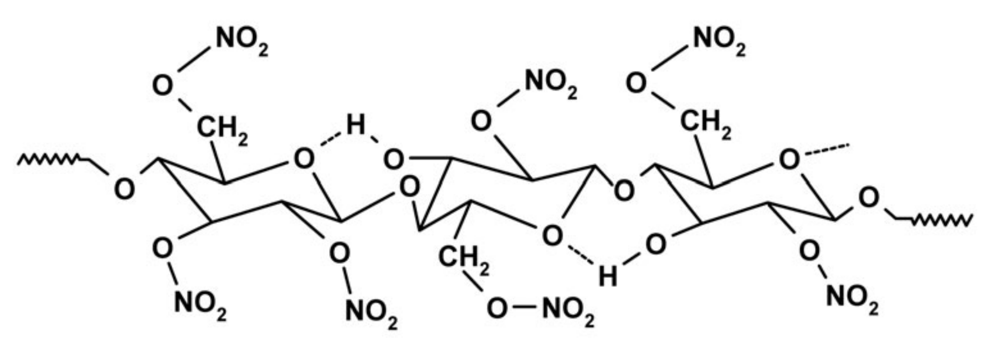


Figure II-1.2: Molecular structure of an ester-soluble cellulose nitrate

Cellulose nitrate grades differ in their content of nitrate ester groups and average molar mass. The molar mass significantly influences the solution viscosity. The analytical method for establishing the degree of esterification consists in measuring the content of nitrogen. Table II-1.1 shows the content of nitrogen as a function of the content of ester groups.

The degree of esterification determines the solubility and compatibility of cellulose nitrate. Grades with a high ester content are readily soluble in esters, ketones, and glycol ether esters and may be blended with alcohols and aromatic hydrocarbons. The molecular structure is shown in Figure II-1.2.

These so-called E-grades are compatible with many other binders. Grades that contain lower amounts of ester groups (the A-grades) are readily soluble in alcohols, glycol ethers, esters and ketones. They offer less scope for blending and are less compatible with other binders than the E-grades. There are also intermediate grades known as M-grades. An overview of the characteristics of cellulose nitrate grades is provided in Table II-1.2.

The different molar masses of the cellulose nitrate grades are reflected in the viscosity of the solutions. For this reason, European suppliers of cellulose nitrate use figures relating to the viscosity in their product nomenclature. The method for determining the viscosity is set forth in the standard DIN 53179. The definition there consists of a letter (E, M, A) to denote the solubility or degree of esterification, and the amount of solid cellulose nitrate in an acetone solution that has a viscosity of 400 ± 25 mPa s, as measured in a falling-ball viscometer. The various suppliers of cellulose nitrate either follow this definition when describing their products, or they quote the viscosity number of specific solutions. Typical available products are listed in Table II-1.3

The molar mass of cellulose nitrate not only influences the solution viscosity and thus the solids content for application, but also some film properties. Large molecules of cellulose nitrate are capable of forming complex molecule coils and such films are therefore flexible. Compared with those, cellulose nitrates containing small molecules yield brittle films. Table II-1.4 [5] shows the relationship between the viscosity of different grades of cellulose nitrate in a defined solution and the mechanical film properties of elongation and ultimate tensile strength. This is the reason why cellulose nitrate of lower average molar mass has to be combined with plasticizers.

Table II-1.2: Content of nitrogen and degree of esterification of different grades of cellulose nitrate

grade of cellulose nitrate	content of nitrogen [%]	number of ester groups per structure unit
A	10.9 to 11.3	1.18 to 1.23
M	11.3 to 11.8	2.06 to 2.20
E	11.8 to 12.3	2.20 to 2.33

Table II-1.3: Examples of supplier products and their classification

standardization		suppliers		
definition (DIN 53 179)	**content of solids [%] (test solution)**	**Hagemann**	**Hercules**	**Wolff**
4E	4.0	H 4	RS 1300”	E 1440
9E	9.0	H 9	RS 15”	E 950
25E	25.0	–	–	E 510
27E	27.0	H 27	RS 1/4”	-
28E	28.0	–	–	E 400
27A	27.0	AH 25	SS 1/2”	A 500
27 M	27.0	–	–	AM 500

Table II-1.4: Mechanical properties of films of different cellulose nitrate types (in relation to viscosity)

viscosity of test solution [mPa · s]	elongation [%]	ultimate tensile strength [N/mm²]
1440	24 to 30	98 to 103
1160	23 to 28	98 to 103
950	23 to 28	88 to 98
840	20 to 25	88 to 98
620	12 to 18	78 to 88
560	10 to 15	74 to 84
510	8 to 12	69 to 78
400	5 to 10	59 to 69
375	< 5	39 to 49
330	< 3	29 to 39

Grades of high molar mass may be used as single resins, e.g. for zapon lacquers. Of course, the products have a low solids content at application viscosity.

Solvents evaporate rapidly during film formation by cellulose nitrate solutions and so the binder is mainly used for paints with short drying times. Cellulose nitrate combined with suitable plasticizers or other partner resins leads to tough, horn-like films. These films are relatively resistant to various agents, but not, of course, to solvents – although they may be resistant to aliphatic hydrocarbons (benzene, petrol, white spirit). The weatherability of coatings containing cellulose nitrate is restricted. Due to the risk of explosion, cellulose nitrate lacquers may not be produced, stored, or applied in combination with paints containing reducing agents, e.g. amines. Furthermore, there is a risk associated with the use of paints containing cellulose nitrate for stoving enamels.

1.1.1.2 Combination partners for cellulose nitrate

Most cellulose nitrate paints consist of grades with relatively low molar mass because only then are acceptable solids levels achieved. In such cases, it is necessary to combine the cellulose nitrate with plasticizers and other resins.

Plasticizers

Plasticizers are chemical compounds that interact with polymers in the same way as solvents. But, unlike solvents, they have very low vapour pressures under application conditions. Thus, they remain in the films. There are two types of plasticizer, the so-called gelling and non-gelling kinds. Their interaction with resins is comparable to that of the various solvents. Gelling plasticizers act like true solvents; at least in films, they form “solid solutions” (gels). Non-gelling plasticizers are comparable to thinners. They must be combined with gelling plasticizers to impart special properties to the films. The use of only non-gelling plasticizers for a polymer runs the risk of exudation. The criteria for selecting plasticizers are: adequate compatibility with the binders, low colour value, and resistance to light and migration. Modern plasticizers have to meet the environmental regulations concerning physiological and ecological safety. Additionally, fuel resistance and the stability to saponification are important.

Table II-1.5: Vapour pressure of bis-2-ethylhexyl-phthalate

temperature [°C]	vapor pressure [mbar]
50	$1.1 \cdot 10^{-5}$
100	$1.8 \cdot 10^{-3}$
140	$4.2 \cdot 10^{-2}$

Chemical classification of plasticizers:

- Ester plasticizers
  - Diesters of phthalic acid, adipic acid or sebacic acid and monoalcohols (e.g. 2-ethylhexanol, isononanol, decyl alcohol, fatty alcohols, benzyl alcohol or glycol monoethers)
  - Triesters of citric acid
  - Phosphoric ester of monoalcohols with long aliphatic chains
  - Esters of fatty acids and monoalcohols with aliphatic chains (e.g. butyl stearate)
  - Diesters of polyethylene glycols
  - Esters of rosin acids with monoalcohols with long aliphatic chains
- Plasticizers based on epoxidised fatty acid esters or epoxidised oils
- Plasticizers based on hydrocarbons
- Plasticizers based on chlorinated paraffin
- Special plasticizers (e.g. di(phenoxyethyl)formal = Desavin [Bayer])

In the past, the diesters of phthalic acid and low molecular aliphatic mono-alcohols (e.g. dibutyl phthalate) and the tri(alkylphenyl) ester of phosphoric acid (e.g. tricresyl phosphate) and halogenated aromatic hydrocarbons (PCBs) were the standard products. But today, the use of all these products is restricted due to their physiological behaviour and environmental risks. Some of them are also water contaminants.

However, some of them are also authorized for food packaging, and have FDA approval (e.g. citric esters).

To illustrate the low vapour pressure of typical plasticizers, the following table shows the data for bis-2-ethylhexyl phthalate at different temperatures [13].

Most ester plasticizers have a gelling action on cellulose nitrate, and their use yields good fuel resistance. The less polar plasticizers – fatty acid derivatives and hydrocarbons – have no gelling action on cellulose nitrate. Gelling plasticizers are combined with cellulose nitrate in weight ratios of about 1 : 2. Such combinations are suitable for topcoats that are easily polished.

Other plasticizers for cellulose nitrate are special polyesters based on adipic acid or sebacic acid, and alkyd resins. The alkyd resins are so-called short oil grades, and the mono-carboxylic acids are synthetic acids, fatty acids from coconut oil, or contain significant amounts of oleic acid (e.g. based on peanut oil). Other alkyd resins for combination with cellulose nitrate are based on castor oil or dehydrogenated castor oil [8].

Special amino resins are also suitable for combination with cellulose nitrate. In particular, carbamide resins are used, e.g. the product of the reaction of butyl carbamate and formaldehyde [8].

Alkyd resins [1 to 3] are combined with cellulose nitrate in weight ratios of about 2 : 1. This combination improves the gloss and appearance (filling power) of films. Alkyd resins may be used to produce pigment pastes for cellulose nitrate paints.

Not so much for plasticizing as for improving gloss and appearance and increasing the application solids of paints, more brittle resins (e.g. ketone resins, rosin esters, phthalate resins) are used for combinations with cellulose nitrate.

1.1.1.3 Applications of cellulose nitrate paints

The long-established zapon lacquers, which consist of high-molecular cellulose nitrate, are used to protect decorative, sensitive metal surfaces (silver, copper, brass) with thin clear coat layers.

On account of their fast physical drying, cellulose nitrate paints are used for air-drying wood paints (primers and topcoats), air-drying effect finishes (hammer finishes, crackle paints), printing finishes and paper lacquers, leather paints and foil paints as well as the formulation of adhesives. To render foil paints heat-sealable, cellulose nitrate A-grades are selected as binders.

Cellulose nitrate paint has played an important role in industrial paint systems, mainly being used for automotive topcoats. In the 1920s, Ford passenger cars were produced on conveyor belts and given their famous black car finishes, which were based on cellulose nitrate and dried very quickly. In those days, carbon black was the only pigment which improved the weatherability of the automotive topcoats. The whole car-coating process utilised fast-drying putties containing a cellulose nitrate binder. If the topcoats based on cellulose nitrate and plasticizers could be polished, they were called “polishing enamels”. Later, these grades were replaced by paints based on binder combinations of cellulose nitrate and alkyd resins (for plasticization), so-called “combination enamels”. For a long time – and in some cases even today – this variant was used for topcoats for trucks and agricultural implements.

The main disadvantage of cellulose nitrate paints is their limited weatherability. Matting and chalking occur on exposure to the elements. The weatherability can be improved by combining cellulose nitrate with other resins. But modern coating systems for topcoats (stoving enamels, two-component paints) are much more durable.

Since cellulose nitrate is widely compatible with many other resins, it is used in different combinations, mainly to improve physical drying. Cellulose nitrate may be contained in two-component paints (the main resins are polyesters or alkyds and polyisocyanate adducts), in alkyd paints, which primarily cure oxidatively (containing unsaturated fatty acids) and in so-called acid-curing paints (based on alkyd resins, amino resins, and acids for crosslinking catalysis).

Table II-1.6 describes a red, glossy topcoat based on cellulose nitrate as a means of illustrating a “classic” combination enamel.

The binder is to be a combination of a medium viscous, ester-soluble cellulose nitrate and an alkyd resin based on peanut oil and a small amount of phthalate plasticizer. The weight ratios are to be 1.0 : 1.5 : 0.2, calculated on solid resin. For pigmentation, a quinacridone red is chosen and the PVC is 15 vol.%. For better pigment wetting, addition of 0.4 wt.% (calculated on delivery form) of a calcium octoate is required. The paint is to have a solids content of 40 wt.%. The solvent composition is to consist of butyl acetate, butanol and xylene in the weight ratio 5 : 4 : 2. Finally – to improve levelling – 4.6 wt.% butyl glycol acetate (a slow-evaporating solvent) will be added.

Calculation of formulation:

Given that the quinacridone red has a density of 1.6 g/cm^3 and the resins have an average density of 1.2 g/cm^3, the definition of PVC at 15 vol.% yields 24 parts by weight of the pigment and 102 parts by weight of the resins, giving a total solids content of 126 parts by weight. The weight ratio of pigment to binder (P/B) is 0.23 : 1.00.

Table II-1.6: Red, glossy cellulose nitrate combination topcoat

pos.	raw material	solids [wt.%]	density [g/cm³]	formulation [wt.%]
pigment dispersion				
01	nondrying peanut oil alkyd (70% in xylene)	18.0	1.2	25.7
02	di-2-ethylhexyl-phthalate*	2.4	1.2	2.4
03	quinacridon red	7.6	1.6	7.6
04	calcium octoate (5% Ca)			0.4
05	butylacetate			6.0
06	xylene			4.3
binder solution				
07	medium viscous cellulose nitrate (66% with butanol)	12.0	1.2	18.2
08	xylene			8.0
09	butylacetate			13.8
adjusting of viscosity				
10	butyl acetate			5.2
11	butanol			3.8
12	butyl glycol acetate			4.6
sum		40.0		100.0

pos. 01: e. g. Alkydal E 41 (Bayer)
*pos. 02: e. g. Palatinol AH (BASF)**
pos. 03: e. g. Hostaperm red E 3 B (Clariant)
pos. 06: e. g. CN E 510 (Wolff)

** currently the di-2-ethylhexyl-phthalate is classified as toxic, it should be replaced by di-isononyl-phthalate (Palatinol DINP [BASF SE]) or by di-isononyl-hexahydro-phthalate (Hexamoll DINCH [BASF SE])*

In line with the binder ratios, the requisite amounts are 12.0 wt.% cellulose nitrate, 18.0 wt.% alkyd resin, and 2.4 wt.% plasticizer (all calculated on solids). If the cellulose nitrate is wetted with butanol in the ratio 2 : 1, 18.2 wt.% the delivery form of the ester-soluble cellulose nitrate has to be used. The alkyd resin is diluted 70 wt.% in xylene; therefore, 25.7 wt.% the solution is used. The formulation consists of 55 wt.% solvents divided into 25.0 wt.% butyl acetate, 20.0 wt.% xylene, and 10.0 wt.% butanol. With regard to the solvents used in the delivery form of cellulose nitrate (6.2 wt.% butanol) and alkyd resin solution (7.7 wt.% xylene), the remaining amounts of solvents are 25.0 wt.% butyl acetate, 3.8 wt.% butanol and 12.3 wt.% xylene. To prepare the solution of cellulose nitrate with 30 wt.% solids, first we need 13.8 wt.% butyl acetate and 8.0 wt.% xylene. The remaining free solvents are then 11.2 wt.% butyl acetate, 3.8 wt.% butanol, 4.3 wt.% xylene, and 4.6 wt.% butyl glycol acetate. For pigment dispersion, an additional 6.0 wt.% butyl acetate and 4.3 wt.% xylene are used.

Production of the topcoat

The alkyd resin solution, the plasticizer, the pigment, the wetting agent and the portions of butyl acetate and xylene (items. 1 to 6) are mixed first, pre-dispersed and then dispersed on a sand or pearl mill to the required fineness. The resultant pigment paste contains 16.4 wt.% pigment and 44.0 wt.% binder including plasticizer.

Meanwhile, the cellulose nitrate solution of the materials in items 07 to 09 is produced as follows. The cellulose nitrate, wetted with butanol (pos. 07), is dispersed with the scheduled amount of thinning agent xylene (pos. 08). Only then is the true solvent butyl acetate added. This guarantees that the solution will be homogeneous. The solution is prepared by intensive stirring until it is clear and free from specks.

The solution is mixed well with the pigment paste. The remaining free solvents (pos. 10 to 12) are then added. The viscosity of the resultant red topcoat is adjusted by adding a thinner containing butyl acetate and xylene in the weight ratio 2 : 1. The application viscosity is 20 s (DIN 53211 flow-cup 4 mm, 23 °C). The topcoat is applied over a primer surfacer. Two applications may be required. The film can be polished after a short drying time.

1.1.2 Physically drying paints based on acrylic resins

Attempts have been made to overcome the main disadvantage of paints based on cellulose nitrate, namely limited weatherability. One alternative is to use paints based on physically drying acrylic resins [1 to 3]. These resins consist mainly of polymers containing molecular chains of different esters of methacrylic acid and monoalcohols, but they may also contain acrylic esters and other comonomers for the polymerization process. In order that adequate film properties may be achieved, the resins have relatively high molar masses. Like paints based on cellulose nitrate, they have a low content of solids for application.

The monomer composition may be varied to influence the hardness of the resins, and the films made there from. Physically drying acrylic resins may be combined with plasticizers. The films of the acrylic paints are resistant to discoloration, mostly highly resistant to fuel, but, of course, not resistant to other solvents. In comparison to cellulose nitrate, acrylic resins are less compatible with other resins and they have poor workability. In general, the composition of paints based on acrylic resins is similar to that of paints based on cellulose nitrate. Systems based on physically drying acrylic resins are still important for automotive repair paints used in the Americas, in Australia and in East Asia. Additionally, they may be used for wood paints and general industrial paints. They are less suitable for primers and primer surfacers.

1.1.3 Paints based on rubber modifications

1.1.3.1 Structure and properties of rubber modifications

Natural rubber is the main ingredient (approx. 35 wt.%) of a latex exuded by special *Euphorbiaceae* trees, the most important being the *Hevea brasiliensis*. The product is a polyisoprene (poly-2-methylbut-2-ene). The chemical structure is shown in Figure II-1.3. The methyl group is arranged in a *cis*-position to the hydrogen atom on the 3rd carbon atom of the isoprene segment. The average molar mass of the polymer is about 10^6 g/mol [4].

Here, too, attempts have been made in the past to render the natural rubber suitable for paints. Current modifications of natural rubber as paint binders are cyclized rubber (RUI) and chlorinated rubber (RUC).

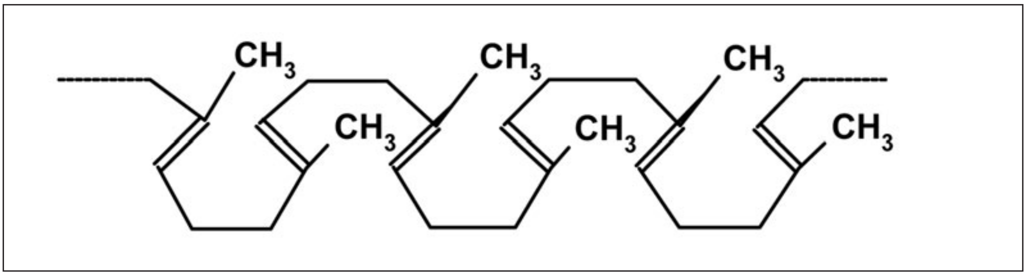


Figure II-1.3: Structure of molecular segments of rubber (polyisoprene, poly-2-methylbut-2-ene)

Cyclized rubber

Cyclized rubber is produced by cyclizing polyisoprene at higher temperatures under the influence of catalysts (strong acids). The isoprene units form six-membered ring systems, and the large molecules decompose to molar masses of 3,000 to 10,000 g/mol. Cyclized rubber is a hard, resin-like material, and melts at temperatures between 120 and 140 °C. It is soluble in aliphatic and aromatic hydrocarbons and in terpenes, thinnable with esters and ketones, but insoluble in alcohols and glycol ethers. For paint formulations, cyclized rubber has to be combined with a plasticizer. Cyclized rubber – like chlorinated rubber – is used for anticorrosive, chemically resistant paints.

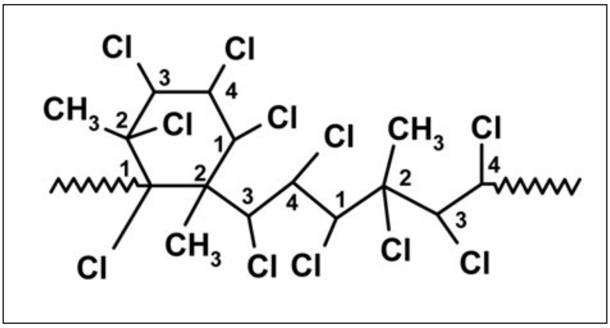


Figure II-1.4: Model of likely molecular structure of a segment of chlorinated rubber

Example of commercial product[8]: Syntotex RR 800 (DSM)

Chlorinated rubber

Chlorinated rubber is adding chlorine to solutions of natural rubber in carbon tetrachloride. Chlorine reacts by addition and substitution, with decomposition of the macromolecules and cyclization. The finished product consists of 67 wt.% chlorine. Average molar masses are 30,000 to 180,000 g/mol. The molecular structure is shown in Figure II-1.4

Chlorinated rubber is no longer produced from natural rubber; it is now derived from synthetic polyisoprene.

Chlorinated rubber is a white powder. It is soluble in aromatic hydrocarbons, in esters and ketones. Its solutions are thinnable with aliphatic hydrocarbons and terpenes, but chlorinated rubber is insoluble in alcohols and glycol ethers. Although the product forms films only by physical drying, they are particularly chemically resistant. Films of chlorinated rubber have excellent adhesion. Grades having a lower molar mass do not need the addition of plasticizers. Their films are sufficiently flexible to enable them to be used as the sole binder in paints. For improved gloss and appearance, chlorinated rubber is combined with plasticizers or other resins. Without stabilization, chlorinated rubber is not weatherable, and is not resistant to light exposure or to elevated temperatures. Hydrochloric acid splits off at temperatures from 90 °C and above. Although unstabilized chlorinated rubber is not flammable, it generates hydrochloric acid and dioxins (e.g. the extremely highly toxic 2,3,7,8-tetrachlorodibenzo-p-dioxin) when burned. But chlorinated rubber can be stabilized with relatively small amounts of metal oxides (e.g. zinc oxide) or with sodium carbonate. Chlorinated rubber is an inexpensive raw material for paints.

Example of commercial products: Pergut S 5, S 10, S 20, S 40, S 90 (Bayer)

1.1.3.2 Applications of rubber modifications

Due to their properties, rubber modifications are preferred for corrosion protection paints (protection against severe corrosion). For example, paints based on chlorinated rubber are used for steel constructions and marine paints. They are suitable for underwater coating systems. Paints based on cyclized rubber penetrate well into concretes. As they are also resistant to alkalis, they are ideal for swimming-pool paints and comparable applications. Chlorinated rubber is also suitable for road-marking paints.

Table II-1.7: Red corrosion protection paint

pos.	raw material	solids [wt.%]	density [g/cm³]	formulation [wt.%]
binder solution				
01	lower viscous chlorinated rubber	18.4	1.6	18.4
02	xylene			12.0
03	aromatic 100			6.4
pigment dispersion				
04	chlorinated paraffin plasticizer	10.9	1.2	10.9
05	red iron oxide	10.0	5.0	10.0
06	titanium dioxide rutile	8.0	4.1	8.0
07	barium sulphate	10.0	4.3	10.0
08	bentonite paste (10% in xylene/butanol)			2.0
09	xylene			6.2
10	aromatic 100			12.0
adjusting of viscosity				
11	aromatic 100			4.1
sum		57.3	–	100.0

pos. 01: Pergut S 10 (Bayer)
pos. 03, 10, 11: Shellsol A (bp: 165 to 185 °C, evaporation index 46) (Shell)
pos. 04: Hordaflex LC 47 (Clariant)
pos. 05: Bayferrox 130 BM (Bayer)
pos. 06: Bayertitan R-KB (Bayer)
pos. 07: Blancfix powder N (Sachtleben)
pos. 08: Bentone 38 (Elementis) 10% in xylene, butanol 8:1

The formulation of coatings particularly resistant to saponification requires the use of plasticizers which are also resistant to saponification, e.g. chlorinated paraffins or diphenoxyethyl formal, Desavin (Bayer). Suitable combination resins for cyclized rubber and chlorinated rubber are alkyd resins (medium oil and long oil grades), also “drying” oils, and resins containing rosin, alkyl and terpene phenolic resins, ketone resins, and bitumens. Low-viscosity chlorinated rubber in combination with bitumen is, for example, eminently suitable for thick-film coatings. Finally, chlorinated rubber may be used to prepare adhesives and printing inks.

As just mentioned, chlorinated rubber has to be stabilized. Stabilization consists of a small amount of metal oxides (e.g. 0.3 wt.% zinc oxide), metal soaps (e.g. 2.0 wt.% calcium naphthenate) or epoxy compounds (e.g. 2.0 to 6.0 wt.% epxidised soybean oil).

But, with regard to the different applications of chlorinated rubber, it should be taken into consideration that it is not compatible with high amounts of zinc oxide, zinc sulphide, or lead carbonate pigments. These may lead to gelling. Furthermore, the use of metal pigments (e.g. aluminium) requires special stabilization.

Formulation of red corrosion protection paint for steel constructions

The chosen [14] binders are a low-viscosity grade of chlorinated rubber and a chlorinated paraffin plasticizer. The pigments consist of titanium dioxide, barium sulphate, and red iron oxide. A bentonite paste is used as antisettling agent. The chosen solvents are Aromatic 100 and xylene. The details are shown in Table II-1.7.

Content of plasticizer expressed in terms of amount of binder: 37 wt.%

Pigment/binder ratio:

$$P/B = \frac{10.0 + 8.0 + 10.0}{18.4 + 10.9} = 0.96 : 1.00$$

Pigment volume concentration:

$$PVC = \frac{10.0 / 5.0 + 8.0 / 4.1 + 10.0 / 4.3}{10.0 / 5.0 + 8.0 / 4.1 + 10.0 / 4.3 + 18.4 / 1.6 + 10.9 / 1.2} \cdot 100\% = 23\%$$

Production:

First, a solution of 50 wt.% chlorinated rubber in xylene and Aromatic 100 (pos. 01 to 03) is prepared. The pigments and extenders are dispersed in the plasticizer and a portion of the solvent, together with the bentonite paste (pos. 04 to 11). Finally, the solution of chlorinated rubber is added and the viscosity is adjusted with the remaining amount of Aromatic 100. A portion of the solution of the chlorinated rubber may also be used to prepare the pigment paste. Additionally, a wetting agent may be added (for example, soya lecithin).

1.2 Oxidative-cure paints

1.2.1 Oxidative-cure reactions

Oxidative-cure of binders is often – but wrongly – called oxidative “drying” or “air-drying”. But the drying of a coating system is defined as the evaporation of solvents or dispersion medium after application. The term oxidative drying or air drying comes from the observation in the past that liquid oils (e.g. linseed oil) are transformed into solid films by absorption of atmospheric oxygen. The subjective impression is that a liquid has become a solid. But this process is a chemical reaction between the ingredients of such oils and the oxygen of the air, which leads to crosslinking.

For oxidative-cure, it is essential that the paint binders contain a significant amount of compounds with a minimum of two double bonds. The double bonds have to be isolated in the 1,4-position or conjugated in the 1,3-position. Such double-bond systems are only available in natural products, mainly fatty oils and their derivatives. The film forming reactions start with the addition of oxygen molecules across the system of double bonds. In the case of isolated double bonds, the addition of oxygen, which may be described as a bi-radical, takes place at the CH_2-group between the two double bonds in the 3rd position. The reaction leads to a hydroperoxide group. In contrast, the conjugated double bonds react mainly via 1,4 addition of oxygen to form a cyclic peroxide. Both types of peroxides may decompose into oxo radicals. This reaction is accelerated by metal cations acting as catalysts. The oxo radicals can initiate a free-radical polymerization process, but they also may react with other radicals in a recombination reaction. In all cases, C-O-C or C-C bridges are generated, and this leads to molecular networks. But the peroxides, the oxo radicals, and the ether bridges may also react by forming aldehydes and carboxylic groups, both reactions leading to cleavage of molecule linkages and restricting optimum film formation. Finally, film formation by means of oxidative-cure entails many different chemical reactions, which appear to be endless. The curing reaction, which yields a crosslinked molecular network, may evolve into a decomposition reaction in the event of aging and exposure. Thus, oxidatively cured films are not totally weatherable, unlike the case for films of other paint systems that also cure chemically. Studies of the reaction mechanisms underlying oxidative-cure have been reported in numerous papers since the 1950s, and are still going on.

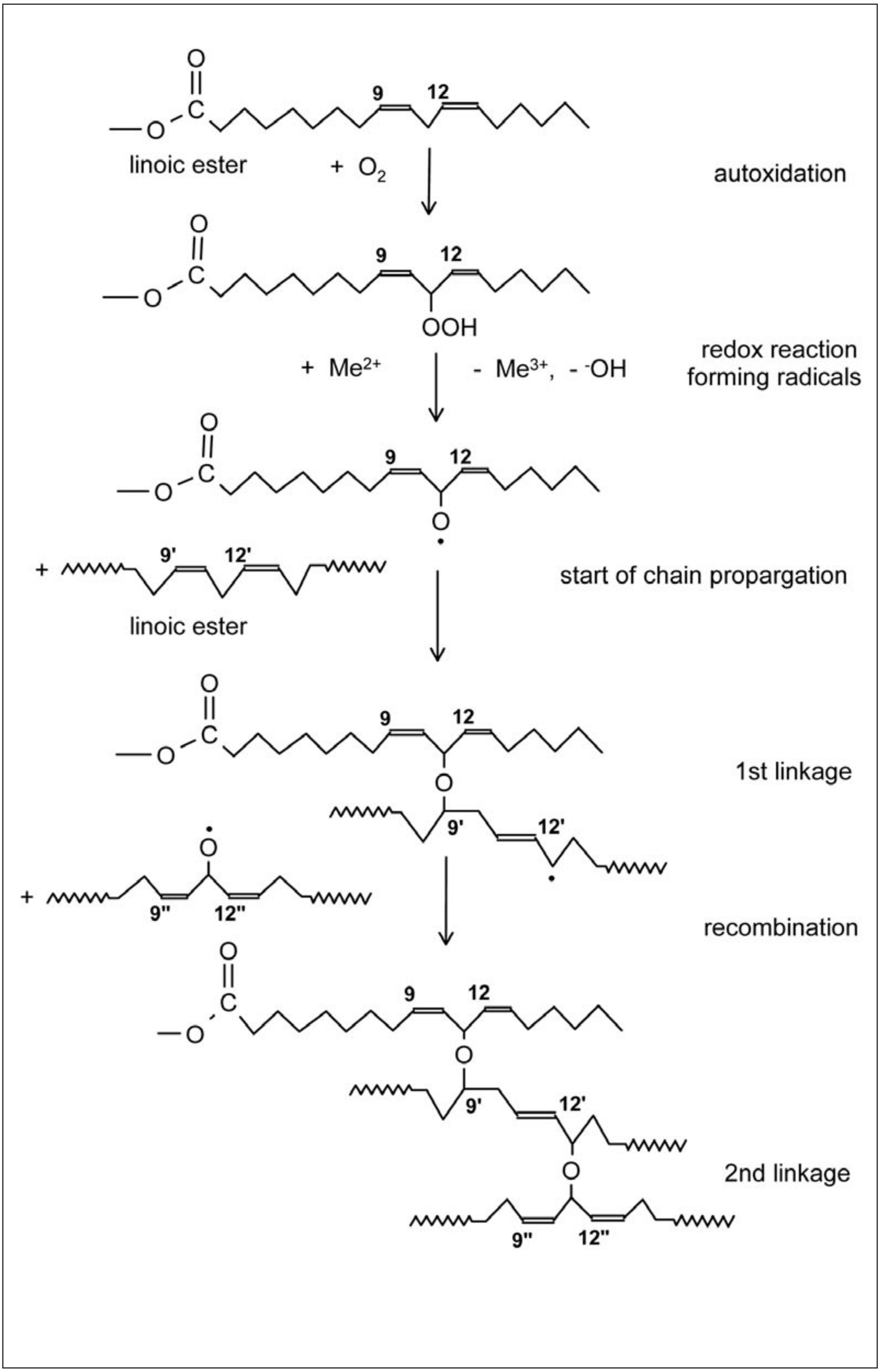


Figure II-1.5: shows a simplified example of the reaction of isolated double bonds.

Double-bond systems with isolated double bonds can take up higher amounts of oxygen, in contrast to systems with conjugated double bonds, which are more likely to form C-C bridges. But isolated double bonds can also be transformed into conjugated double bonds by isomerisation.

The reaction rate is accelerated by catalytic quantities of metal cations (see Chapter 1.2.3). Raising the temperature has only a minor effect on the reaction temperatures. However, conjugated double bonds at higher temperatures can react by means of a polymerization mechanism. They may be used for so-called 80 °C systems.

The base resins of oxidative-cure paints are renewable raw materials, and the curing reaction is harmless. Their use should therefore be supported, but the systems are not so common for industrial paint formulations, because the film-forming reactions do not fit in with the cycle times of industrial application processes, and they cannot be accelerated.

1.2.2 Binders for oxidative curing

“Drying” oils

The use of paint raw materials for oxidative-cure is linked to polyunsaturated compounds (i.e. those containing two or more double bonds) derived from natural fatty oils (triglycerides) [4]. When such oils contain significant quantities of polyunsaturated fatty acids, they are defined as “drying” oils (but see the comment in Chapter 1.2.1) and may serve as the sole binders. Since oils have relatively low molar masses (e.g. the triglyceride of 9,12,15-linolenic acid has a molar mass of 872 g/mol), they must contain enough functional groups for curing to be effective. Natural “drying” oils are linseed oil, perilla oil, fish oils, wood oil, and oiticica oil.

“Semi-drying” oils

Oils that contain a significant amount of fatty acids with two double bonds, but do not form wholly crosslinked films are called semi-drying oils. When these oils are the basis for binders used in high-molecular resins (e.g. alkyd resins), they can be effectively formulated as oxidative-cure systems. The natural bases for these fatty acids are cottonseed oil, soya bean oil, sunflower oil and safflower oil. Another important source of this type of fatty acid is tall oil, a by-product of the chemical wood pulping that consists of fatty acids with a fairly high content of linoleic acid and rosin acids.

“Non-drying” oils

Oils that contain fatty acids with only one double bond (e.g. oleic acid) and triglycerides that contain saturated fatty acids (e.g. coconut fat, palm kernel oil) are classified as non-drying oils and fats. Resins from these sources are unable to take up oxygen to form cured films. The fatty acids are used for incorporating plasticizing effects into binders (e.g. in combination with physically drying polymers, see Chapter 1.1.1) or for binders that crosslink by another reaction mechanism, such as stoving enamels and acid-cured systems.

Oxidatively curing resins modified with fatty acids having 2 & more double bonds include: alkyd resins, oil-modified phenolic resins, epoxy esters and special polyurethanes.

Alkyd resins

Alkyd resins are still the most important class of binders for paint materials. A great many different grades are commercially available. They are produced from phthalic anhydride, polyalcohols with three or four functional groups (pentaerythritol, glycerol, and trimethylolpropane) and the above-mentioned fatty acids or oils. In some cases, different raw materials may be used – isophthalic acid instead of phthalic anhydride, benzoic acid or rosin acids instead of the fatty acids, and mixtures of pentaerythritol with diols instead of the triols. The grades chosen for oxidative-cure paints have high molar masses, low hydroxyl numbers (mainly less than 50 mg KOH/g), and low acid numbers (between 3 and 20 mg KOH/g).

Alkyd resins are classified roughly into three groups on the basis of their content of oil or fatty acids.

• Long oil alkyds	More than 60% oil or fatty acid
• Medium oil alkyds	40 to 60%
• Short oil alkyds	Below 40%

Oxidative-cure alkyds are mainly medium to long oil grades since the amount of fatty acids has to be adequate for the curing process. Long oil alkyds are based mainly on pentaerythritol as polyalcohol. A molecular structural unit of such an alkyd resin containing 1 mole phthalic acid, 1 mole pentaerythritol and 1.8 moles linoleic acid (see Figure II-1.6) contains 64.0 wt.% fatty acid, 17.2 wt.% pentaerythritol and 18.8 wt.% phthalic ester.

Although alkyd resins have relatively high molar masses due to the high content of aliphatic fatty acids, they are still viscous liquids. Solidification of the films is achieved only after thorough curing. The products exhibit optimum wetting, good levelling, and appearance (filling power).

Where faster initial drying is required, medium oil alkyds are chosen. The best way to formulate such types of alkyds is to replace some of the fatty acid in the above-mentioned penta-alkyds with benzoic acid. This still provides scope for the production of alkyds with fairly high molar masses. The molecular structure of such an alkyd is shown in Figure II-1.7, and contains 1 mole phthalic acid, 1 mole pentaerythritol, 1.2 moles fatty acid and 0.6 moles benzoic acid, and so consists of 48.4 wt.% fatty acid, 21.4 wt.% phthalic ester, 19.6 wt.% pentaerythritol and 10.6 wt.% benzoic acid. Due to the lower quantity of fatty acids containing double bonds, the curing rate is lower, but the initial physical drying is much faster.

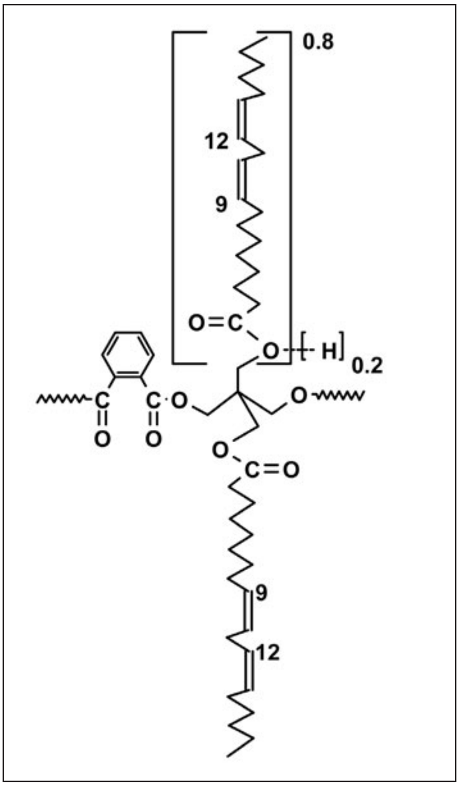


Figure II-1.6: Structural unit of a long oil alkyd resin

As alkyd resins containing fatty acids of linseed oil contain significant amounts of linolenic acid with three isolated double bonds, they undergo very rapid chemical cure and, additionally, have excellent wetting properties. Since this fatty acid can react continuously with oxygen, films of such alkyds tend to yellow and embrittle during weathering. Such alkyds may be improved in their curing efficiency and flexibility by combining linseed oil with a small portion of wood oil. Alkyds with better initial drying properties contain mixtures of linseed fatty acids and rosin acids.

As described, there are numerous ways to modify oxidative-cure alkyd resins.

A special product group are combinations of long oil alkyds with an excess of drying oils. The total content of fatty acids may be higher than 70 wt.%. These combinations are suitable for the formulation of high-solids house paints. Due to the high content of fatty oil, the curing process is very effective, but the initial solidification time is relatively long.

Styrene-modified alkyd resins [1 to 3]

Alkyd resins modified with styrene consist of copolymers of alkyds and styrene. They are characterized by excellent initial drying. Comparable resins are copolymers of alkyds and vinyl toluene or methacrylic esters.

Thixotropic alkyd resins

A partial reaction between alkyd resins and polyamides (from polymeric fatty acids and polyamines) leads to thixotropic alkyd resins [1 to 3]. Due to their rheology, they serve as the basis for oxidative-cure paints with controlled sag.

Urethane alkyds and urethane oils

Replacing some of the phthalic anhydride in an oxidative-cure alkyd resin with toluene diisocyanate yields urethane alkyds. Total replacement of phthalic anhydride leads to so-called urethane oil [1 to 3]. In comparison to conventional alkyds, the two resin grades are distinguished by faster initial drying and better mechanical resistance of their films.

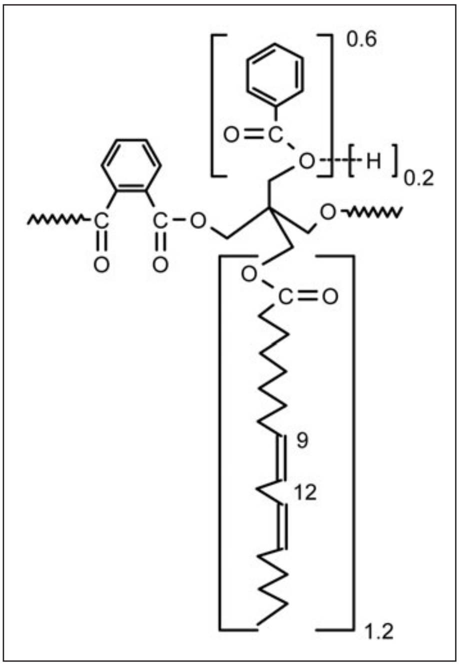


Figure II-1.7: Structural element of a medium oil alkyd modified with benzoic acid

Additionally, there are oxidative-cure alkyd resins that are modified with silicone resins, epoxy resins, and metal alcoholates (e.g. aluminium isopropylate).

Aromatic epoxy resins and polyunsaturated fatty acid form the oxidative-cure epoxy esters [1 to 3]. Films containing epoxy esters have excellent adhesion and good chemical resistance (see Chapter 1.2.6).

1.2.3 Siccatives and anti-skinning additives

Siccatives

As already mentioned, the oxidative-cure reaction is accelerated by adding catalysts. These catalysts are the salts of special metals and organic acids. The products are called driers or siccatives [9]. Empirical trials and studies showed that salts of cobalt, manganese and lead are particularly effective. Since soluble chemical compounds of lead are toxic, and also cobalt salts are classified as harmful to health and environmental, efforts were made to find substitutes. Today, organic salts of zirconium are preferred to those of lead. Replacements for cobalt salts must be found by the end of 2012. Current candidates include organic salts and complex compounds of vanadium, manganese, cerium, and iron.

The catalytic effect is based on the redox potential of the metal cations, which have different oxidation valencies. The oxidation of metal cations reduces the hydroperoxide of the autoxidation process, leading to the formation of an oxonium ion and an oxo radical (see Figure II-1.5).

The preference of the aforementioned metals is probably also linked to their ability to form associates. It is assumed that the metal cations form complexes with the oxygen compounds. This assumption stems from the observation that metal cations which exist only in one oxidation state also support the oxidative-cure reactions. Probably, they are able to form oxygen complexes. Organic salts in use are those of calcium, barium, magnesium, strontium, zinc, and lithium. The products are called auxiliary driers. Polyvalent metals of the series may also react with the carboxylic groups of alkyd resins, and in this way support the crosslinking process. Some of the metal salts (e.g. calcium octoate) are capable of wetting pigments.

Thanks to observations that mixtures of siccatives produce positive synergistic effects, combinations of metal salts are often used and are also available as commercial products. In the past, the best known combinations were those of cobalt and lead. The different acceleration effects of the two metal cations optimizes the balance between surface cure and full cure. Accordingly, combinations of cobalt and lead driers were used in the past. A more modern combination employs organic vanadium and zirconium salts.

The organic acids for the siccatives are selected for optimum solubility and compatibility. In the past, acids with long aliphatic chains (e.g. technical grade linoleic acid or oleic acid for linolates or oleates) and rosin acids (for resinates) were used. These later ceded ground to salts of naphthenic acid (the naphthenates) obtained from petroleum. Currently, most siccatives are salts of synthetic monocarboxylic acids, which are produced by the oxo process. Until now, 2-ethylhexanoic acid was the most commonly employed product. However, its use is restricted due to concerns about its harmful effects on health. Suitable replacements are iso-nonanoic acid (3,5,5-trimethylhexanoic acid) and neo-decanoic acid (mostly 2,2,3,5-tetramethylhexanoic acid).

Since the oxidative-curing process – as mentioned above – is a really complex reaction in which crosslinking and rupturing of bonds occur simultaneously, the dosage of siccatives is critical. Minimal amounts are needed for efficient curing. Adding too much impairs film formation and film properties.

The quantities of some siccatives that cause discoloration are also restricted (organic salts of cobalt, manganese, and iron). And, of course, some of them are expensive additives.

Commercially available siccatives are characterized by their metal content.

Some pigments are also capable of accelerating the oxidative-cure process, e.g. iron oxides (mainly the transparent grades due to their large surface area), metallic zinc pigments, zinc oxides, calcium carbonates and lead pigments (but their use is restricted on account of their toxicity). Other pigments may act as inhibitors for the oxidative-curing process, e.g. carbon blacks, ultramarine pigments and some phthalocyanine pigments. They adsorb siccatives on their surfaces. Thus, either the amount of siccative addition has to be increased or some siccative is added when the paint is taken out of storage.

Anti-skinning additives

Due to the reaction of atmospheric oxygen with the surface of oxidative-cure liquid paints stored in containers, there is the possibility that crosslinking will take place. In such cases, an insoluble layer resembling a skin is formed on the surface of the paint. This effect is enhanced if the siccatives – due to their surfactant-like molecular structure – concentrate on the surface of the paint material. It may be counteracted by the use of anti-skinning additives.

Principally, anti-skinning additives are reducing compounds which react with the oxygen and so prevent oxidative-curing reactions from starting. Additionally, the anti-skinning agents can form complex compounds with the siccative, and that reduces their redox efficiency. There are two groups of additives: alkyl phenols (e.g. di-tert.-butyl-p-cresol) and ketoximes. The phenols are not volatile and inhibit the reaction at the start of the curing process. That is not necessarily a disadvantage since a delay in oxidative crosslinking at the start of curing may be beneficial for levelling, gloss and full curing. In general, ketoximes are volatile. During the initial drying process, the complex compounds formed with the siccatives decompose, and the curing reaction is not hindered. But investigations have uncovered physiological risks associated with the most common grade in the past, methyl ethyl ketoxime, which is suspected of being carcinogenic. It is going to be replaced by other ketoximes or hydroxylamines and their derivatives. Often, a combination of phenols and ketoximes is used for anti-skinning in oxidative-cure paints.

1.2.4 Oil varnishes

Oil varnishes are the classic oxidative-cure paints [4]. Oil varnishes have been used since ancient times for the protection of articles and by artists. The most commonly used oil was linseed oil. Since then, there have been a lot of trials to fasten the “drying” efficiency of oils. The first observation was that white lead (lead II oxide), used as a pigment, additionally shortens the “drying” time. This observation probably led to the use of siccatives. Another was that oils stored in sunlight became much more viscous and the resultant stand oils had much better film forming properties. To accelerate film formation by additional physical drying, oils and stand oils were combined with rosin. But as the use of recent rosins in oil varnishes yields soft films at elevated temperatures (they become tacky), fossil rosins (copal and amber) were used for combination with oils. As demand grew for relatively fast curing paints and the raw rosin materials became scarce, paint chemists stepped onto the scene and finally synthetic resins were developed which led to combinations with oxidative-cure oils.

The most important were the oil-reactive alkyl and aryl phenolic resins. These resins were combined mainly with oils containing conjugated double bonds (tung oil) in a hot blend process. The products containing these combinations made excellent oxidative-cure varnishes for marine paints and bench lacquers. They are still used today, but in smaller amounts. Combinations of oxidative-cure oils with rosin esters, lime-hardened rosins and ketone resins are no longer used for paints, but there are still some applications to be found in printing inks. Today, oxidative-cure oils and stand oils play a minor role in the formulation of high-solids house paints. And, of course, oxidative-cure oils are still the basis of artist’s paints.

1.2.5 Alkyd resin paints

Alkyd resin paints are still the most widely used solvent-borne systems.

Long oil alkyds, which are derived from fatty acids with high contents of 9,12-linoleic acid (sources are cottonseed oil, sunflower oil, safflower oil and tall oil acids with a low content of rosin acids) are used for house paints, DIY systems and topcoats (low yellowing and relatively good weatherability). They are also used for corrosion protection paints. Grades with particular high oil contents are used for high-solids paints (see example).

Alkyd resins with **medium oil lengths** that cure oxidatively and are based on the same grades of fatty acids as mentioned above find application in non-yellowing, faster-drying paint systems, e.g. paints for trucks and agricultural implements, automotive repair coats, radiator paints and other industrial paint systems.

Long oil alkyds based on linseed oil are preferred for house paints, wood paints, and printing inks. They have a tendency to yellow.

Medium long oil alkyds based on linseed oil are used mainly in corrosion protection paints.

Medium oil and short oil alkyds that are modified with rosin acids in addition to unsaturated fatty acids are used for oxidative-cure primer surfacers, fillers and putties.

Oxidative-cure **alkyds modified with styrene, vinyltoluene and methacrylic acid esters** that contain linseed fatty acids or are rich in 9,12-linoleic acid are used for fast-drying machine enamels, corrosion protection paints, paints for agricultural implements and comparable applications.

Thixotropic alkyd resins are mainly used for DIY paints.

Urethane alkyd resins and **urethane oils** are preferred for the production of fast-drying wood paints, for parquet varnishes and for printing inks.

Alkyd resins modified with epoxies are mainly used for all kinds of primers.

Alkyds modified **with metal alcoholates** are particularly used for industrial primers and fast-drying machinery enamels.

Examples of commercial grades of long oil alkyds:

Setal F 48 (Bayer), Setal 198 (Nuplex), Synthalat SR 46 (Synthopol Chemie), Vialkyd AF 474 (Cytec, Surface Specialties Vianova)

Examples of commercial grades of medium oil alkyds [8]:

Alkydal F 48 (Bayer), Setal 198 (Nuplex), Synthalat SR 46 (Synthopol Chemie), Vialkyd AF 474 von (Cytec, Surface Specialties, Vianova)

Examples of commercial linseed alkyds [8]:

Setal 234 (Nuplex), Uralac AD 142 (DSM), Synthalat L 555 (Synthopol Chemie), Vialkyd AL 544 (Cytec Surface Specialties Vianova)

Table II-1.8: Oxidative curable, white, glossy topcoat for industrial application

pos.	raw material	solids [wt.%]	density [g/cm³]	formulation [wt.%]
pigment dispersion				
01	alkyd resin, curing oxidatively, 48% fatty acid, (55 wt.% in white spirit, xylene 38/7)	11.81	1.2	21.48
02	titanium dioxide rutile	28.80	4.1	22.80
03	calcium-wetting agent (10 wt.% Ca)			0.87
04	aromatic 100			7.20
completion of paint				
05	alkyd resin, curing oxidatively, 48% fatty acid, (55 wt.% in white spirit, xylene 38/7)	29.34	1.2	42.42
06	alkyl phenolic resin (50 wt.% in xylene)	0.70	1.2	1.40
07	siccative iron complex compound			0.25
08	silicone oil (1 wt.% in xylene)			1.05
09	antiskinning agent (oxime-free)			0.33
10	methoxy propyl acetate			2.20
sum		64.65		100.00

pos. 01, pos. 05: Alkydal F 48 (Bayer)
pos. 02: Crenox R-KB-4 (Crenox)
pos. 03: Octa Soligen Calcium (Borchers)
pos. 04: Solvesso 100 (Exxon)
pos. 06: Tungophen (Bayer)
pos. 07: Borchers OXY-Coat (Borchers)
pos. 08: Baysilon paint additive MA (Borchers)
pos. 09: Borchi Nox M2 (Borchers)
pos. 10: solvent (BASF SE)

Formulation of an oxidative-cure, glossy, white topcoat for industrial applications:

A medium oil alkyd [20] is chosen that consists of a 48 wt.%, vegetable fatty acid rich in 9,12-linoleic acid. The pigment is titanium dioxide (rutile). It is ground in the alkyd solution with the aid of calcium octoate as wetting agent. The resultant pigment paste is let down with another portion of the alkyd solution. A small portion of an alkyl phenolic resin is added for gloss optimization. The siccative is a special iron complex which is effective in small amounts and avoids discoloration (cobalt-free system). To promote optimum levelling, a silicone oil solution combined with methoxypropyl acetate is added. The anti-skinning additive is oxime-free. All details of the formulation are presented in Table II-1.8.

Production: The ingredients of items 01 to 04 are mixed and pre-dispersed on a dissolver. The resulting pigment paste is ground on a sand or pearl mill to the required fineness. Then the pigment paste is let down with the raw materials of items 05 to 11 in the given order. After each addition, the mixture has to be stirred intensively. The viscosity of the topcoat is then adjusted to spray viscosity by adding a mixture of xylene and Aromatic 100 (in the ratio 5 : 5).

Pigment/binder ratio:

$$P/B = \frac{0.8}{1.0}$$

Pigment volume concentration:

$$PVC = \frac{26.70 / 4.1}{26.70 / 4.1 + 33.71 / 1.2} \cdot 100\% = 19\%$$

Exercise

Develop formulations for two oxidative-cure alkyd paints which differ significantly in the amount of pigment (PVC). More particularly, one pigment dispersion is to be used for completing both paints. The paints should be based on an oxidative-cure alkyd resin with a high amount of unsaturated fatty acid (long oil alkyd). The pigment to binder ratio has to be a) 1 : 1 and b) 4 : 1. The non-volatiles content is to be 85 wt.%. The pigmentation is to consist of red iron oxide and an extender in the ratio 1 : 1.

Selection of raw materials:

1. Long oil alkyd : oil content 80 wt.%, acid number <15 mg KOH/g, delivery form: 100%, (e.g. Synthalat HS 80, Synthopol)
2. Pigment: red iron oxide, ρ = 5.1 g/cm³ (e.g. Bayferrox 180, Bayer)

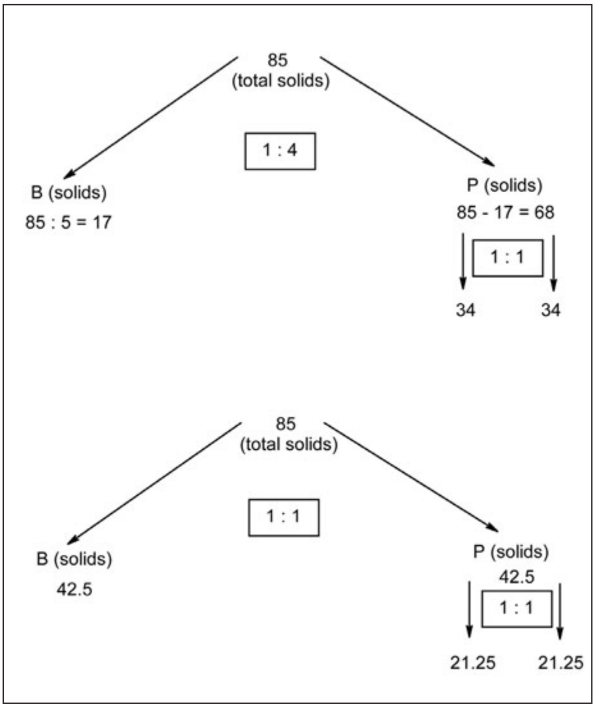


Figure II-1.8: Development of formulations of oxidative-cure alkyd paints

3. Extender: barium sulphate, $\rho = 4.1$ g/cm^3, (Blanc fixe N, Sachtleben)
4. Solvents: white spirit, xylene, butanol, methoxypropyl acetate
5. Additives:
   Siccative: based on the mixture of Co, Ba and Zr salts (Dryer 173, Borchers)
   Anti-skinning additive: phenol derivative (Ascinin P, Borchers)
   Dispersing agent: salt of an anionic copolymer (Disperbyk 180, Altana-Byk)

The development of both formulations is presented in Figure II-1.8

The developed paint formulation with a P/B of 4 : 1 (see Figure II-1.8) yields the calculation recipe presented in Table II-1.8:

Table II-1.9: Formulation of the alkyd paint with P : B = 4 : 1

pos.	raw material	solids [wt.%]	density [g/cm³]	formulation [wt.%]
01	alkyd resin (100%)	17.0	1.2	17.0
02	red iron oxide	34.0	5.1	34.0
03	extender	34.0	4.1	34.0
04	dispersing agent			3.3
05	siccative			0.6
06	antiskinning agent			0.4
07	solvent mixture			10.7
sum		85.0		100.0

The PVC of the paint with a P/B = 4 : 1 is calculated as follows:

$$\text{PVC} = \frac{34.0 / 5.1 + 34.0 / 4.1}{34.0 / 5.1 + 34.0 / 4.1 + 17.0 / 1.2} \cdot 100\% = 51.4\%$$

The developed paint formulation with a P/B = 1 : 1 (see Figure II-1.8) yields the calculation recipe presented in Table II-1.9:

Table II-1.10: Formulation of the alkyd paint with P : B = 1 : 1

pos.	raw material	solids [wt.%]	formulation [wt.%]
01	alkyd resin (100%)	42.50	42.50
02	red iron oxide	21.25	21.25
03	extender	21.25	21.25
04	dispersing agent		2.10*
05	siccative		1.50**
06	antiskinning agent		1.00**
07	solvent mixture		10.40
sum		85.00	100.00

* *calculated on the different amount of pigment*
** *calculated on the different amount of binder*

The PVC of the paint with a P/B = 1 : 1 is calculated as follows:

$$\text{PVC} = \frac{21.25 / 5.1 + 21.25 / 4.1}{21.25 / 5.1 + 21.25 / 4.1 + 42.5 / 1.2} \cdot 100\% = 20.9\%$$

Production:
For the pigment paste (mill base), the ratio of pigment to binder is chosen to be 4 : 1. The paint with the high content of pigment (P/B = 4 : 1) is easily completed by adding solvents and additives. But the paint with lower content of pigment (P/B = 1 : 1) can also be produced by adding alkyd resin, solvents and additives.

The formulation for the pigment dispersion is presented in Table II-1.10.

The formulation for completion of the paint with a P/B = 4 : 1 is presented in Table II-1.11.

For completion of the paint with P/B = 1 : 1, the mill base is let down with an amount of alkyd resin such that the final formulation contains the same amounts of pigment and binder. The formulation for this is presented in Table II-1.12

Both paints, produced in the laboratory, are applied to steel panels. The drying time is one week at room temperature. For a second test series, some of the panels are additionally dried for two hours at 80 °C. The results of tests on the films are presented in Figure II-1.9.

The test results clearly show that the higher pigmentation reduces the gloss and the flexibility, but has no effect on hardness. The postcuring (2 hours at 80 °C) generally reduces gloss and flexibility and the hardness increases. That means that the oxidative-cure reaction still has not finished after one week at room temperature. If the hardness is low, it is

Table II-1.11: Formulation for pigment dispersion with P : B = 4 : 1

pos.	raw material	parts by weight
01	alkyd resin (100%)	17.9
02	red iron oxide	35.8
03	extender	35.8
04	dispersing agent	3.5
05	solvent mixture (partly amount)	7.0
sum		100.0

A loss during dispersing process is not taken into consideration.

Table II-1.12: Completion of the pigment paste for the paint with P : B = 4 : 1

pos.	raw material	formulation [wt.%]
01	pigment paste (70 wt.%)	94.9
02	siccative	0.6
03	antiskinning agent	0.4
04	solvent mixture (partly amount)*	4.1
sum		100.0

** = adjust on required viscosity*

Table II-1.13: Completion of the pigment paste for the paint with P : B = 1 : 1

pos.	raw material	formulation [wt.%]
01	pigment paste (70%)	59.4
02	alkyd resin (100%)	31.9
03	siccative	1.5
04	antiskinning agent	1.0
05	solvent mixture (partly amount)*	6.2
sum		100.0

** = adjust on required viscosity*

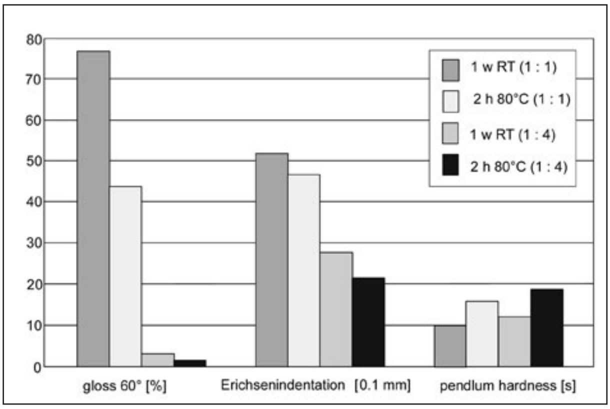


Figure II-1.9: Gloss, indentation (Erichsen) and pendulum hardness of the two alkyd paints

necessary to optimize the type and quantity of siccative.

1.2.6 Paints based on epoxy ester resins

Epoxy ester resins (EPE) are synthesized from bisphenol A-epoxy resins (e.g. type 4) and suitable unsaturated fatty acids (Figure II-1.10) at elevated temperatures.

Like "drying" alkyd resins, epoxy esters are used as oxidatively curing binders. It should be noted that only cobalt soaps are added as siccatives ("driers") to paints based on epoxy esters. Recently, toxicological concerns have been expressed with respect to cobalt driers. Thus, alternatives such as manganese or vanadium driers should be considered. The epoxy resin chain is nonsaponifiable whereas alkyd resins are saponifiable. Thus, epoxy esters lead to coatings whose humidity resistance is greater than that of alkyd resins. Furthermore, epoxy esters adhere well on metals and have corrosion-protection properties. They are therefore mostly used in anticorrosive primers.

The poorly saponifiable epoxy esters are used especially as binder in one-component, zinc-rich primers, which differ significantly from other types of anticorrosive primers in terms of their pigment/binder ratio. For this reason, zinc-rich primers will now be discussed more in detail.

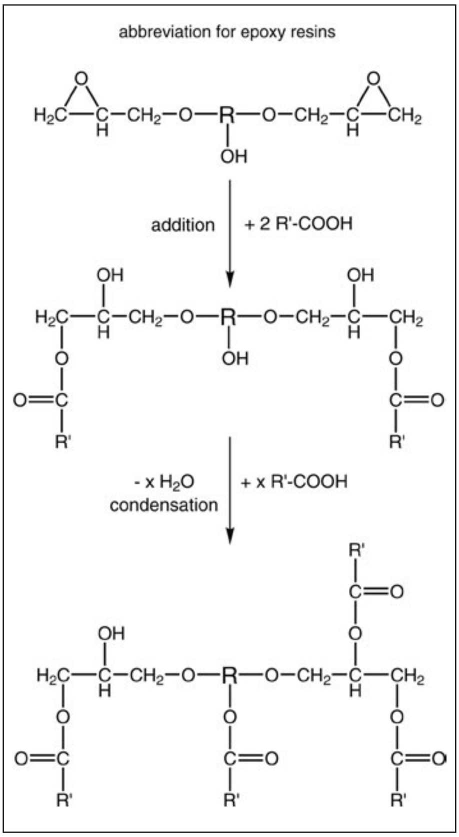


Figure II-1.10: Synthesis of epoxy ester resins

Zinc dust is an active anticorrosion pigment which is produced in two different ways:

- Distillation and condensation of zinc metal (m.p. 419 °C, b.p. 907 °C)
- Atomization of a zinc melt

Both processes yield more or less spherical zinc dust of different particle sizes, and the particle-size distribution is frequently broad (Figure II-1.11, Table II-1.14).

The most important requirement that enables zinc-rich primers to afford corrosion protection is a PVC close to or above the CPVC. In such cases, the zinc pigment particles are in metallic contact both with each other and with the iron substrate. As a result, the iron is cathodically protected because zinc is electrochemically less noble than iron. Zinc therefore acts as a sacrificial anode.

The weight ratio of zinc dust : binder in zinc-rich primers ranges from 90 : 10 to 95 : 5.

Therefore, the pigment/binder ratio P/B is 9 : 1 to 19 : 1. On this basis, the volume ratios of zinc dust : binder computes to 60 : 40 to 76 : 24. The PVC is 60 to 76 vol.% and, therefore, in the range of the hexagonal close packing of uniform spheres of 74 vol.%. Because of the high PVC, the mechanical properties of zinc-rich primers are mostly not very good.

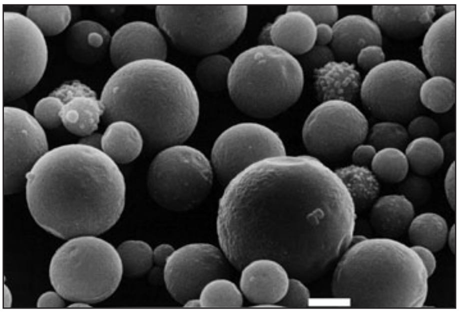


Figure II-1.11: Scanning electron micrograph of zinc dust ("super- fine") scale bar 1 µm

The corrosion-protection action of zinc-rich primers is based on three effects:

- Electrochemical protection (see above)
- Sealing action
  Over the course of time, sparingly soluble corrosion products of zinc are formed, e.g. basic zinc carbonate [$ZnCO_3 \cdot x\ Zn(OH)_2$]. These products reinforce the coating and fill out minor damage ("cementation"). The initially porous coating becomes densified.
- Chemical protection
  Corrosion products of zinc, such as ZnO and $Zn(OH)_2$, act as active corrosion-protection pigments because they are able to bind corrosion-stimulating substances, e.g. chloride ions in the sparingly soluble base zinc chloride [$ZnCl_2 \cdot 4\ Zn(OH)_2$].

Zinc-rich primers are mostly used in maintenance coatings, such as coatings for steel constructions and marine coatings. They can be coated with a topcoat, which needs to be carefully formulated with regard to the zinc-rich primer [16].

The formulation of zinc-rich primers (Table II-1.15) proceeds as follows.

Pigment/binder ratio P/B = 75 : 7.8 = 91 : 9

$$PVC = \frac{75 / 7.1}{75 / 7.1 + 7.8 / 1.2} \cdot 100\% = 62\%$$

Because of the coarse particle size and the high density of zinc dust (Table II-1.14), zinc-rich primers (Table II-1.15) always need an antisettling agent; hydrophobic fumed silica is the most important of these [17]. The zinc pigment and fumed silica are dispersed in the epoxy ester solution by means of a dissolver. During storage of zinc-rich primers, zinc pigments may react with traces of water to evolve hydrogen ("gassing"):

Table II-1.14: Data for zinc dust

zinc dust	characteristic
particle shape	spherical
particle diameter	4 to 8 µm
zinc content (total)	98.5 to 99.7%
zinc content (metal)	94.0 to 97.5%
density	7.1 g/cm³

Table II-1.15: One-component zinc-rich primer based on epoxy ester

pos.	parts by weight		solids
01	13.0	epoxy ester resin (60% in xylene)	7.8
02	75.0	zinc dust	75.0
03	1.0	hydrophobic fumed silica	1.0
04	0.5	dehydrating agent	0.5
05	0.1	cobalt siccative (6% Co)*	
06	5.4	xylene	
07	5.0	Solvesso 100	
sum	100.0		84.3

pos. 01: epoxy ester resin based on "drying" conjugated fatty acids, 40% oil content, 60% epoxy content; e.g. Worléedur D 46
pos. 03: hydrophobic fumed silica as antisettling agent; e.g. Aerosil R 972
pos. 04: dehydrating agent to remove traces of water; e.g. molecular sieve Sylosiv A 4
** replace if necessary*

$Zn + 2\ H_2O \rightarrow Zn(OH)_2 + H_2$

For this reason, dehydrating agents are added to bind traces of water [18].

The grey zinc-rich primers can be coloured with small amounts of, e.g., iron oxide red to facilitate application on blasted steel substrates, which are grey too.

Zinc-rich primers can also formulated as two-component, amine-cured epoxy systems (see Chapter II-1.3.2).

1.3 Two-component systems

Most of the coating systems which cure by chemical reactions have two resin components. But only systems whose two reaction components have to be mixed immediately before application satisfy the definition of a two-component system. That means they have to be delivered separately. This is a necessary condition if the two components of such a resin system are to be able to react at ambient temperatures. The best known examples of such systems are two-component polyurethane paints and two-component epoxy paints. The larger part of such a system, which also mostly contains the pigments, is defined as the base component (or A-component). The smaller part – mostly without any pigment – is called the hardener (or B-component).

As mentioned above, the components have to be mixed just before application. Often, mixing is carried out in a container fitted with a stirrer. But many applications require the possibility of manual mixing. Mixing may also take place in a two-component spray gun containing a static mixer. Once both components have been mixed, the application time is limited; this time restriction is called the pot-life. The pot-life is the period of time during which the mixed system can be applied without any problems. A rough indication of the pot-life is the time required for the viscosity to double. During this time, the application viscosity may be adjusted by adding solvents. The pot-life should range from 3 to 6 hours.

There are other paint systems whose components are added just before application: initiators to UP resin systems, and acid catalysts to acid-curable paints. But these systems are not defined as two-component paints because the additives are not resin components that form a part of the film structure. They are more comparable with other additives and solvents which may be added.

1.3.1 Two-component polyurethane paints

1.3.1.1 Reactions of isocyanates

Isocyanates are very reactive. At ambient temperatures (room temperature and even below), they can react with partner compounds containing active hydrogen atoms, such as amines (primary and secondary) and alcohols. This property is exploited in the formulation of paint systems in so far as, in particular, polymers bearing reactive hydroxyl groups are combined with isocyanates, which act as hardener. Because the crosslinking reaction yields urethane groups, the systems are called two-component polyurethane paints. This term should not be confused with the polyurethanes used as plastics or as binders for paints that dry physically.

The reaction of isocyanates with resins containing hydroxyl groups proceeds sufficiently at room temperature. The reaction may be accelerated by adding catalysts and/or raising the temperature. Raising the temperature has less impact on acceleration than in the case of other crosslinking reactions (e.g. crosslinking with amino resins). Furthermore, the reaction rate is dependent on the type of isocyanate group. Aromatic isocyanates react much

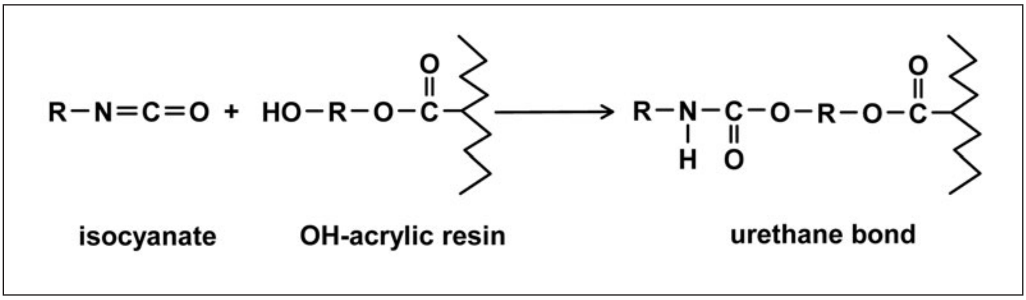


Figure II-1.12: Reaction of isocyanates with resins containing hydroxyl groups

faster than the aliphatic kind, which in turn react faster than cycloaliphatic isocyanates. Steric effects additionally have an influence. The differences are shown in Figure II-1.13.

The rate of the reaction between isocyanates and primary and secondary amines is very high. Accordingly, this combination is unsuitable for paint systems. However, there are ways of slowing down the rate that allow this combination to be used in paints. The preferred methods are masking or blocking of the reactive groups (amines or isocyanates; see Part IV).

Isocyanates react with water to form carbaminic acids, which are unstable and decompose into primary amines and carbon dioxide. The primary amines react very rapidly with the remaining isocyanate groups to form urea linkages. These reactions offer scope for formulation systems which cure by means of atmospheric humidity. The reaction is a side reaction if two-component systems are applied at ambient temperatures and high relative humidity. The crosslinking reaction generates urethane and urea linkages. Several studies have shown that the urea groups which form have less negative impact than was initially assumed. Admittedly, the stoichiometric relationships are changed by this reaction.

Traces of water are present in some of the raw materials of two-component polyurethane systems. As they have to be eliminated, special compounds are added to react with the water. These include toluene sulphonic isocyanate, ethyl orthoformate, oxazolidines, as well as molecular sieves.

1.3.1.2 Isocyanate crosslinkers (hardeners for two-component polyurethanes)

Crosslinking of resin systems bearing more than two hydroxyl groups requires the use of isocyanates that also have at least two functional groups. The following diisocyanates are available (on an industrial scale): toluene diisocyanate (TDI, mostly the 2,4-isomer, with a lesser amount of 2,6-isomer), methylene diphenyl diisocyanate (MDI, 4,4'-diisocyanato-diphenylmethane), hexamethylene diisocyanate (HDI, 1,6-hexane diisocyanate), isophorone diisocyanate (IPDI, 3-isocyanatomethyl-3,5,5-trimethyl-cyclohexylisocyanate), hydrogenated MDI (HMDI, 4,4'-diisocyanato-dicyclohexyl-methane), xylyene diisocyanate (XDI),

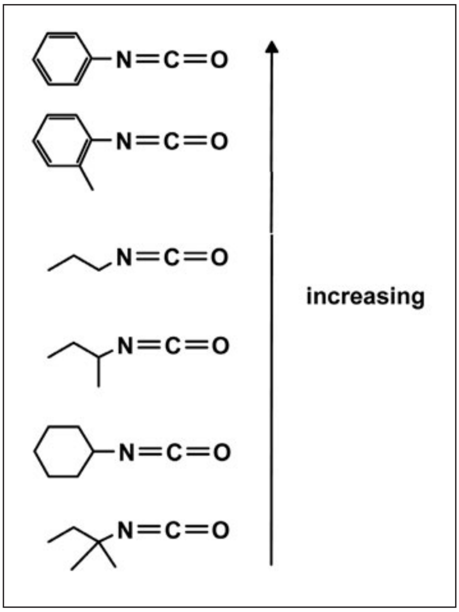


Figure II-1.13: Reaction rates of different isocyanates

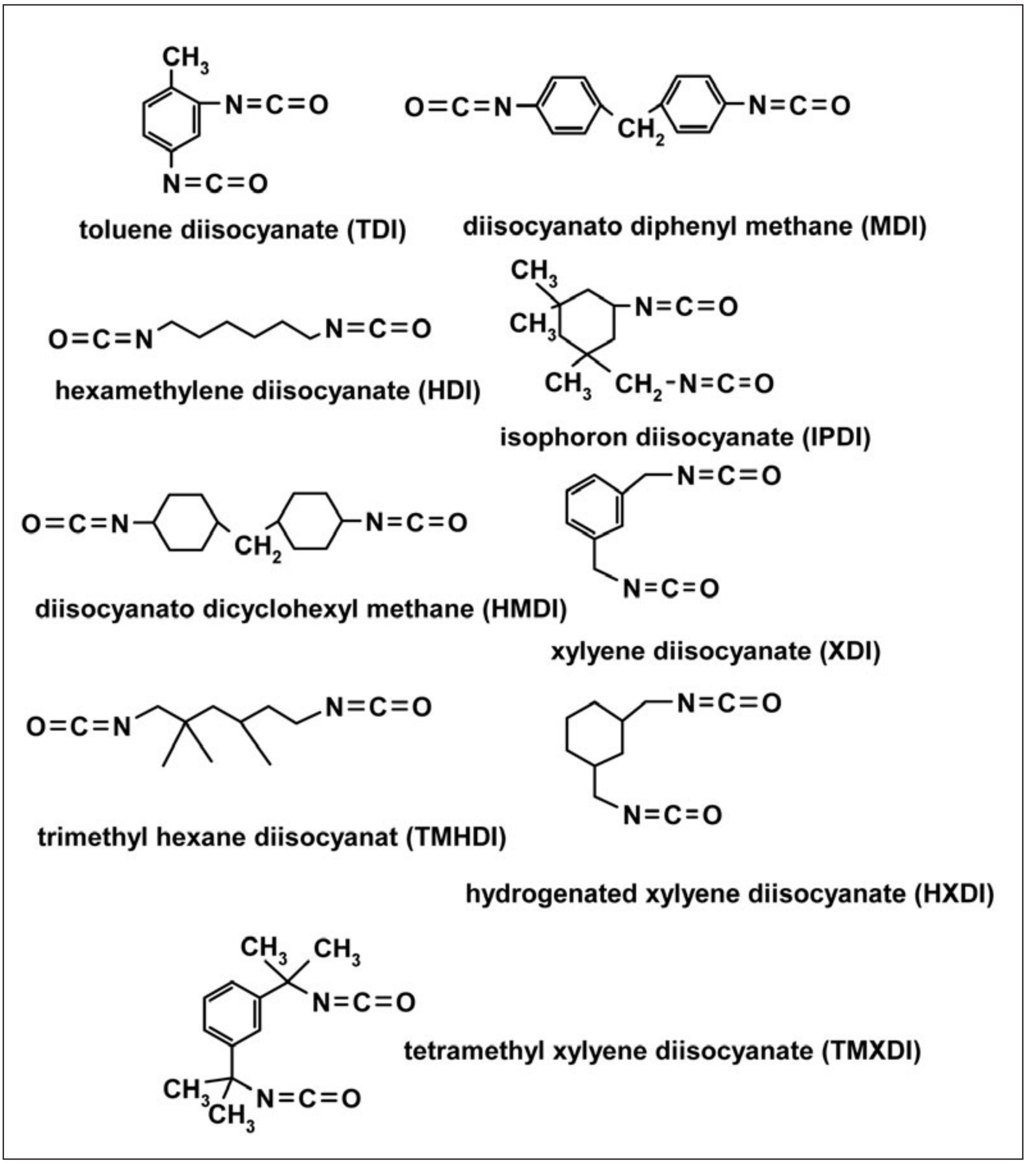


Figure II-1.14: Diisocyanates for hardeners

hydrogenated XDI (HXDI), 2,2,4-trimethyl hexane diisocyanate (TMHDI) and tetramethyl xylyene diisocyanate (TMXDI). The molecular structures of the diisocyanates are presented in Figure II-1.14.

MDI is available in derivatives which are liquids if they consist of mixtures of isomers and homologues. Some have more than two functional groups per molecule. These derivatives are therefore suitable for crosslinkers for solvent-free paint systems (see Chapter IV-1.1).

All the aforementioned diisocyanates, except pure, solid MDI, are classified as toxic. In particular, the aromatic isocyanates are strong poisons. All these diisocyanates have a measurable vapour pressure at room temperature and so, besides skin protection equipment (e.g. gloves), it is essential that breathing apparatus be employed when these products are handled. Naturally, the diisocyanates are not suitable for use in hardeners for paint systems.

However, if various processes are employed to modify the diisocyanates to yield oligomers, the outcome is products that still require protective measures, but that have very low vapour pressures at ambient temperatures and are no longer classified as toxic by inhalation. They are suitable for hardeners for two-component polyurethane systems. Additionally, there is a technical advantage: often the oligomerisation leads to polyisocyanates of higher functionality and so crosslinking is more effective.

Methods of oligomerisation include:

- Formation of biurets, principally by reaction of three molecules of diisocyanate with one molecule of water
- Reaction of excess diisocyanates with triols to form urethanes
- Catalytic trimerisation of diisocyanates to form isocyanurates
- Catalytic dimerisation of diisocyanates to form carbodiimides
- Formation of allophanates from two molecules diisocyanate and one molecule of alcohol

The molecular structures of some oligomers are presented in Figure II-1.15.

All these oligomers are used as hardeners. Although they are safer than the free diisocyanates, contact with skin and mucous membranes has to be avoided.

The film properties of two-component polyurethane systems are characterized by the formation of effective, homogenous networks which lead to optimum resistance to chemicals, solvents and other agents and offer an optimum balance of hardness and flexibility. This flexibility is promoted by the hydrogen bonds of the urethane groups in the film. Most commercial hardeners are based on the isocyanates TDI, HDI and IPDI [6, 7].

Aromatic polyisocyanate adducts are very reactive and form films of high hardness and especially resistance to solvents and chemicals. They are comparatively inexpensive. However, the films are not resistant to weathering. During weathering, the films, consisting of aromatic polyisocyanate hardeners, undergo yellowing, embrittlement, and finally decompose. For this reason, aromatic polyisocyanates hardeners are preferred for primers, primer surfacers for corrosion protection lacquers, for industrial paint systems and for wood paints offering high resistance to chemicals.

The film properties may be optimized with isocyanate oligomers formed from mixtures of TDI and HDI. The HDI in these mixtures confers flexibility and weatherability. The TDI confers hardness and resistance to chemicals.

When used in combination with suitable resins containing hydroxyl groups, oligomers of HDI form films that not only are sufficiently resistant to chemicals, but also exhibit excellent weatherability. Such combinations are used for high-quality industrial coatings, paints for trucks, general transport equipment and agricultural implements, automotive OEM coatings and repair paints. Due to the low glass transition temperature and the supporting action of the hydrogen bonds in the urethane groups, films containing HDI oligomers are highly flexible. After mechanical impact, the films are self-healing (re-flow).

Oligomers of IPDI yield completely different film properties. IPDI oligomers have higher glass transition temperatures. The cycloaliphatic isocyanate groups are less reactive. The films are hard, feature a diffusion barrier and good weatherability, but are less flexible. IPDI hardeners are preferred for coating systems characterized by a combination of hardness, relatively good chemical resistance and weatherability.

Due to the different properties resulting from the use of HDI and IPDI hardeners, it makes sense to combine both to achieve balanced film properties.

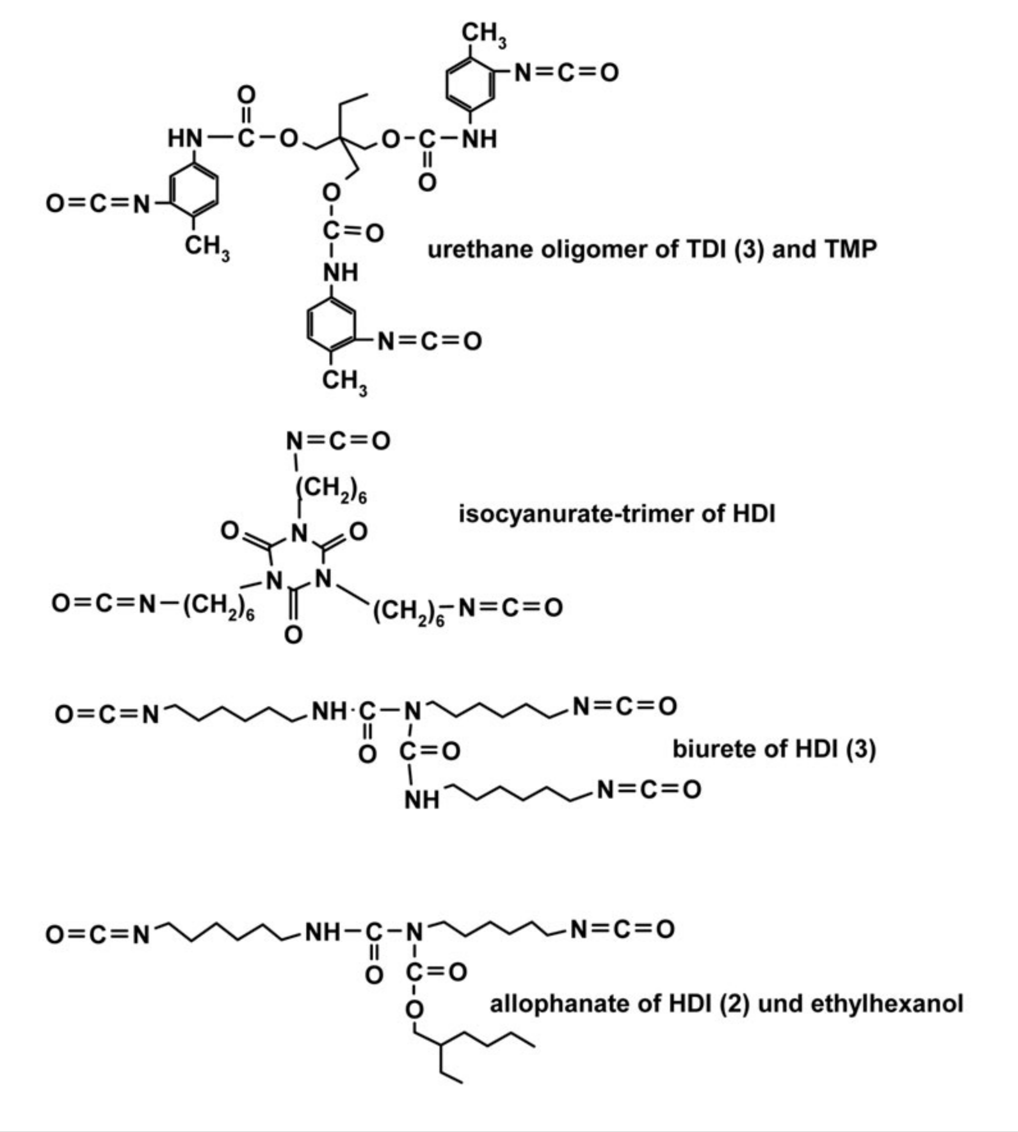


Figure II-1.15: Polyisocyanate oligomers; hardeners for two-component polyurethane systems, idealised molecular structures

It should also be mentioned that aliphatic and cycloaliphatic isocyanate products are fairly expensive.

Currently, particularly low-viscosity polyisocyanates adducts are available that are suitable for two-component high-solids systems. These adducts are either oligomers with a very narrow molar mass distribution (in the case of isocyanurate adducts) or compounds which principally yield a low viscosity (e.g. allophanates of long chain alcohols), but have lower functionality.

The reason why high-solids compositions are feasible with polyisocyanate adducts is that the isocyanates react very effectively and that opens up the possibility of starting the crosslinking reaction from relatively low-molecular compounds. But, of course, the partner resins for crosslinking also have a significant influence on the application viscosity.

Table II-1.16: NCO-% and glass transition temperatures of polyisocyanate adducts

polyisocyanate	%-NCO (solids)	glass transition temperature [°C]
TDI-isocyanurate	16	+75
TDI-TMP-adduct	18	+69
TDI-HDI-isocyanurate	17	+60
HDI-biurete	22	- 59
HDI-isocyanurate	22	- 64
IPDI-isocyanurate	17	+61

Polyisocyanate adducts for hardeners are characterized primarily by their chemical composition, and then by their delivery form, their viscosity and their content of isocyanate groups. The content of isocyanate groups is mainly quoted as wt.% isocyanate. This represents the mass fraction of isocyanate groups (molar mass: 42 g/mol) in 100 g of adduct or its delivery form. It is therefore important in all calculations to add the wt.% delivery form. The basis for the calculation is:

$$\text{NCO-\%} = \frac{n_{NCO} \cdot M_{NCO} \cdot 100}{m_{NCO}}$$

n_{NCO} = Number of NCO groups [mol])
M_{NCO} = Molar mass of the isocyanate group [g/mol] (= 42 g/mol)
m_{NCO} = Mass of the isocyanate product [g]

Table II-1.16 lists examples of various polyisocyanate adducts (with NCO-% content and glass transition temperatures)

Suitable solvents for polyisocyanate adducts are esters (e.g. butyl acetate), glycol ether esters (e.g. methoxypropyl acetate), and aromatic hydrocarbons (e.g. xylene, Aromatic 100). Of course, it is impossible to use solvents bearing free hydroxyl groups (e.g. alcohols or glycol monoethers) as they would react with the isocyanate groups by forming urethanes. Additionally, it is important to check the water content of the solvents. If possible, they should be free of water.

Examples of commercial polyisocyanate adducts (often the figures quoted have a numerical extension that represents the concentration of the delivery form).

- TDI trimethylolpropane adduct: Desmodur L (Bayer)
- TDI isocyanurate: Desmodur IL (Bayer)
- TDI/HDI isocyanurate: Desmodur HL (Bayer)
- HDI biuret: Desmodur N (Bayer), Tolonate HDT (Rhodia), Basonat HI (BASF), Luxate HT (Lyondell)
- HDI allophanate: Desmodur N 34 (Bayer), Basonat HB (BASF), Luxate HI (Lyondell)
- IPDI isocyanurate: Desmodur Z 44 (Bayer), Basonat HB (BASF), Vestanat T 1890 (Evonik-Degussa), Luxate IT (Lyondell)

1.3.1.3 Hydroxyl resins for two-component polyurethane systems

A large number of resins may be combined with polyisocyanates for crosslinking:

- Saturated polyesters
- Alkyd resins
- Acrylic resins
- Polyethers
- Epoxy resins and epoxy ester resins
- PVC copolymers
- Polyvinyl acetals

Saturated polyesters

Saturated polyesters are usually produced from isophthalic acid, phthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid or their anhydrides, mixtures of different diols and the triol trimethylolpropane. More flexible grades may also contain adipic acid or other long-chain polycarboxylic acids. The saturated polyesters mainly have large amounts of hydroxyl groups (high hydroxyl numbers), but low acid numbers. The molar masses are usually low (800 to 3,000 g/mol). The resins are diluted in mixtures of aromatic hydrocarbons and either esters or glycol ether esters. Of course, the solvents should not contain hydroxyl groups.

Due to the effective reactivity of the hydroxyl groups of polyester and isocyanate groups, there is great scope for variation in polyesters. They may contain hard or flexible structural elements, have different hydroxyl numbers and have different branching. Consequently, a large number of different polyesters are available and it is possible to satisfy a wide range of quality requirements imposed on coating films. In comparison to other paint systems, an optimum balance between hardness and flexibility can be achieved. The use of aliphatic or cycloaliphatic polyisocyanate adducts confers excellent weatherability on pigmented topcoats. Good weatherability of clear coats is achieved only if the polyesters do not contain aromatic structural elements.

Such combinations of saturated polyesters and polyisocyanate adducts are preferred for high quality wood paints, plastic paints (all kinds), primers, primer surfacers (automotive repair and industrial systems) and for two-component topcoats. A special version of polyesters for the formulation of high-solid polyurethane coatings consists of adducts of polyols and ε-caprolactone.

Alkyd resins

Alkyd resins for two-component polyurethane systems consist of phthalic anhydride, triols or tetraols and saturated fatty acids, as well as of fatty acids that contain oleic acid, linoleic acids (9,12- or 9,11-isomers) and ricinolic acid. Candidates are grades with low or medium oil length, high hydroxyl numbers, and low acid numbers. The crosslinking reaction with polyisocyanate adducts is less effective than is the case for saturated polyesters. But alkyd resins are characterized by excellent wetting properties (substrates and pigments), and confer high gloss and a good appearance. Thus, alkyd resins in combination with polyisocyanate adducts are preferred for the formulation of high-quality pigmented topcoats (for wood, plastic, transport vehicles, industrial goods, corrosion protection systems and for automotive repair coatings).

Acrylic resins

Acrylic resins for two-component polyurethane paints consist of acrylic esters and methacrylic esters and may contain other comonomers (e.g. styrene). Incorporation of suitable amounts of hydroxyalkyl acrylates or hydroxyalkyl methacrylates into the monomer compositions confers high hydroxyl numbers on the copolymer resins (hydroxyl numbers of 120 to 140 mg KOH/g). Small amounts of acrylic acid or methacrylic acid lead to relatively low acid numbers. Resins of low molar mass are preferred; the number average molar masses are 2,000 to 4,000, which yield high-solids paint systems.

Acrylic resins do not crosslink with polyisocyanate adducts as effectively as polyesters, but offer advantages in film forming due to the rapid physical drying. The crosslinked acrylic systems are characterized by excellent stability to chemicals and solvents. If acrylic resins do not contain aromatic elements (e.g. styrene) or, if so, only in small amounts, and if they are crosslinked with aliphatic or cycloaliphatic polyisocyanate adducts, the films produced by these systems offer excellent weatherability in pigmented topcoats and in clear coats.

A further disadvantage of acrylic resins over polyesters and especially alkyd resins is that of limited wetting. But this can be compensated by using acrylic resins modified with a glycidyl ester of branched synthetic fatty acids (e.g. Cardura E [Hexion]). This modification produces an alkyd-resin-like character and improves not only the wetting of substrates and pigments, but also the levelling and flow during film formation. Due to their generally optimum balance of properties, combinations of acrylic resins and polyisocyanate adducts are the preferred resins for topcoats and clear coats, especially for plastic paints, automotive repair paints (topcoats and clear coats) and automotive OEM clear coats. The OEM two-component clear coats are applied with electrostatic spray equipment, whose spray guns are equipped with static mixing units. For the OEM process – and to accelerate film formation – the clear coats are stoved at 130 to 140 °C for 20 to 30 min.

Polyethers

Polyethers are produced by the reaction of ethylene oxide or propylene oxide with different types of polyols. To an extent depending on the type and functionality of the starting alcohol and the ratios of ethylene or propylene oxide to starting alcohol, polyethers have different molar masses and different branching and functionalities. They are relatively inexpensive. Crosslinking with polyisocyanate adducts yields very flexible films. However, the films of polyethers and polyisocyanates are not weatherable. Such systems are mainly used for plastic paints.

Others

Epoxy resins, epoxy ester resins, PVC copolymers, polyvinyl acetals are sometimes used for two-component polyurethane paints.

Characteristics

If resins containing hydroxyl groups are used for crosslinking with polyisocyanate adducts, they are characterized by *inter alia* their hydroxyl number or their OH-% content.

The hydroxyl number is the amount in mg of potassium hydroxide which is equivalent to the hydroxyl groups of 1 g resin. The OH-% content is the mass of hydroxyl groups in 100 g resin. They are calculated with the aid of the equations below.

$$\text{OH-number} = \frac{n_{OH} \cdot M_{KOH} \cdot 1000}{m_{OH}}$$

$$\text{OH-\%-content} = \frac{n_{OH} \cdot M_{OH} \cdot 100}{m_{OH}}$$

n_{OH} = Number of hydroxyl groups [mol]
M_{OH} = Molar mass of hydroxyl groups (17.0 g/mol)
M_{KOH} = Molar mass of potassium hydroxide
m_{OH} = Mass of resin containing hydroxyl groups [g]

Solving both equations for n_{OH} and comparing the results, we arrive at the following relationships:

$$\frac{m_{OH} \cdot \text{OH-\%}}{M_{OH} \cdot 100} = \frac{m_{OH} \cdot \text{OH-nb.}}{M_{KOH} \cdot 1000}$$

$$\frac{\text{OH-nb.}}{\textit{OH-\%}} = \frac{M_{KOH} \cdot 1000}{M_{KOH} \cdot 100} = \frac{56110}{1700} = 33.0$$

The final result is:

$$\text{OH-nb.} = \text{OH-\%} \cdot 33.0$$

1.3.1.4 Catalysts and accelerators for two-component polyurethane paints

Table II-1.17: Relative efficiency of catalysts for two components polyurethane systems

catalyst	concentration [wt%]	relative reactivity
comparison (without)	–	1
DABCO	0.1	130
DABCO	0.2	260
DABCO	0.3	330
DBTL	0.1	210
DBTL	0.5	670
DBTL + DABCO	0.1 + 0.2	1000

The calculated sum of 0.1 wt% DBTL and 0.2% DABCO would be 470, but the result is 1000, that is the evidence for synergism.

As mentioned above, the reaction rate of aliphatic and cycloaliphatic polyisocyanates at room temperature is relatively low. To accelerate the reaction effectively, different catalysts are used. The recommendations are to use either electrophilic compounds (Lewis acids) or nucleophilic compounds (Lewis bases). Catalysts which act as Lewis acids include organic metal salts of the subgroups of the periodic table. The effect of Lewis acids is to support the electrophilic reaction of the isocyanate group. Recent studies (*W. Blank* et al, King Industries) show that the metal ions can interact with the hydroxyl groups in a different way [15]. The preferred catalysts are salts of tin, zinc, zirconium, and bismuth. The anions are salts of long-chained aliphatic acids (ethyl hexanoate, iso-nonanate, laurate). The best-known product is dibutyltin dilaurate (DBTL). Besides tributyl tin compounds (used in the past as biozides, mostly for marine coatings), dibutyl tin compounds are classified as harmful to both human health and the environment. Dibutyl tin dilaurate has to be replaced by compounds which are less hazardous. It has been proposed that combinations of organic zinc salts with tertiary amines or basic heterocyclic compounds would make suitable candidates.

Lewis bases increase the nucleophilic reaction of the hydroxyl group. The preferred compounds are mainly tertiary amines, with the most effective being triethylene diamine (DABCO = diazabicyclooctane).

The above-mentioned studies and others show that both types of catalysts can be combined to produce in synergistic catalytic effects [11]. The efficiency of the catalysts is shown in the following Table II-1.17:

Of course, the use of catalysts shortens the pot-life of mixed polyurethane paints. Excessive use of catalyst should be avoided because weatherability and heat stability deteriorate. Recommended additions are 0.02 to 1.00 wt.% for metal salts and 0.01 to 0.50 wt.% for tertiary amines, calculated on base component [8].

1.3.1.5 Development of formulations for two-component polyurethane paints

The crosslinking reaction between resins containing hydroxyl groups and polyisocyanates is long well-defined. It therefore makes sense to calculate the stoichiometric mixing ratios. Experience shows that the best performance is achieved by choosing equivalent amounts as follows:

$$n_{NCO} = n_{OH}$$

These formulas, along with the hydroxyl number and the NCO-% content, can be used to arrive at the following. Additionally, the NCO-% content and the OH-% content can be used.

$$\frac{m_{OH} \cdot \text{OH-nb.}}{M_{KOH} \cdot 1000} = \frac{m_{NCO} \cdot \text{NCO-\%}}{M_{NCO} \cdot 100}$$

$$\frac{m_{OH}}{m_{NCO}} = \frac{\text{NCO-\%} \cdot M_{KOH} \cdot 1000}{\text{OH-nb.} \cdot M_{NCO} \cdot 100} = \frac{\text{NCO-\%}}{\text{OH-nb.}} \cdot 13.36$$

If, for example, an acrylic resin of hydroxyl number 140 mg KOH/g, is combined with an isocyanurate trimer of HDI, with an NCO-% content of 22.0, the calculation yields a mixing ratio of 2.1 : 1.0.

Setting the weight of hydroxyl resin at 100 parts allows the so-called isocyanate base value for the mass of polyisocyanate to be calculated. It is defined as the amount of polyisocyanate necessary for equivalent crosslinking of 100 g of resin containing hydroxyl groups.

$$\text{NCO-base-value} = \frac{\text{OH-nb.} \cdot M_{NCO} \cdot 10}{\text{NCO-\%} \cdot M_{KOH}} = \frac{\text{OH-nb.}}{\text{NCO-\%}} \cdot 7.49$$

Of course, the isocyanate base value may also be calculated from the OH-% content.

$$\text{NCO-base-value} = \frac{\text{OH-\%} \cdot M_{NCO} \cdot 100}{\text{NCO-\%} \cdot M_{KOH}} = \frac{\text{OH-\%}}{\text{NCO-\%}}$$

For the above-mentioned example, the result of both equations is 47.6 g. This means that, for 100 g of the acrylic resin, 47.6 g of the polyisocyanate is needed to balance the stoichiometric ratios for crosslinking.

The alternative way of performing the calculation is to start with the equivalent weight (EW). The equivalent weight is the amount in g of a resin containing one mole hydroxyl groups or one mole isocyanate groups. The equivalent weights are obtained from the formulas above by defining the number of functional groups as 1 and solving the equation for the weights.

$$EW_{NCO} = \frac{M_{NCO} \cdot 100}{\text{NCO-\%}}$$

$$EW_{OH} = \frac{M_{KOH} \cdot 1000}{\text{OH-nb.}}$$

The equivalent weights for the reaction partners in the example compute to 190.9 g/equivalent for the polyisocyanate and 400.7 g/equivalent for the acrylic resin.

Finally, all the definitions and equations lead to the same combination ratios:

$$\frac{m_{OH}}{m_{NCO}} = \frac{2.1}{1.0} = \frac{100}{47.6} = \frac{400.7}{190.9}$$

Although it is recommended that balanced stoichiometric mixing ratios be calculated first, it is possible to change the ratios. Experience shows that variations in the stoichiometric proportions of polyisocyanate to hydroxyl resin from 0.90 : 1.00 and 1.15 : 1.00 do not significantly affect the resultant film properties. Less polyisocyanate yields more flexible films with excellent adhesion properties, but less resistance to chemicals and solvents. An excess of polyisocyanate leads to better resistance to chemicals and solvents. It must be remembered that the excess isocyanate groups will react with atmospheric moisture to form primary amines immediately transferred into urea linkages. This side reaction may also occur in the event of equivalent stoichiometric proportions if the crosslinking is carried out at ambient temperatures and at high relative air humidity. Of course, some hydroxyl groups remain in the film. But in that case there are nearly no disadvantages for film properties. Under these conditions, however, it is possible to select an excess of polyisocyanate to schedule an additional crosslinking reaction with the view to obtaining a higher crosslinking density (see also: Two-component, water-borne paints in Part III).

The following two problems and their solutions illustrate how the formulations for different two-component polyurethane paints are developed.

a) Formulation of a two-component polyurethane clear coat for automotive repair.

The two-component polyurethane clear coat for automotive repair[22] consists of an acrylic resin modified with the glycidyl ester of neo-decanoic acid. The hydroxyl content is 4.5%,

Table II-1.18: Two-component polyurethane clear coat for automotive repair coatings

pos.	raw material	solids wt.%	density [g/cm^3]	formulation wt.%
base component				
01	acrylic resin, 4.5 OH-%, 60% in mixed solvents	51.66	1.2	86.10
02	methoxy propyl acetate			3.87
03	xylene			3.87
04	butyl acetate			3.87
05	HALS: N-alkyltetramethylpiperidine derivate			0.45
06	UV-absorber: hydroxyphenylbenzotriazole			1.35
07	silicon intermediate			0.20
08	catalyst: bismuth neodecanate (70%)			0.20
09	N,N-dimethylethanolamine			0.09
sum		51.55		100.00
hardener				
10	HDI-biuret adduct (75% in butylacetate)	26.10	1.2	19.60
11	butylacetate			24.80
12	aromatic 100			6.20
13	xylene			10.30
sum		26.10		76.10
total-sum		77.65		176.10

pos. 01: Macrynal SM 510n (Cytec Surface Specialties, Vianova)
pos. 02: BASF SE
pos. 05: Tinuvin 292 (BASF Swiss, Ciba-Specialties)
pos. 06: Tinuvin 1130 (BASF-Swiss, Ciba-Specialties)
pos. 07: Borchi Gol LA 2 (Borchers)
pos. 08: Borchi Kat 315 (Borchers)
pos. 10: Desmodur N 75 (Bayer)
pos. 12: Solvesso 100 (Exxon)

expressed in terms of the solids. The clear coat is to be crosslinked in balanced stoichiometric proportions. The hardener consists of a biuret adduct of hexamethylene diisocyanate. The NCO content is 22.0%, expressed in terms of the solids. The delivery form is 75% in butyl acetate. The base component consists of the acrylic resin while the solvents are methoxy propyl acetate, xylene and butyl acetate. An UV absorber (1.35 wt.% of a hydroxyphenyl benzotriazole) and a free-radical scavenger (0.45 wt.% of a N-methyl tetramethyl piperidine derivative, HALS) are added. The flow additive is an organic modified polysiloxane in a proportion of 0.20 wt.%. The catalysts are 0.20 wt.% bismuth neo-decanate and 0.09 wt.% diethylethanolamine (tin-free formulation).

The hardener solution is thinned with butyl acetate, aromatic 100, and xylene. The mixing ratio of the base component to hardener is 100.0 : 75.1.

Stoichiometric calculation

86.10 wt.% of acrylic resin solution is equivalent to 51.66 wt.% of solid resin. 100 parts of the resin, with a hydroxyl content of 4.5 wt.% contain 0.2647 moles of hydroxyl groups. Therefore 51.66 parts contain 0.1367 moles. 34.80 weight amounts of polyisocyanate adduct solution contain 26.10 weight amounts of solid hardener. 100 parts of solid hardener with an NCO content of 22 wt.% is equivalent to 0.5238 moles NCO. Therefore 26.10 weight amounts contain 0.1367 moles. The stoichiometric mixing ratio is exactly 1 : 1 per mole. It is important that the batch be stirred thoroughly after mixing. The viscosity of the mixture meets the application conditions for spraying, approximately 20” (DIN 53211, flow cup 4 mm at 20 °C). The mixture has a solids content of 45 wt.%. The mixture is applied on a dry repair metallic basecoat. After application, the film thickness (dry) is to be 40 to 45 µm. The pot-life is seven hours. The initial drying time is approx. 30 minutes. The second drying stage takes 2 hours. The pendulum hardness (EN ISO 1522, Koenig tester) is approx. 88” after one day, and 212” after seven days at ambient temperatures. The resultant smooth, high-gloss (92.4% at 60° angle) two-layer topcoat system can be polished and may be re-coated after one night at the latest and exhibits excellent resistance to weathering.

The resultant smooth, highly glossy, two-layer topcoat system can be polished and may be re-coated after one night at the latest and exhibits excellent resistance to weathering. There is also the possibility of forced drying at 60 °C for 45 min.

b) Develop formulations for two different two-component polyurethane paints, based on an acrylic resin containing hydroxyl groups and crosslinked first with the aid of an aliphatic HDI adduct and secondly an aromatic TDI adduct as hardener. The NCO/OH ratio is to be 1 : 1. The pigment / binder ratio is to be 1.2 : 1. The non-volatiles of the mixed system are to be 62 wt.%. The pigmentation is to consist of titanium dioxide and an extender in the ratio of 2.5 : 1 by weight.

The first step is to select the resins, which have to be compatible, and then to select the other raw materials.

Acrylic resin: 60 wt.% in xylene, hydroxyl number approx. 80 equivalent to 2.4% OH (expressed in terms of solids), e.g. Synthalat A 077 (Synthopol Chemie)

HDI adduct: 75 wt.% in methoxypropyl acetate/xylene, 22% NCO (solids), e.g. methoxypropyl acetate/xylene, 22%-NCO (on solids), e.g. Desmodur N 75 (Bayer)

TDI adduct: 67 wt.% in methoxypropyl acetate/xylene, 17.3% NCO (solids), e.g. Desmodur L 67 (Bayer)

Pigment: Titanium dioxide, rutile, density 4.1 g/cm^3, e.g. Kronos 2160 (Kronos)

Extender: Barium sulphate, density 4.5 g/cm^3, e.g. EWO powder (Alberti)

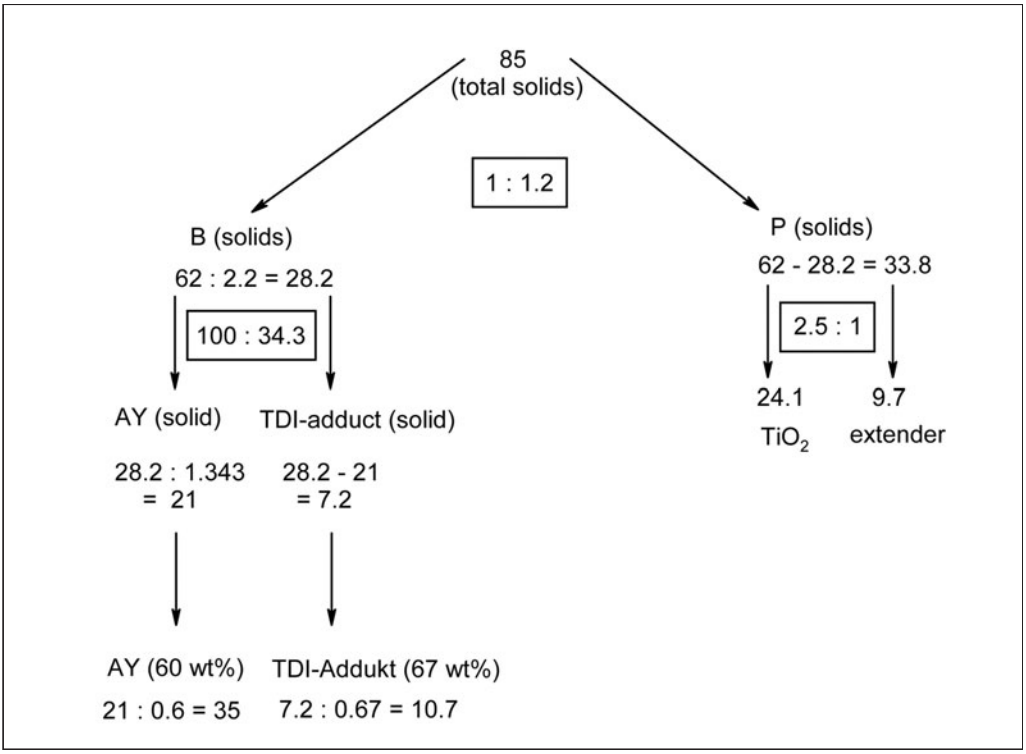


Figure II-1.16: Development of recipe for the base lacquer for the TDI adduct

Solvents: Xylene, butyl acetate, methoxypropyl acetate.

For the first laboratory batch, there is no need to consider any additives. But, of course, it is possible to add a catalyst for the aliphatic polyisocyanate.

The first step in the calculation is to determine the isocyanate base value of the acrylic resin for both polyisocyanates.

$$\text{NCO-base-value (TDI)} = \frac{42 \cdot 2.4 \cdot 100}{17 \cdot 17.3} = 34.3 \text{ (solids)}$$

$$\text{NCO-base-value (HDI)} = \frac{42 \cdot 2.4 \cdot 100}{17 \cdot 22} = 27.0 \text{ (solids)}$$

Table II-1.19: Formulation of the paint for TDI-adduct

pos.	raw material	solids [wt.%]	formulation [wt.%]
01	acrylic resin (60%)	21.0	35.0
02	TDI-adduct	7.2	10.7
03	titanium dioxide, rutil type	24.1	24.1
04	extender barium sulphate	9.7	9.7
05	solvent mixture		20.5
sum		62.0	100.0

Because the paint containing the TDI adduct needs higher amounts of hardener and therefore a lower amount of acrylic resin, it makes sense to start with this formulation. After that, it is easier to develop the formulation for the base component for the HDI crosslinker, because it is done by adding acrylic resin. This method is presented in Figure II-1.16

The result of the development recipe for the base lacquer for the TDI adduct is the calculation recipe in Table II-1.19

The PVC of this formulation is:

$$\text{PVC} = \frac{24.1 / 4.1 + 9.7 / 4.5}{24.1 / 4.1 + 9.7 / 4.5 + 28.2 / 1.2} \cdot 100\% = 25.5\%$$

It is common to write a two-component polyurethane system in the form of two recipes, one for the base component and one for the hardener. The base component is prepared by dispersing pigments in the acrylic resin. The hardener has to be stored separately (see Table II-1.20).

The addition of hardener containing the HDI adduct is calculated as follows:

$$\text{hardener (HDI) on base} = \frac{42 \cdot 2.4 \cdot 23.5}{17 \cdot 22} = 6.3 \text{ (solid)}$$

Compared with the system containing the TDI adduct (8.0 parts by weight solid polyisocyanate), 1.7 parts by weight of total solid resin is missing. To compensate (comparable level of P/B ratio), 1.7 parts by weight of binder has to be added. The amount has to be divided 100 : 27 in the ratio of acrylic resin to polyisocyanate (see isocyanate base value). The addition is 1.30 g of acrylic resin (2.2 g of delivery form) and 0.40 g of HDI adduct (0.5g of delivery form). The resultant formulation is presented in Table II-1.21.

Table II-1.20: Formulation of base component and hardener (TDI-adduct)

pos	raw material	solids [wt.%]	formulation [wt.%]
01	acrylic resin (60%)	23.5	39.2
02	titanium dioxide, rutile	27.0	27.0
03	extender barium sulphate	10.9	10.9
04	solvent mixture		22.9
sum		61.4	100.0

hardener: 12.0 parts per weight TDI-adduct (67%, 8.0 parts solid)

Additionally, the PVC value is calculated to verify the calculation above.

$$\text{PVC} = \frac{27 / 4.1 + 10.9 / 4.5}{27 / 4.1 + 10.9 / 4.5 + 31.5 / 1.2} \cdot 100\% = 25.5\%$$

The PVC value is equal to the PVC value of the paint system containing TDI adduct. Therefore, it is possible to formulate two different polyurethane paint systems, but with the same PVC, starting from one mill base.

Table II-1.21: Formulation for base component and HDI-hardener

pos.	raw material	solids [wt.%]	formulation wt.%
01	acrylic resin (60%)	23.5 + 1.3	39.2 + 2.2
02	titanium dioxide, rutile	27.0	27.0
03	extender barium sulphate	10.9	10.9
04	solvent mixture		22.9
sum		61.4	100.0

the addition of hardener is 8.4 + 0.5 = 8.9 parts per weight of HDI-adduct (75%, 6.7 parts solid)

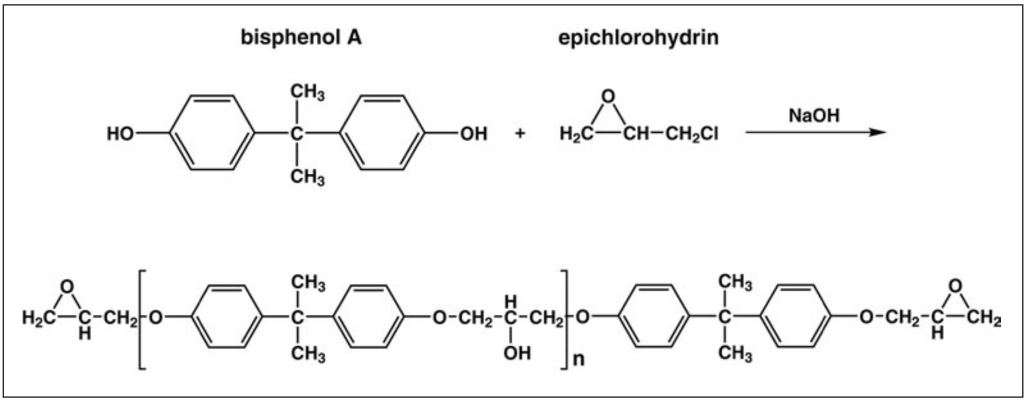


Figure II-1.17: Synthesis of epoxy resins based on bisphenol A (n = 0 : bisphenol A - diglycidyl ether)

1.3.2 Two-components epoxy paints

Coatings based on epoxy resins are characterized by hardness, abrasion resistance, chemical resistance and excellent adhesion (Chapter I-1.6.2) on different metals. A preferred application of two-components epoxy coatings is corrosion protection and maintenance coatings. A disadvantage may be their reduced weatherability caused by the aromatic structure of bisphenol A resins. The paint discussed in this chapter consists of a base component (A-component: epoxy resin, pigments, additives, solvents) and a hardener (B-component: polyamines or derivatives of polyamines and sometimes pigments) which are mixed just before application to yield a mixture of limited pot-life. In contrast to two-components polyurethane paints, pigments can be dispersed in the hardener of two-components epoxy paints. Two-components epoxy paints cure by polyaddition at ambient temperature (see below).

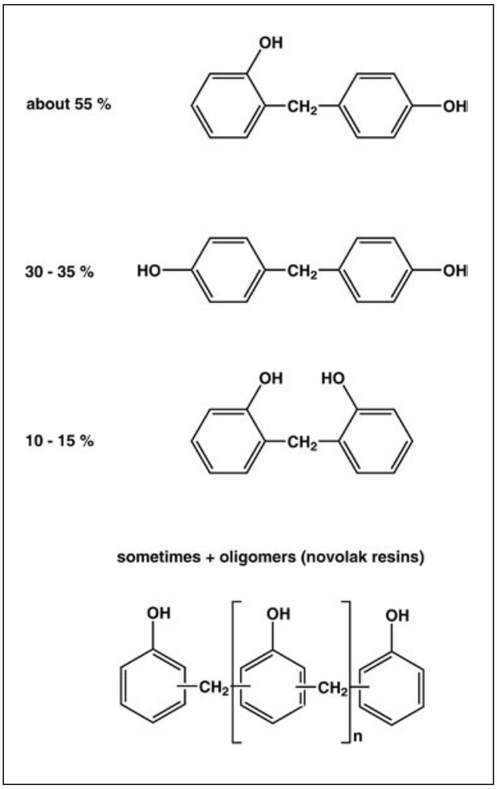


Figure II-1.18: Bisphenol F and novolak resins

1.3.2.1 Base component: epoxy resins

The most important epoxy resins are based on bisphenol A, which is synthesized from 2 mols phenol and 1 mol acetone. Worldwide 3.8 million tons of bisphenol A are produced per year, one third of this is used for expoxy resins [23]. The reaction between bisphenol A and 2 mols epichlorohydrin yields bisphenol A - diglycidyl ether. Changes in the reaction conditions and especially the molar ratio of the reactants allows epoxy resins of higher molar mass to be synthesized by this method (Figure II-1.17). In the epoxy resin (type 1) commonly used in solvent-borne two-components paints, n is 2 to 2.5.

Among others, the raw materials market offers epoxy resins based on bisphenol F, which is produced from 2 mols phenol and 1 mol formaldehyde (Figure II-1.18).

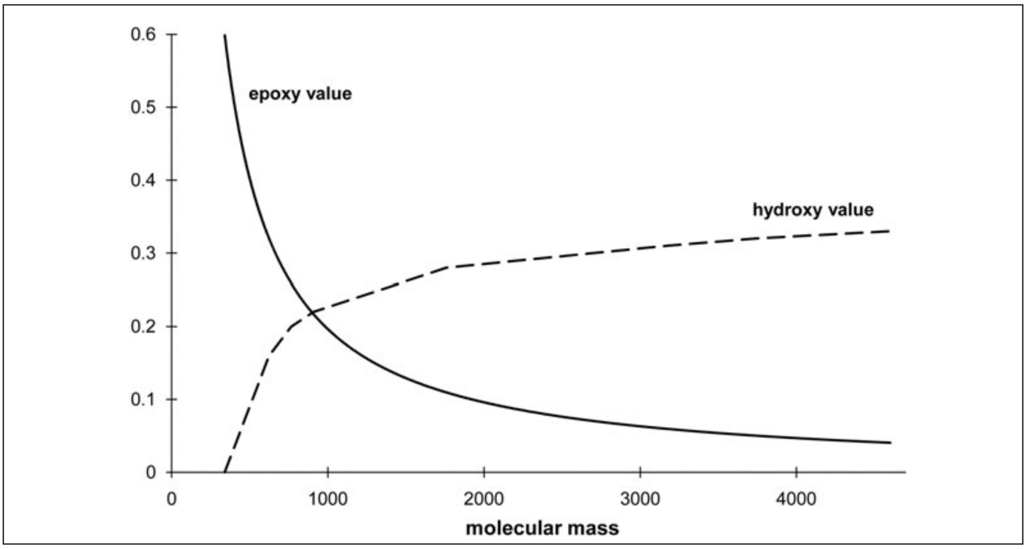


Figure II-1.19: Approximate dependence of the epoxy and hydroxy values on the molar masses of epoxy resins based on bisphenol A

Unlike bisphenol A, bisphenol F is a mixture of isomers [sometimes also with oligomers (novolak resins)]. This has the advantage that epoxy resins based on bisphenol F have a lower viscosity and a lower tendency to crystallize than those based on bisphenol A. Mixing epoxy resins based on bisphenol A with resins based on bisphenol F can minimize the tendency to crystallize.

Epoxy resins are characterized by the following values:

- The epoxy equivalent mass (also called the epoxy equivalent weight: eew) indicates how many grams of epoxy resins contain 1 mol of epoxy groups (oxirane rings). Thus, a high epoxy equivalent mass indicates a low content of epoxy groups.

  Approximation for epoxy resins based on bisphenol A:
  epoxy equivalent mass ≈ (molar mass) / 2

- The epoxy value shows the number of mol epoxy groups in 100g epoxy resin:

  epoxy value = 100/(epoxy equivalent mass)

  Approximation for epoxy resins based on bisphenol A:

  epoxy value ≈ 100 / [(molar mass) / 2]

- The hydroxy equivalent mass shows how many grams of epoxy resins contain 1 mol hydroxyl groups (OH groups).

  Approximation for epoxy resins based on bisphenol A:

  hydroxy equivalent mass ≈ (molar mass) / n

- The hydroxy value shows the number of mol hydroxyl groups in 100g epoxy resin:

  hydroxy value = 100 / (hydroxy equivalent mass)

Table II-1.22: Data for bisphenol A-epoxy resins

epoxy resin (type)	epoxy equivalent mass	approximate molecular mass (M_n)	T_g [°C]
1	450 to 500	880	26
4	806 to 909	1480	49
7	1550 to 2000	2870	67
9	2273 to 3846	4000	80

Source: Data sheets "Epikote" 1001 - 1009 (www.resins.com)

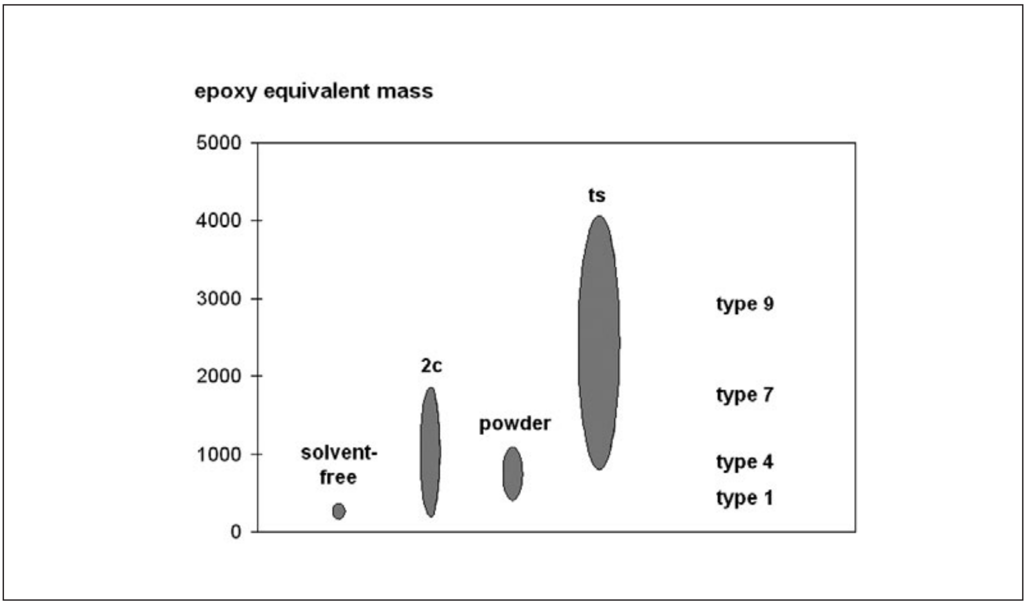


Figure II-1.20: Applications of epoxy resins as a function of their epoxy equivalent mass
Solvent-free: *Low-molecular, liquid epoxy resins for solvent-free two-components coatings (see Chapter IV-1.2)*
2c: *Solid epoxy resins for solvent-borne two-components paints (optimum: epoxy resin type 1)*
Powder: *Solid epoxy resins for powder coatings (see Chapter IV-3.4.2)*
ts: *Thermosetting, solid epoxy resins for solvent-borne stoving enamels (epoxy resin type 4 to 9; see Chapter II-2.3)*

Approximation for epoxy resins based on bisphenol A:
hydroxy value ≈ 100 /[(molar mass) / n]

The dependence of the epoxy values and hydroxy values on the molar masses of bisphenol A – epoxy resins calculated from the above equations is shown in Figure II-1.19. With increase in molar mass, the content of epoxy groups (epoxy value) decreases whereas the content of hydroxyl groups (hydroxy value) increases.

In actual practice, the dependences presented in Figure II-1.19 are qualitatively valid. However, with increase in epoxy equivalent mass, the molar masses calculated therefrom (molar mass = 2 · epoxy equivalent mass) deviate more and more (Table II-1.22). Thus, the synthesis of resins of higher molar mass leads to side reactions which cause a loss of epoxy groups [19]. Moreover, Table II-1.22 shows that the glass temperatures (T_g) of epoxy resins increase with increase in molar mass.

Epoxy resins find application in different paint systems in accordance with their respective epoxy equivalent mass (Figure II-1.20). These will be described in the course of this book. Water-borne epoxy resins are discussed in Chapter III-3.2.2.

1.3.2.2 Hardeners: polyamines and derivatives

As is common in two-components systems, the aminofunctional hardener and the base component (epoxy resin) are mixed just before application. Curing (crosslinking) of two-components epoxy coatings takes place by addition reaction between the aminofunctional hardener and the oxirane groups of the epoxy resins (Figure II-1.21). Because of steric hindrance, secondary amines are less reactive than primary amines (tertiary amines are non-reactive). The first part of the reaction sequence is therefore faster than the second (Figure II-1.21).

During the curing reaction, the glass temperature T_g of the coating increases rapidly (Figure II-1.22), the low T_g a few minutes after application may caused by the solvents in the film which act as plasticizers.

Aminofunctional hardeners are characterized by the NH-equivalent mass (also called H-active-equivalent mass). The NH-equivalent mass is the molar mass of the amine hardener divided by the number of reactive hydrogen atoms on the amino groups. Thus, the NH-equivalent mass is the mass of amine hardener [g] which contains 1 mol of reactive hydrogen.

For a stoichiometric reaction of 100 parts by weight of epoxy resin, the amount of amine hardener to be added [parts by weight] is calculated as follows:

Hardener addition = epoxy value · NH-equivalent mass

The calculated stoichiometric addition level for aminofunctional hardener is not always the optimum. Often, an excess of 10 to 20% hardener is added, which may lead to coatings with improved properties.

For ambient temperature curing, it is common practice to employ two-components epoxy paint hardeners, such as polyamines, adducts of polyamines and polyaminoamides (polyamide resins). Theses types of hardener are described below.

Aliphatic and cycloaliphatic polyamines

Aliphatic polyamines (Figure II-1.23) have low viscosities and are highly reactive and therefore a short pot life. Disadvantageous are the corrosivity and the unpleasant odour of low-molecular aliphatic polyamines. The reaction between carbon dioxide and water (airborne) leads to the formation of amine carbonates; during curing at high humidity, this may cause surface defects in coatings. Theses difficulties can be avoided by using adducts of polyamines and epoxy resins (see below). Cycloaliphatic polyamines (Figure II-1.23) are less reactive than aliphatic amines for steric reasons. Aromatic amines are suspected carcinogens and should be avoided.

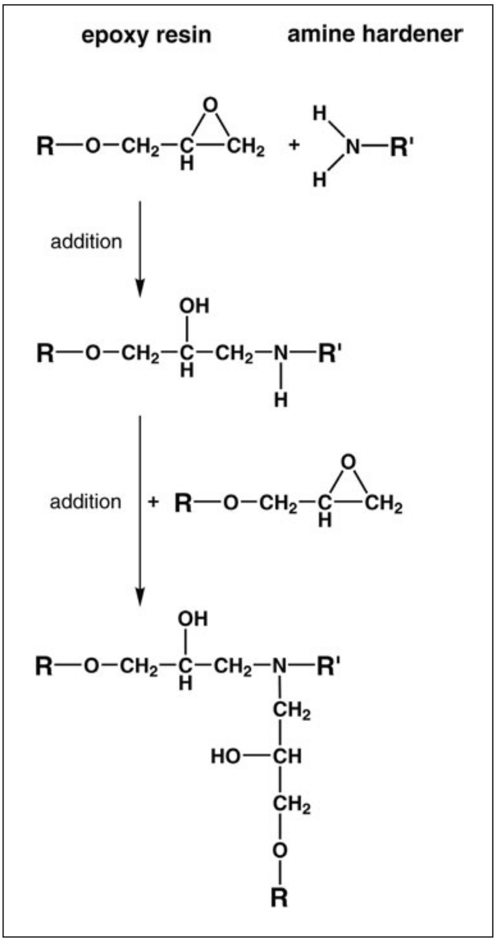


Figure II-1.21: Curing reaction of epoxy resins and hardeners

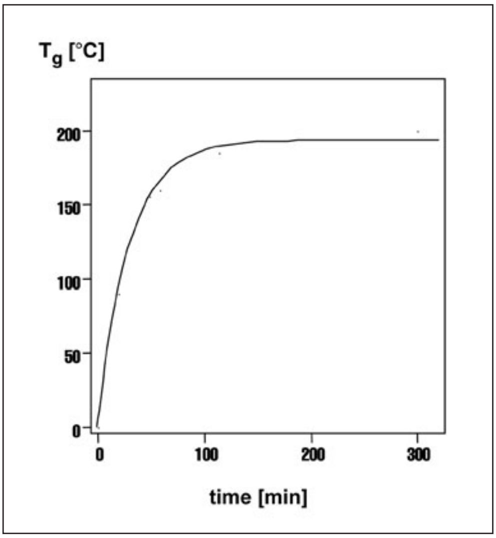


Figure II-1.22: Simplified diagram of the dependence of the glass temperature T_g on time

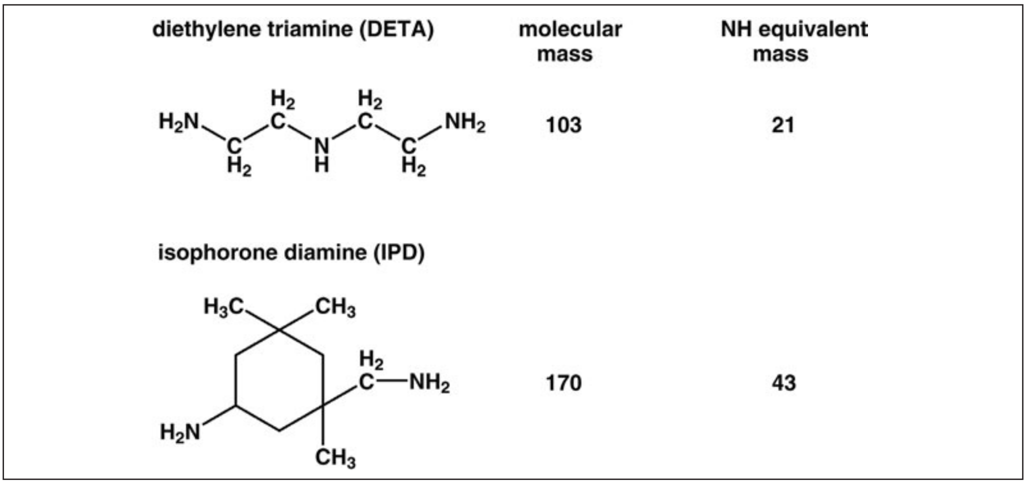


Figure II-1.23: Examples of an aliphatic and a cycloaliphatic amine

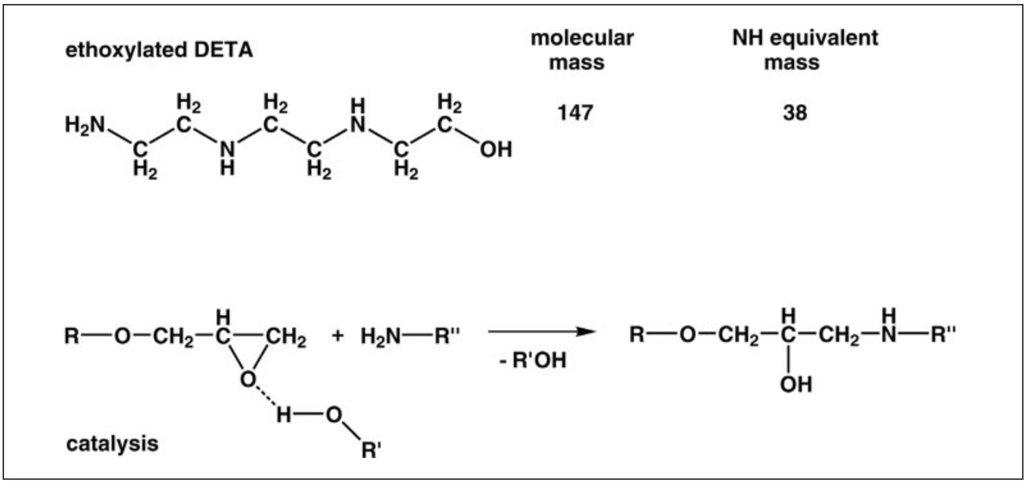


Figure II-1.24: Example of an aminoalcohol hardener

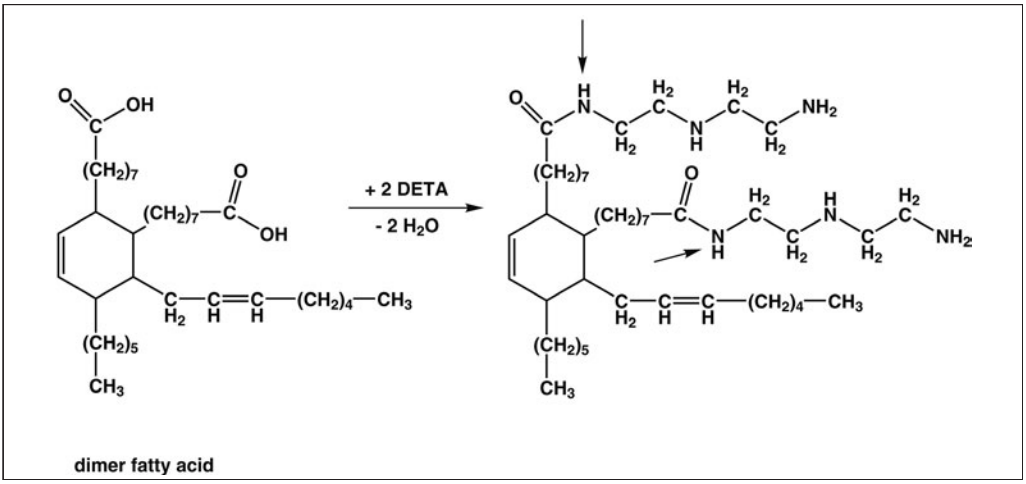


Figure II-1.25: Idealized diagram of a polyaminoamide based on dimer fatty acid and DETA

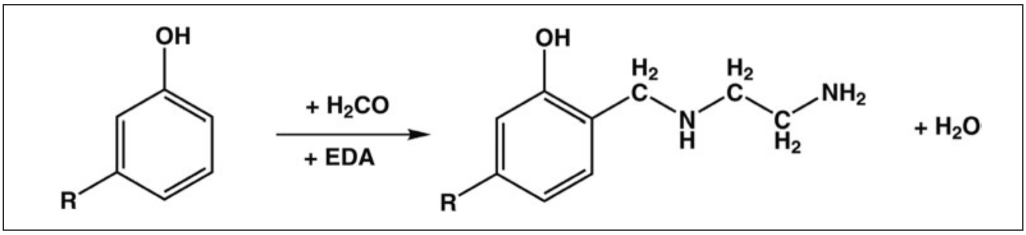


Figure II-1.26: Simplified diagram of the Mannich reaction between phenol derivatives formaldehyde and ethylene diamine (EDA). R = H or alkyl group

The reaction between amines and ethylene oxide leads to highly reactive aminoalcohol hardeners; these are able to catalyze the curing reaction (Figure II-1.24). Similar catalysis is effected by adding water, salicylic acid or lactic acid.

Polyaminoamides

Because of their higher molar mass, polyaminoamides (Figure II-1.25) react more slowly than polyamines. They yield more hydrophobic coatings because of their fatty acid structural parts. For this reason, polyaminoamides are commonly used in anticorrosion coatings.

As an exercise, the NH-equivalent mass of the polyaminoamide (Figure II-1.25) will be calculated.

Dimer fatty acid (2 · C_{18} fatty acid): $C_{36}H_{64}O_4$, molar mass 560.9

DETA: $C_4H_{13}N_3$, molar mass 103.2

Dimer fatty acid +2 DETA (-2 H_2O): $C_{44}H_{86}O_2N_6$,
molar mass 731.2

NH-equivalent mass 731.2/6 = 122

When calculating the NH-equivalent mass, it is important not to count the two non-reactive amide NH-atoms (indicated by an arrow in Figure II-1.25). Amides are much less nucleophilic than amines; amides usually do not react with epoxy groups (oxirane rings) at ambient temperature.

Mannich bases

The reaction between phenol and formaldehyde and amines yields Mannich bases (Figure II-1.26), which are used as highly reactive hardeners, even at low temperatures (accelerating action of phenol; see aminoalcohols in Figure II-1.24). The Mannich reaction (Figure II-1.26) may lead to mixtures of products.

If R in Figure II-1.26 is an unsaturated C15 alkyl group, phenalkaneamines are obtained by the Mannich reaction. C15 substituted phenol derivatives are obtained from cashew nutshell oil [21]; the most important of the substances obtained are the Cardanols [23]. The doubly unsaturated Cardanol is shown in Figure II-1.27. In the crosslinked epoxy coating, the aliphatic C15 chain of Cardanol improves corrosion protection, due to its hydrophobic character [21].

Mannich bases from formaldehyde and secondary amines can serve as accelerators (Figure II-1.28).

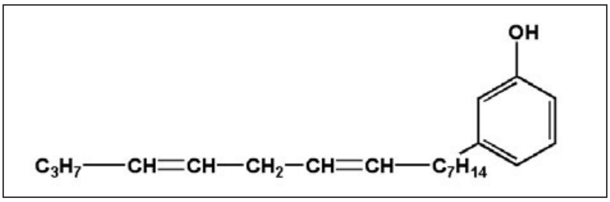


Figure II-1.27: Doubly unsaturated Cardanol

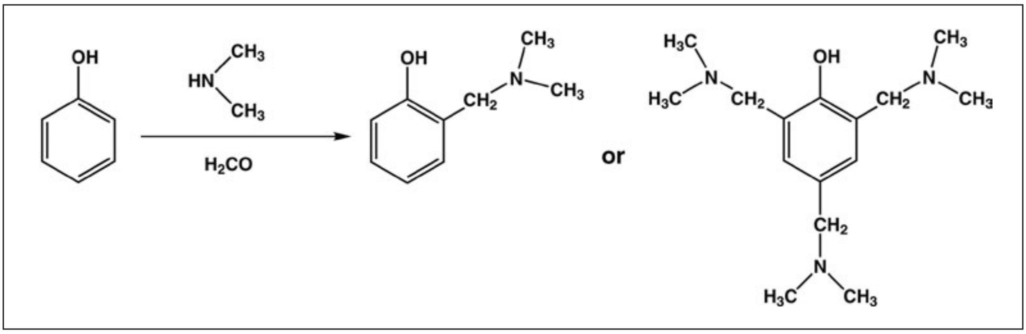


Figure II-1.28: Mannich reaction between phenol and different amounts of formaldehyde and dimethyl amine

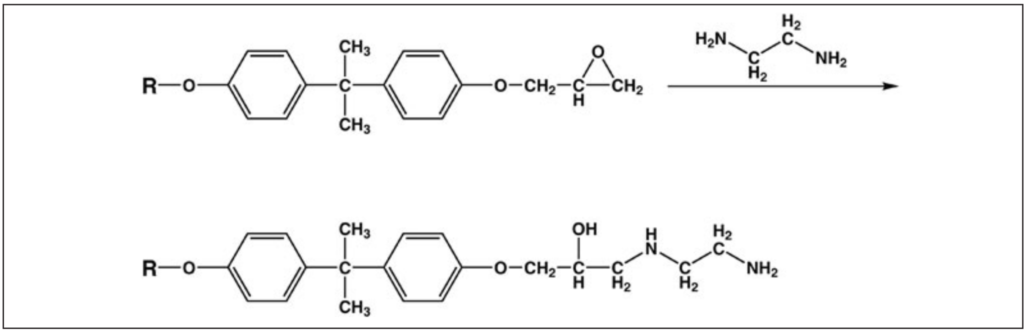


Figure II-1.29: Simplified diagram of a polyamine adduct

Polyamine adducts

The reaction between polyamines (in excess) and epoxy resins yields polyamine epoxy resin adducts (polyamine adducts) having a significantly higher NH-equivalent mass (Figure II-1.29). Polyamine epoxy resin adducts are less reactive than polyamines because of their increased molar mass. Polyaminoamides (see Figure II-1.25) may also be used in the form of adducts.

1.3.2.3 Formulation of two-components epoxy paints

The solvents for two-components epoxy paints have to be chosen carefully. Not only are application properties such as levelling and drying time influenced by solvents but also the pot life of the mixed two-components paint and the chemical resistance of the coating. Chemical resistance and especially the water and acid resistance are lowered by adding high boiling solvents that are miscible with water (e.g. diacetone alcohol, butyl glycol); solvent retention and swelling by water may occur. Ketones react with aminofunctional hardeners to form imines and therefore prolong the pot life whereas alcohols shorten it.

A solvent mixture for two-components epoxy paints (based on epoxy resin type 1; see Figure II-1.20) contains true solvents, such as methoxypropanol, methoxypropyl acetate and methyl isobutyl ketone (MIBK), as well as latent solvents, such as xylene and 1-butanol. It should be noted that epoxy resins of type 1 frequently contain xylene as diluent (e.g. are delivered as a 75% solution in xylene) but are not totally miscible with xylene. In two-components epoxy paints, a certain amount of alcohol (e.g. 1-butanol or methoxypropanol) is necessary, as otherwise compatibility problems with amine hardeners may occur.

Esters and ketones should not be added to the amine hardener as chemical reactions may take place in storage.

It should be noted that pigments which react chemically with the hardener (e.g. metal pigments) can only be dispersed in the base component.

To save on costs, compatible hydrocarbon resins can be added; the mixing ratio of hydrocarbon to epoxy resin is about 40 : 60.

When mixtures of different epoxy resins or hardeners are used, average equivalent masses have to be calculated as follows:

$$\text{Equivalent mass (mixture)} = \frac{\text{mass (mixture)}}{\text{mass 1 / equivalent mass 1 + mass 2 / equivalent mass 2 + …}}$$

Similar averages can calculated for other characteristic values of mixtures.

Formulations

Typical formulations are the following two-components aircraft primer and two-components anticorrosion primers containing zinc phosphate as chemically active anticorrosion pigment.

Coatings in aircraft interiors are especially characterized by their FST properties. FST is the abbreviation for fire, smoke and toxic. This means that these coatings are characterized by low flammability and reduced and non-toxic smoke formation, allowing sufficient time for evacuation of the aircraft in the case of fire. As an example, Table II-1.23 presents an FST primer for metals based on a two-component epoxy resin. Of special importance is the flame retardance pigment (item 11) which simultaneously acts as anticorrosive pigment.

The characteristic values of this aircraft coating are shown in (Table II-1.23).

Hardener calculation: g hardener on 100 parts by weight epoxy resin (solids) = 0.205 • 198 = 40.6 (• 0.164) = 6.7

i.e. 15% excess of hardener in the formulation

Pigment/binder ratio (without additives): P/B = (6.7 + 15.5 + 6.2 + 14 + 0.1) : (16.4 + 7.8) = 42.5 : 24.2 ≈ 1.8 : 1

Table II-1.23: Two-components epoxy FST-primer for aircraft interiors

pos.	raw material	parts by weight	solids
base component (component A)			
01	epoxy resin, type 1 (75%)	21.9	16.4
02	methoxy propanol	6.2	
03	methyl isoamyl ketone	1.5	
04	xylene	13.4	
05	wetting and dispersing agent	0.5	
06	organo clay	0.5	0.5
07	hydrophobic fumed silica	0.5	0.5
08	talc	6.7	6.7
09	baryte filler	15.5	15.5
10	titanium dioxide rutile	6.2	6.2
11	flame retardance pigment	14.0	14.0
12	carbon black	0.1	0.1
sum		87.0	59.9
hardener (component B)			
13	polyamide resin (100%)	7.8	7.8
14	xylene	5.2	
total		100.0	67.7

01: Beckopox EP 301/75X (Cytec), 75% in xylene, epoxy equivalent mass (solid) 450 to 525, epoxy value = 100/487.5 = 0.205 (solid)
03: 5-methyl hexane-2-one
05: Antiterra 204 (Byk)
06: Bentone 38 (Elementis) and /or Tixolgel VP (Rockwood), rheological additive
07: Aerosil R 972 (Evonik Degussa), rheological additive
08: Finntalc M15 (Finnminerals) d = 2.75 g/cm^3
09: Albaryt (Sachtleben) d = 4.3 g/cm^3
11: multiphase pigment based on zinc-borate-orthophosphate-hydrate, Heucophos BZN (Heubach) d = 3.0 g/cm^3
12: carbon black pigment, e.g. Flammruß 101 (Evonik Degussa) d = 1,8 g/cm^3
13: Versamid 115 (100% solids), NH-equivalent mass 198 (Cognis)

Table II-1.24: Two-components epoxy anticorrosion primers

pos.	raw material	parts by weight formulation 1	 formulation 2
base component (component A)			
01	epoxy resin, type 1 (75% in xylene)	28.0	27
02	iron oxide red	14.2	15
03	zinc phosphate	14.2	15
04	baryte filler	9.5	10
05	talc	9.5	10
06	methyl isobutyl ketone	8.0	8
07	xylene	13.0	12
08	1-butanol	3.6	3
sum base component		100.0	100
hardener (component B)			
09	polyaminoamide (70%)	15	
10	polyaminoamide adduct (60%)		22.0
11	xylene		2.4
12	1-butanol		0.6
sum hardener		15	25.0
sum total		115	125.0
solids [%]		69	67.0

pos. 01: 75% in xylene, epoxy value 0.205 (solid) respectively 0.155 (solution), epoxy equivalent mass 488 (solid)
pos. 09: polyaminoamide based on dimer fatty acid, 70% in xylene. NH-equivalent mass 240 (solid) respectively 340 (solution), e.g. Aradur 115/70X (Huntsman)
pos. 10: polyaminoamide adduct, 60% in xylene/1-butanol = 4/1, NH-equivalent mass 520 (solution), e.g. Aradur 423 (Huntsman)

PVC (without additives) = [(6.7/2.75 + 15.5/4.3 + 6.2/4.1 + 14/3 + 0.1/1.8) : [(6.7/2.75 + 15.5/4.3 + 6.2/4.1 + 14/3 + 0.1/1.8 + 16.4/1.2 + 7.8/1.2)] • 100% ≈ 38%

For the analysis of the second formulation, let us calculate the characteristic values of the anticorrosion primers (Table II-1.24).

Hardener addition:

Formulation 1: $0.155 \cdot 340 = 52.7$ ($\cdot$ $0.28 = 14.8$)

Formulation 2: $0.155 \cdot 520 = 80.6$ ($\cdot$ $0.27 = 21.8$)

I.e., roughly stoichiometric addition levels.

Pigment/binder ratios:

Formulation 1
P/B = $(14.2 + 14.2 + 9.5 + 9.5) : (28 \cdot 0.75 + 15 \cdot 0.7) = 47.4 : 31.5 = 1.5 : 1$

Formulation 2
P/B = $(15 +15 +10 +10) : (27 \cdot 0.75 + 22 \cdot 0.6) = 50 : 33.45 = 1.5 : 1$

Pigment volume concentrations:

Densities (g/cm^3): Baryte filler 4.3; talc 2.7; zinc phosphate 3.3; iron oxide red 5.0; cured epoxy resin about 1.2

Formulation 1

$$\text{PVC} = \frac{9.5 / 4.3 + 9.5 / 2.7 + 14.2 / 3.3 + 14.2 / 5}{9.5 / 4.3 + 9.5 / 2.7 + 14.2 / 3.3 + 14.2 / 5 + (21 + 10.5) / 1.2} \cdot 100\% = 32.9\% \approx 33\%$$

Formulation 2

$$\text{PVC} = \frac{10 / 4.3 + 10 / 2.7 + 15 / 3.3 + 15 / 5}{10 / 4.3 + 10 / 2.7 + 15 / 3.3 + 15 / 5 + (20.25 + 13.2) / 1.2} \cdot 100\% = 32.8\% \approx 33\%$$

In other words, the two formulations exhibit roughly the same pigment/binder ratios and pigment volume concentrations.

Note that both these formulations (Table II-1.24) contain talc, which is said to improve adhesion. These starting formulations could be optimized by adding a rheology modifier.

The two formulations (Table II-1.24) have the disadvantage that, for the production of lab batches, two different mill bases are necessary. It would be much more economical to formulate the recipes in a way that only one mill base is needed for both epoxy paints. This method of paint formulation is explained below. Also discussed is the development of paint formulations that goes far beyond the analysis of existing formulations (Tables II-1.24 and II-1.23).

Development of paint formulations

The objective is as follows:

Develop formulations for 2 two-components topcoats (white) based on epoxy resin type 1 (see Figure II-1.20) and polyaminoamide or polyaminoamide adduct as hardeners. The pigment/binder ratios (of the mixtures of base component and hardener) P/B should be 0.75 : 1; the non-volatile content should be 60%. Both paints are to be produced from just one mill base.

The first step in solving this problem is to choose the appropriate raw materials; the epoxy resin and the hardeners should be compatible with each other.

Epoxy resin type 1: 75% in xylene, epoxy value 0.155 (as delivered) and 0.205 (solid)

Polyaminoamide: 60% in xylene/methoxypropanol = 4 : 1, NH-equivalent mass 790 (as delivered) and 474 (solid), e.g. Aradur 100/60 XMP (Huntsman)

Polyaminoamide adduct: 60% in xylene/1-butanol = 4 : 1, NH-equivalent mass 520 (as delivered)

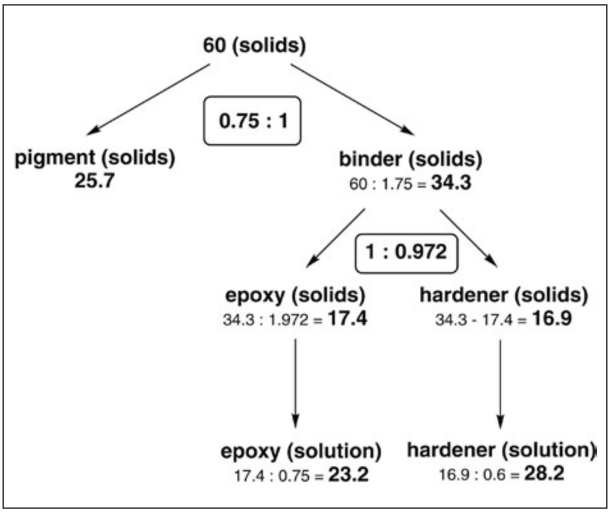


Figure II-1.30: Development of a paint formulation for polyaminoamide

Table II-1.25: Formulation of the polyaminoamide-based paint

parts by weight	raw material	solids
23.2	epoxy resin type 1 (75%in xylene)	17.4
28.2	polyaminoamide (60%)	16.9
25.7	titanium dioxide rutile	25.7
10.0	methyl isobutyl ketone	
10.0	xylene	
2.9	1-butanol	
100.0	sum	60.0

Table II-1.26: Formulation of the base component and hardener addition (polyaminoamide)

base component (A-component)		
parts by weight	**raw material**	**solids**
32.3	epoxy resin, type 1 (75% in xylene)	24.2
35.8	titanium dioxide rutile	35.8
13.9	methyl isobutyl ketone	
13.9	xylene	
4.1	1-butanol	
100.0	sum	60.0
hardener (B-component)		
39.3	polyaminoamide (60%)	23.6

and 312 (solid), e.g. Aradur 423 (Huntsman)

The pigment is titanium dioxide rutile, density 4.1 g/cm^3; to simplify formulation, only titanium dioxide will be used here; in practice, small amounts of iron oxide yellow and black are added to improve hiding.

Solvents: Methylisobutyl ketone (MIBK), xylene and 1-butanol in the ratio 1 : 1 : 0.3.

Additives are not necessary for the first lab batch.

The next step is to calculate the level of hardener addition (parts by weight) for a stoichiometric reaction with 100 parts by weight of epoxy resin type 1:

Hardener addition = epoxy value of epoxy resin type 1 (solid) · NH-equivalent mass (solid) of

poly aminoamide = 0.205 · 474 = 97.2

Polyaminoamide adduct addition = 0.205 · 312 = 64

In other words, more polyaminoamide is needed. Therefore, we start developing the formulations with the polyaminoamide because this formulation contains less epoxy resin at constant pigment/binder ratio. The paint containing polyaminoamide adduct has more epoxy resin and can be produced from the mill base or base component of the first one (polyaminoamide) by letting down.

The calculations for polyaminoamide (Figure II-1.30) lead to the paint formulation (Table II-1.25). With the help of the law of proportions, this is converted to a formulation for the base component and the hardener addition (Table II-1.26).

For stoichiometric crosslinking, the 24.2 parts by weight epoxy resin (solid) in the base component (Table II-1.26) need 64 · 0.242 = 15.5 parts by weight polyaminoamide adduct (solid). In other words, the formulation containing polyaminoamide adduct needs 23.6 – 15.5 = 8.1 parts by weight of binder (solid) because the pigment/binder ratio should be constant. These 8.1 parts by weight of binder must be added to the ratio epoxy resin (solid) : polyaminoamide adduct (solid) = 100 : 64 (see above). Thus, we arrive at the following:

Addition of epoxy resin (solid) 8.1 : 1.64 = 4.9 and 4.9 : 0.75 = 6.5 parts by weight of epoxy resin (as delivered).

Addition of polyaminoamide adduct (solid) 8.1 - 4.9 = 3.2; i.e., in total 3.2 + 15.5 = 18.7 parts by weight of polyaminoamide adduct (solid) and 18.7 : 0.6 = 31.2 parts by weight of polyaminoamide adduct (as delivered).

Thus, we can produce the two paint formulations from just one mill base or base component. To verify our procedure, we calculate the PVC of both formulations (according to Table II-1.26).

Polyaminoamide:

$$PVC = \frac{35.8 / 4.1}{35.8 / 4.1 + (24.2 + 23.6) / 1.2} \cdot 100\% = 18\%$$

Polyaminoamide adduct:

$$PVC = \frac{35.8 / 4.1}{35.8 / 4.1 + (24.2 + 4.9 + 18.7) / 1.2} \cdot 100\% = 18\%$$

The PVC is constant for both paints and that indicates that our recipes are correct.

1.4 References

[1] H. Wagner, H. F. Sarx, Lackkunstharze, Publisher Carl Hanser Munich (1971)

[2] D. Stoye, W. Freitag (editor), Lackharze, Publisher Carl Hanser Munich Vienna (1996)

[3] W. Krauß (editor), Kittel, Lehrbuch der Lacke und Beschichtungen, Volume 2: Bindemittel für lösemittelhaltige und lösemittelfreie Systeme, Publisher S. Hirzel Stuttgart - Leipzig (1998)

[4] K. D. Ledwoch (editor), Kittel, Lehrbuch der Lacke und Beschichtungen, Volume 1: Geschichte, Grundlagen, Naturstoffe, anorganische Bindemittel, Publisher S. Hirzel Stuttgart - Leipzig (1998)

[5] Brochure of Wolff Walsrode AG, Walsroder NC

[6] P. Thomas (editor), Polyurethanes, J. Wiley and Sons; London etc (1998)

[7] M. Bock et al., Polyurethane für Lacke und Beschichtungen, Publisher Vincentz Network, Hanover (1999)

[8] O. Lückert, Karsten – Lackrohstofftabellen, 10. Auflage, Publisher Vincentz Network Hannover (1996)

[9] R. Wissmann, R. W. Hein, Sikkative, Farbe & Lack 106, No. 3 (2000) p. 38

[10] W. J. Muizebelt et al., Oxidative Curing, Progr. Org. Coat. 24 (1994) p.263, Progr. Org. Coat. 31 (1997) p. 331 and J. Coat. Tech. 70, No. 876 (1998) p. 83

[11] L. Thiele, R. Becker, H. Frommelt, Synergien von 2K-Katalysatoren; Zeitschr. für Polymerforschung 28 (1977) p. 405

[12] Relative Aktivität einiger PUR-Katalysatoren; Kunststoffhandbuch, Volume 7, p. 95, C. Hanser Verlag Munich (1983)

[13] Datasheet of BASF SE

[14] Brochure of Clariant (former Hoechst)

[15] W. J. Blank et al. (King Industries): Crosslinking with Polyurethanes, W. J. Blank et al. (King Industries), Catalysis of the Isocyanate-Hydroxyl Reaction by Non-Tin-Catalysts

[16] E. V. Schmid: Zwanzig Jahre Erfahrungen mit Zinkstaubanstrichen; Farbe & Lack, 88 (1982) p. 435-442

[17] H. Ferch: Spezielle Effekte bei Einsatz hydrophober Kieselsäure in Beschichtungssystemen, Farbe & Lack, 85 (1979) p. 651-657

[18] O. Lückert: Wissenswertes über Zinkstaubfarben; Farbe & Lack, 74 (1968) p. 469-472

[19] H. Kittel, Lehrbuch der Lacke und Beschichtungen, Volume 2, Chapter 2.2.2, Epoxidharzbindemittel (epoxy resin binders), 2nd ed., Publisher S. Hirzel (1998)

[20] Borchers, Guide formulation, RR 1.12

[21] J.-L. Dallons, Europ. Coat. Journ. (2005) No. 6, p. 34-37

[22] Borchers, Guide formulation, RR 1.25

[23] http://en.wikipedia.org/wiki/Cardanol

[24] B. Osterath, Nachr. Chem. 59, Febr. 2011, p. 121-123

2 Stoving enamels

2.1 Definitions

Stoving enamels are paints which cure at elevated temperatures. Such paints meet the requirements of industrial coating processes well. In particular, they lend themselves to serial-application methods. Because of the different kinds of systems in existence, effective stoving temperatures are between 80 °C and 250 °C. Stoving periods at these temperatures range from one minute to one hour. Under these conditions – during film formation – crosslinking takes place. Thus, while organosols and plastisols solidify at elevated temperatures, they do so only by a physical process and therefore are not classified as typical stoving enamels (see Chapter II-1.1 Physically drying paints).

Most stoving enamels contain two or more resin compounds that can react chemically with each other to form crosslinked molecular structures. There are also a few types of resins capable for self-crosslinking. Stoving enamels are additionally defined as reactive paints. The resin compounds are selected such that the reaction rate at ambient temperatures is low to enable the finished paint to be stored for an acceptable length of time. The most common storage time for such paints is 6 months. With some exceptions, stoving enamels are delivered as finished (ready mixed) systems. For most of them, it is necessary to add some solvent to lower the viscosity just prior to application. The exceptions are two-component paints, which can crosslink at ambient temperatures but are cured at elevated temperatures so as to accelerate film formation in industrial coating processes (e.g. two-component OEM clear coats, see Chapter II-1.3).

2.2 Stoving enamels based on amino resins

2.2.1 Chemical structure of amino resins

The common definition of “amino resin” is not chemically correct because the base raw materials for amino resins are amides not amines. These are **urea** (diamide of carbonic acid), **carbamates** (esters of carbaminic acid, the monoamide of carbonic acid), **melamine** (triamide of cyanuric acid, or 2,4,6-triaminotriazine), **benzoguanamine** (2-phenyl-4,6-diaminotriazine) and **glycoluril** (acetylene diurea). The chemical structures of these components are presented in Figure II-2.1

Hydrogen atoms attached to amide nitrogen atoms are reactive if the neighbouring double bond exerts an influence. Among other reactions, they can add formaldehyde to form methylol compounds. Figure II-2.2 shows the reaction between urea and formaldehyde.

Methylol compounds are also reactive and will form methylene bridges with other amide hydrogen atoms. Methylol groups react which each other to form dimethylene ether bridges. All reactions involve the cleavage of one molecule of water. Figure II-2.3 shows the methylol reactions that lead to the formation of large molecules.

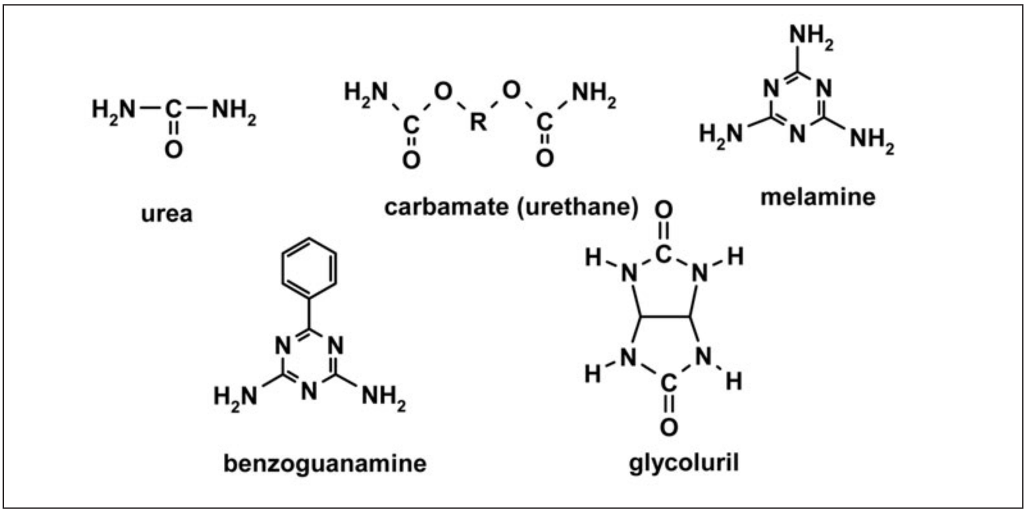


Figure II-2.1: Chemical structures of components for amino resins

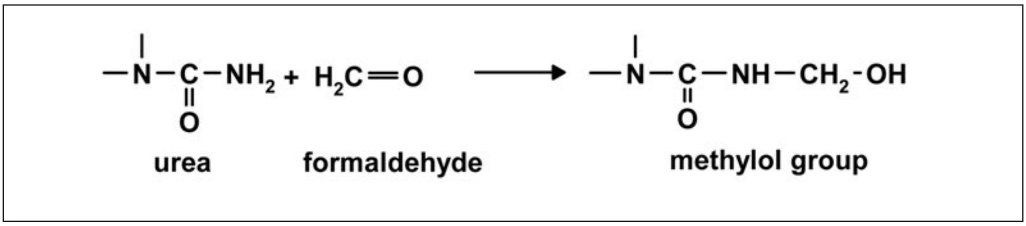


Figure II-2.2: Reaction between urea and formaldehyde

The result is molecules of so-called non-modified amino resins, which consist of amides connected via methylene bridges and dimethylene ether bridges, methylol end groups and residual hydrogen atoms on the nitrogen atoms. The compounds are branched, but there is also the possibility of forming cyclic structures. The use of excess amounts of formaldehyde can lead to the formation of polyacetals.

Non-modified amino resins are highly polar compounds. They are soluble in water and lower alcohols. They therefore find little use in paint formulations. However, they are used in large quantities for adhesives, laminated sheets, and textile coatings.

Amino resins are modified for use in paint systems. The modification consists in etherifying the free methylol groups with monoalcohols. Suitable monoalcohols are methanol, isobutanol, and 1-butanol. Etherified amino resins are much more soluble in the usual solvents and compatible with other resins. Also, they have a better storage stability. Figure II-2.4 shows the reaction of methylol groups with monoalcohol to form ether groups.

Amino resins for paint systems are characterized by the average molar mass and the number of different functional groups (residual amide hydrogen, methylol groups, and etherified methylol groups). These characteristic values are influenced by the ratios of components (molecular ratio of amide : formaldehyde : monoalcohol), the use and amounts of catalysts for the addition and condensation reactions (acids and bases), and the reaction conditions (temperature, reaction time, concentration of solution). Amino resins are usually produced in aqueous solutions. At the end of the production process, the process water and the water from the condensation reaction are distilled off. Low-molecular, highly etherified amino resins are delivered as such (100%). The other amino resins are delivered in solutions

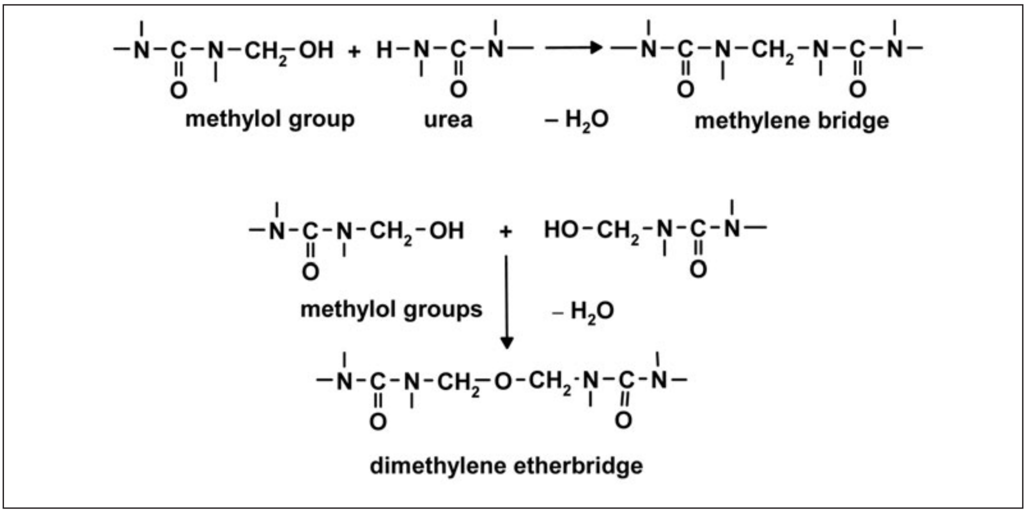


Figure II-2.3: Methylol reactions leading to the formation of large molecules

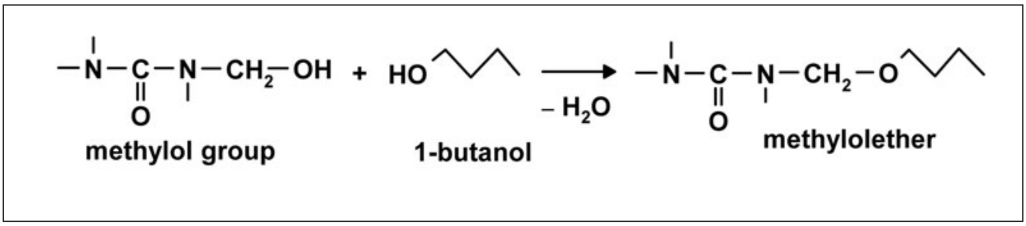


Figure II-2.4: Reaction of methylol groups with monoalcohols to form methylol ethers

in alcohols or mixtures of alcohols (e.g. butanols) and aromatic solvents (e.g. xylene). The alcohols employed may contain excess amounts of the monoalcohol of the ether modification. Amino resins which are modified by etherification with high amounts of methanol are water-soluble or at least water-thinnable.

2.2.2 Types and properties of amino resins

Amino resins are classified first by their amide component. There are urea resins, carbamate resins, melamine resins, benzoguanamine resins and glycoluril resins.

Urea resins

Urea resins produced from urea, formaldehyde, and monoalcohols (mostly butanol) are very inexpensive crosslinkers for suitable partner resins (alkyd resins, saturated polyesters, epoxy resins). Combinations in paints produce hard films on stoving that offer excellent resistance to solvents. But the films are less flexible and not weatherable. Due to the aforementioned properties, combinations of urea resins are preferred for stoving primers and primer surfacers. Optimum stoving temperatures for urea combinations depend on the molar mass and degree of etherification of the amino resin, and lie between 140 and 180 °C.

Curing takes the form of crosslinking at the hydroxyl groups of the combination resin (co-crosslinking) and by self-crosslinking of the urea resin. The first reaction is a transetherification in which monoalcohol is cleaved. The self-crosslinking consists in the formation of methylene and dimethylene ether groups, with cleavage of water, just like during synthesis of the resin. But monoalcohols and formaldehyde are also by-products of the stoving process. The crosslinking rate may be accelerated by adding catalysts, acids and so-called blocked acids. Adding relatively high amounts of strong acids significantly lowers the curing temperatures and crosslinking takes place at ambient temperatures (in so-called acid-curing paints).

Examples of commercial products are [8]:

Plastopal-types, (BASF SE); Setamine U-types (Nuplex); Viamin H-types (Cytec Surface Specialties, Vianova); Beetle BE-types (Cytec BP); Dyomin U-types (Cytec-Dyno).

Additionally, there is a group of modified urea resins called plasticizied urea resins. These are pre-condensates of urea resins with saturated polyesters containing hydroxyl groups. The pre-condensation is a partial etherification or trans-etherification reaction. The plasticization effect results from flexible structural elements in the polyesters (e.g. adipic acid).

Examples of commercial products are [8]:
Plastopal A-types (BASF SE).

Carbamate resins

Carbamate resins are also called urethane resins. Although this term is correct – because esters of carbaminic acid are urethanes – it should be avoided, as otherwise misunderstandings arise through comparison with urethane resins from polyisocyanates. Usually carbaminic esters are butanol carbamates or dicarbamates of 1,4-butanediol. The resins are products of the reaction of carbamates with formaldehyde and monoalcohols. Due to the influence of the carbamates, the resins are marked plasticizing resins. They are therefore used as plasticizers in physically drying paints (see Chapter II-1.1). But they also serve in stoving enamels, where they introduce flexibility through crosslinking. They are less resistant to solvents than are urea resins. The combinations are not weatherable.

Examples of commercial products are [8]:
Plastopal BTB (BASF); Resamin HF 450 (Cytec Specialties Vianova)

Melamine resins

Melamine resins are the most important amino resins in the paint industry. They consist of melamine, formaldehyde and monoalcohols, e.g. methanol, 1-butanol and isobutanol. Classification by structure and properties yields three groups:

a) Low-molecular, highly methylolated, fully etherified melamine resins
b) Relatively low-molecular, highly etherified melamine resins, which still contain residual NH groups (imino grades)
c) Partially etherified melamine resins containing free methylol groups, with different molar masses and different reactivities.

a) Low-molecular, highly methylolated, fully etherified melamine resins

The best known low-molecular, highly methylolated, fully etherified melamine resins are those which contain methanol by way of etherification monoalcohol. On the basis of their idealised structure, they are called hexamethoxymethylmelamine resins (HMMM resins). This structure is shown in Figure II-2.5.

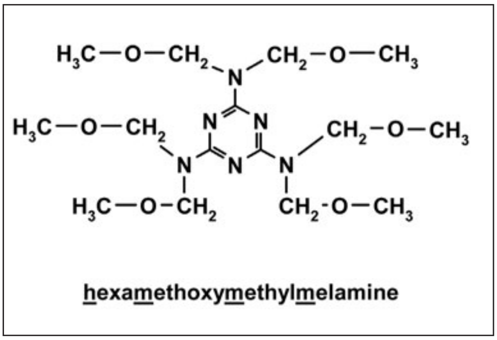


Figure II-2.5: Structure of hexamethoxymethylmelamine

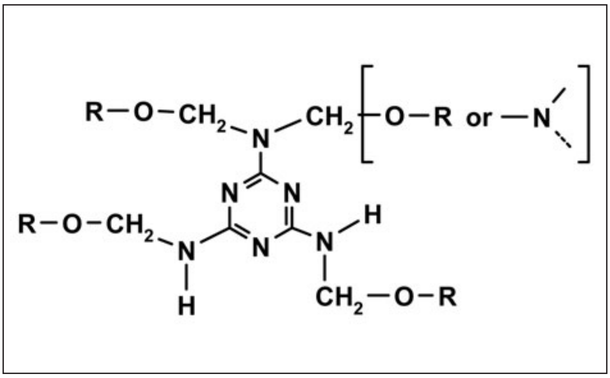


Figure II-2.6: Melamine resin containing imino groups

The HMMM resins are delivered as 100% products. They are either viscous liquids or waxy and are more or less water-soluble. As the trans-etherification reaction of etherified methylol groups is the slowest of all the crosslinking reactions, relatively high stoving temperatures (180 to 200 °C) or efficient catalysis is required. The preferred catalysts are acids, particularly sulphonic acids, although acidic phosphoric esters or their amine salts may be used (see Chapter II-2.2.5). Given an optimum balance of temperature, time, and catalyst, film formation of the paints effectively leads to co-crosslinked structures. These films are distinguished by significant weatherability and good flexibility and intercoat adhesion.

Analysis of the trans-etherification reaction of HMMM resins shows that up to three of the etherified methylol groups of one resin molecule participate effectively in the crosslinking reaction. HMMM resins are relatively low-molecular products, the molar mass of the HMMM molecule being 390.4 g/mol. However, actual products additionally contain molecules which have not just one triazine unit. Nevertheless, and due to their optimum solubility, the resultant low viscosity of HMMM resins offers latitude for formulating high-solids paints. But, of course, the viscosity of the combination partner has to be taken into consideration. Generally, HMMM resins are used for stoving enamels in industrial coatings, particularly for automotive OEM paints and for coil coating and can coating.

Examples of commercial HMMM resins are [8]:
Luwipal 066, 068 (BASF); Maprenal MF 900, MF 904 (INEOS, Vianova), Cymel 301, 303 (Cytec); Resimene 743, 747 (INEOS, Monsanto)

There are also low-molecular resins which are highly etherified with butanol. These resins are mainly used for acid-curing paints. Solubility and reactivity are optimized by employing mixed etherification. These resins consist of mixtures of methanol and butanol ethers in different ratios.

Examples of commercial products are [8]:
Luwipal 044, fully etherified with butanol (BASF); Resimene 753, 755 (INEOS, Monsanto), Cymel 1168 (Cytec) (mixed ethers).

b) Relatively low-molecular, highly etherified melamine resins which still contain residual NH groups (imino types)

Relatively low-molecular, highly etherified melamine resins that still contain residual NH groups (imino types) are significantly more reactive than the completely etherified types. The structure of the resins is presented in Figure II-2.6. At usual stoving temperatures (120 to 160 °C), they do not need any catalysts. However, acid catalysts may be used, too. The residual NH groups may react with methylol groups to form methylene bridges, cleavage of monoalcohol (self-crosslinking). But, by virtue of their acidity, they also accelerate the reaction rate of the methylol ether group on the same nitrogen atom, which forms ether groups with hydroxyl groups of combination resins (co-crosslinking), with cleavage of monoalcohol. Another explanation is the intermediate formation of methylene imine, followed by etherification.

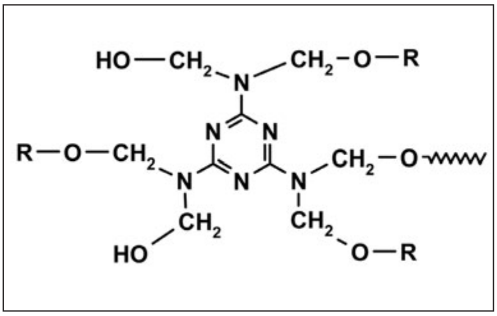


Figure II-2.7: Partly etherified melamine resin

Compared with completely etherified types, the imino grades are less soluble. This leads to higher-viscosity resins, although there are also grades with relatively low average molar masses. Like the completely etherified grades, the imino grades contain butanol or methanol as methylol ethers. These resins are usually delivered in alcohol, most commonly butanols; solids contents are 60 to 90 wt.%. Due to the low content of methylol, the amount of free formaldehyde is lower than in other grades. Together with the fact that relatively low amounts of free formaldehyde are generated during stoving and curing, this is an advantage with regard to requirements on the avoidance of harmful pollution.

Examples of commercial products are [8]:
Luwipal 072 (BASF), Maprenal MF 927 (INEOS, Vianova), Cymel 323, 325, 327 (Cytec), Setamine MS 152 (Nuplex) are grades with methanol ethers.

Luwipal 018 (BASF), Maprenal VMF 3611, 3615 (INEOS Vianova) Cymel 1158 (Cytec), Setamine US 138, US 146 (Nuplex) are grades with butanol ethers.

Grades with high average molar masses are Luwipal 014 (BASF), Maprenal MF 580 (INEOS Vianova).

c) Partially etherified types containing free methylol groups with different molar masses and different reactivities.

Partially etherified melamine resins containing free methylol groups are produced with an excess of formaldehyde but lower amounts of monoalcohol. The excess of formaldehyde and the reactions conditions influence the resultant molar mass. The degree of etherification influences the reactivity. A great many different commercial products are available. Most of the grades in this group have higher molar masses than the resins in the other groups.

Crosslinking takes place by etherification of methylol groups with hydroxyl groups of partner resins, or trans-etherification of etherified methylol groups (co-crosslinking). But there is always a significant amount of self-crosslinking of the methylol groups themselves. The Examples of molecular structure is presented in Figure II-2.7. For stoving at usual temperatures (120 to 160 °C), there is no need for catalysis.

But if the curing temperatures are below 100 °C, acid catalysts must be added. If the molar masses of the melamine resins are high and the viscosities too, the resins promote the physical drying. Melamine resins of this type which contain high quantities of free methylol groups will mainly react by self-crosslinking. Consequently more formaldehyde is generated during stoving. The resultant films are less resistant to acids than are other melamine resin grades.

Examples of commercial products are [8]:
Luwipal 012, 016 (BASF); Maprenal MF 590 (INEOS) Resins grades with higher molar masses are: Luwipal 010, 013 (BASF); Maprenal MF 650 (INEOS)

Benzoguanamine resins

Benzoguanamine resins consist of benzoguanamine, formaldehyde and butanol or methanol (etherification alcohols). Benzoguanamine resins react in the same way as melamine resins. But, due to the lower functionality (benzoguanamine contains only two amide groups), the resultant films are more flexible than melamine resins. The phenyl group on the triazine ring is believed to be responsible for excellent pigment wetting. Films made from benzoguanamine resins are not weatherable. Thus, benzoguanamine resins are mainly suitable for primers and primer surfacers that are characterized by good application behaviour, films of good appearance (filling power) and excellent mechanical properties (stone-chip resistance). Due to the aforementioned properties, benzoguanamine resins are also used in can-coating paints. Benzoguanamine resins are more expensive than melamine resins.

Examples of commercial products are [8]:
Luwipal B 17 (BASF); Cymel 1123, 1125 (Cytec); Maprenal MF 980, 988 (INEOS)

Glycoluril resins

Like benzoguanamine, glycoluril (acetylene diurea) can add four molecules of formaldehyde to form the tetramethylol compound. Tetramethylol glycoluril is a solid (with a softening temperature of 90 to 110 °C). The product is a crosslinker for polyesters that contain hydroxyl groups and is used in powder coatings (see ChapterIV-3.4.2.3.2). Methylol glycolurils can form oligomers by condensation. The methylol groups may also be etherified with monoalcohols. Etherified glycoluril resins are crosslinkers for resins that contain hydroxyl groups. Due to their low reactivity, acid catalysts are required. The resultant films have good intercoat adhesion; they are hard and solvent-resistant. The combinations are preferred for can-coating and primers. Due to the good solubility of this type of amino resin, they can be used for high-solids paints. Glycoluril resins are also suitable for water-borne resins, but the resins are less stable at high pH values.

Examples of commercial products are [8]:
Cymel 1170, 1171 (Cytec)

2.2.3 Combination partners for amino resins

All combination partners for amino resins are resins which contain a significant amount of hydroxyl groups. The important partners for stoving enamels are alkyd resins, saturated polyesters, and acrylic resins (containing hydroxyl groups). Of minor importance are epoxy resins, epoxy esters and special vinyl resins.

2.2.3.1 Alkyd resins

Alkyd resins [1 to 4] belong to the class of polymers known as polyesters. Besides the usual structural elements of polyesters (polyols and polycarboxylic acids), alkyd resins consist additionally of monocarboxylic acids. Monocarboxylic acids are natural fatty acids, synthetic fatty acids as well as benzoic acids and acids from natural resins (rosin). The polycarboxylic acid in alkyd resins is phthalic acid (used as anhydride), with only few exceptions. There are tri- and tetra-functional polyols.

Alkyd resins for stoving enamels have relatively low molar masses; the content of monocarboxylic acid ranges from 25 to 50 wt.%. The hydroxyl numbers lie between 50 and 150 mg KOH/g, while the acid numbers are between 10 and 20 mg KOH/g. For curing under stoving conditions, a significant amount of co-crosslinking may be expected. The crosslinking reaction takes place between hydroxyl groups and methylol or methylol ether groups of the amino resin.

Since there is no need for oxidative crosslinking, the alkyds selected consist mainly of so-called non-drying fatty acids. Saturated fatty acids are preferred. Nowadays, the saturated fatty acids are produced synthetically and yield particularly yellowing-resistant and weatherable films. Generally, fatty acid modification in alkyd resins promotes flexibility, solubility in less polar solvents, compatibility with many other resins, good pigment wetting, and good wetting of substrates, and leads to optimum application behaviour, excellent appearance and gloss, and levelling of films.

Most of these alkyd resins are soluble in aromatic solvents and esters, and dilutable with alcohols and glycol ethers. Thus, the delivery forms contain mostly aromatics, but also small amounts of esters, alcohols, or glycol ethers.

Films formed from stoving enamels containing alkyds and amino resins are distinguished by an optimum balance of hardness and flexibility. If melamine resins are used, the films offer adequate weatherability. The resistance of these coatings to chemicals and weathering is only surpassed by films made from paint systems containing aliphatic and cycloaliphatic isocyanate crosslinkers.

Alkyd resins with relatively low fatty acid content and, especially, grades which contain long aliphatic chains (e.g. soya fatty acid and dehydrogenated castor fatty acids) are combined with urea resins and benzoguanamine resins, and used for stoving primers and primer surfacers. Such combinations are notable for good resistance to solvents, adequate hardness (for sanding), and good wetting of pigments and substrates. They also have adequate flexibility, and, where benzoguanamine resins are used, they offer excellent flexibility. But also the choice of pigments and extenders can promote intercoat adhesion, levelling, and filling power, and sanding properties. Sometimes primer surfacers contain coloured pigments and that requires good pigment-loading properties for the resin combinations.

Examples of commercial alkyd resins with low amounts of long-chain fatty acids for stoving enamels are [8]:
Alkydal F 26 (Bayer), Vialkyd AC 274 (Cytec Surface Specialties, Vianova)
Types with DCO fatty acid (dehydrated castor oil)
Vialkyd AR 280, AR 427 (Cytec Surface Specialties, Vianova), Setal 118, 123, 126 (Nuplex), Worléekyd SM 400 (Worlée)

A combination of alkyd resins containing saturated fatty acids and melamine resin is the binder composition typically used in topcoat stoving enamels. In Europe, this combination is also used for OEM topcoats. The systems are characterized by optimum pigment wetting, excellent levelling and appearance of the films, and yellowing resistance. Where optimum flexibility is a particular requirement, the choice falls on alkyd resins that contain small amounts of unsaturated fatty acid in addition to saturated fatty acid. However, this comes at the expense of limited yellowing resistance, particularly in the case of overstoving.

Examples of commercial alkyd resins with saturated fatty acids for stoving enamels are [8]:
Setal 84 (Nuplex), Alkydal F 251, F 300 (Bayer), Vialkyd AC 451 (Cytec Surface Specialties, Vianova)

For paints which are cured at low temperature (the so-called 80 °C enamels), the combination choice is melamine resins and alkyd resins that contain significant levels of conjugated fatty acids. These are fatty acids with significant amounts of 9,11-linoleic acid, and prepared from dehydrogenated castor oil or by isomerisation of fatty acids with a high amount of 9,12-linoleic acid (e.g. from soya oil, cottonseed oil or sunflower oil). The conjugated fatty acids do not support crosslinking by an oxidative mechanism, but rather crosslinking via C-C polymerization of double bonds (1,4-polymerization). Together with the reaction between the melamine resin and the alkyd hydroxyl groups, the supporting reaction guarantees optimum film formation at low temperatures. There is relatively good stability to chemicals and – particularly important for these conditions – stability to condensation water.

Examples of commercial products are [8]:
Setal 123 (Nuplex), Synthalat SFR 341 (Synthopol-Chemie), Vialkyd AR 280 (Cytec Surface Specialties, Vianova)

2.2.3.3 Saturated polyester

Saturated polyesters [1 to 4] for stoving enamels consist mainly of aromatic polycarboxylic acid, especially isophthalic acid. In some cases, isophthalic acid is combined with other dicarboxylic acids, mainly aliphatic acids (e.g. adipic acid). There are also grades that contain phthalic acid. Special grades contain hexahydrophthalic acid (for freedom from aromatic compounds). Saturated polyesters mainly contain mixtures of different diols for optimum solubility and avoiding crystallinity. Besides aliphatic dicarboxylic acids, diols with long aliphatic chains influence the flexibility. The most important branching unit are triols, with trimethylolpropane particularly favoured. The number average molar masses of these polyesters are relatively low. The hydroxyl numbers lie between 80 and 150 mg KOH/g, while the acid numbers range from 5 to 25 mg KOH/g.

Compared with other resin combinations used in stoving enamels, a combination of branched saturated polyesters and melamine resins strikes an optimum balance of hardness and flexibility. The reason is the effective availability of the functional groups (hydroxyl groups) of saturated polyesters. Since flexibility is the sum of plasticity (resulting from the type of structural elements) and elasticity (resulting from effective crosslinking), polyester melamine resin films have greater elasticity than other resin combinations. Consequently, saturated polyesters and melamine resins are mainly used for primer surfacers, basecoats, can coating, coil coating and for plastic coatings. This combination also exhibits adequate weatherability. But if polyester resins contain – as is usually the case – relatively high amounts of aromatic structural elements (mainly isophthalic acid), a combination with melamine resins is not weatherable in clear coats. In such cases, it is necessary to use polyesters that are free of aromatic structural elements. Polyesters containing cycloaliphatic (e.g. hexahydrophthalic acid) or aliphatic structural elements (e.g. adipic acid and all usual polyols) are combined with melamine resins for clear coats and offer outstanding weatherability.

Examples of commercial products are [8]:
Setal 173, 183, 186, 1600, 1703 (Nuplex), Alkynol 1665 (Bayer), Dynapol LH 820, LH 812, LH 828, LH 700 (Evonik Degussa); Uralac SN 820, SN 822, SN 830 (DSM); K-Flex 188 (King Industries); Vialkyd AN 950 (Cytec Surface Specialties, Vianova)

There is a special class of saturated polyesters, namely the linear, high-molecular polyesters containing aromatic dicarboxylic acid and short-chained diols. The number average molar masses are as high as 20,000 g/mol. Although there are hardly any available functional groups (hydroxyl numbers are about 5 mg KOH/g), the polyesters are combined with melamine resins, especially HMMM resins. The films formed from this combination at relatively high stoving temperatures, and added acid catalysts, are highly flexible and resistant to chemicals and solvents. It is suspected that the melamine resin self-crosslinks, but is physically coiled with the long polyester molecules, and is thus able to produce the above-mentioned properties. The molecular film structure could be likened to the structure of reinforced steel concrete. Due to these particular properties, these combinations are used for coil coating and can-coating enamels.

Examples of commercial products are [8]:
Dynapol L 205, L 206, L 411 (Evonik Degussa)

2.2.3.3 *Acrylic resins crosslinked by amino resins*

Acrylic resins [9] for solvent-borne stoving enamels are produced by polymerization of acrylic or methacrylic esters (monomers). The standard process is solution polymerization. The resins contain specific amounts of functional groups, hydroxyl groups, and carboxyl groups. The hydroxyl groups result from monomers which contain monoesters of diols and acrylic acid or methacrylic acid. The carboxyl groups are generated by using the free acid as monomer. Hydroxyl number and acid number of the acrylic resins are easily controlled via the levels of hydroxyl monomers and free unsaturated acids. Acrylic resins may contain other monomers that can polymerize with the acrylic or methacrylic esters, so-called comonomers. The most common comonomer is styrene. Styrene in an acrylic resin increases hardness and gloss. But high amounts of it limit the weatherability of clear coats.

Acrylic resins may be classified by the molar masses, the molar mass distributions, the hydroxyl number, the acid number and the monomer composition. First, the monomer composition determines the solubility of the resins. Second, the monomer composition is important for the hardness (physical) of the film, as opposed to plasticization. The glass transition temperature reflects the optimum value for the balance between hardness and plasticization. It is the temperature at which polymers leave the glass-like state and transfer into the rubber-like phase, as measured by the modulus of elasticity. Acrylic resins containing adequate amounts of acrylic and methacrylic esters with short side chains or quantities of styrene have high glass transition temperatures, which lead to films that have high hardness but are less soluble and less compatible. In contrast, acrylic resins containing monomers with long side chains have low glass transition temperatures and the polymers are more soluble and compatible, and form films of greater plasticity. Resins containing methacrylic esters are generally much more viscous than resins containing the corresponding acrylic esters in the same solution, although they have the same molar masses. Furthermore, their films are harder.

Generally, though, the molar mass and molar mass distribution determine the viscosity of the polymer solution, which also determines the application solids. The quantity and type of hydroxyl groups (primary or secondary) influence the reactivity and the crosslinking efficiency. Effective crosslinking confers durability and weatherability. Carboxylic groups in acrylic resins act as catalysts for crosslinking with amino resins. Combinations of acrylic resins and amino resins in stoving enamels are notable for fast physical drying (which leads to less redissolving of two-coat wet-on-wet applications), good mechanical and chemical resistance, and yellowing resistance. The use of melamine resins for crosslinking yields films that offer good weatherability. Thus, the aforementioned combinations are preferred for stoving enamels (topcoats and clear coats) for high-quality industrial coatings and automotive OEM coatings.

2.2.3.4 *Comparison of alkyd resins, polyesters and acrylic resins in stoving enamels*

Alkyd resins, saturated polyesters, and acrylic resins exhibit different properties in stoving enamels. That is why they are preferred for different application fields.

Due to the effect of modification with fatty acids, the alkyd resins offer – relative to the two other groups – optimum pigment and substrate wetting, and excellent levelling, high gloss, and filling power (generally good appearance) of films. Therefore, their use is focused on coloured topcoats and one-coat systems. If suitable components are selected, their weatherability is very good. Alkyd resins containing small amounts of unsaturated fatty acids are used in primer surfacers.

The advantage of saturated polyesters is the efficiency with which their functional groups (hydroxyl) crosslink. The other two resin groups crosslink less efficiently. The hydroxyl groups of alkyd resins are less reactive due to steric hindrance of fatty acid chains. The hydroxyl groups in acrylic resins are less reactive because of the intensive coiling of the large linear molecules. Given a suitable composition of diols for the polyesters, the solubility and compatibility are almost on a par with those of alkyd resins and the wetting properties of pigments and surfaces. The high crosslinking efficiency yields an optimum balance of hardness, flexibility, and chemical resistance. That is the reason why polyesters are selected for coating systems which have to offer high mechanical resistance (for example stone-chip resistance). Polyester amino resin combinations are preferred for basecoats, primer surfacers, coil coating, can coating, and other industrial stoving enamels which have to meet demands for high flexibility.

Relative to the aforementioned resin groups, acrylic resins in stoving enamels are characterized by fast physical drying, yellowing resistance, weatherability, and chemical resistance. In the two Americas and the Far East, combinations of acrylic resins and melamine resins are generally preferred for stoving enamels. In Europe, this combination is also used in a great many industrial stoving enamels, but the main application area is that of automotive OEM clear coats. Nonetheless, excellent weatherability, which is the most important requirement imposed on the clear coats, is only obtained if the content of aromatic compounds (styrene) in the acrylic resins is limited.

2.2.4 Crosslinking reactions

In most cases, the aim is co-crosslinking of hydroxyl groups and functional groups of amino resins. However, self-crosslinking by the amino resins also occurs in all cases.

Co-crosslinking is the result of reactions between hydroxyl groups of alkyds, polyesters, and acrylic resins with the methylol groups or methylol ether groups of the amino resins. Water or monoalcohols are the cleavage products. The reactions follow an etherification or a trans-etherification mechanism. The reaction rate is supported by the directing effect of the amide nitrogen. The principles behind such reactions are presented in Figure II-2.8.

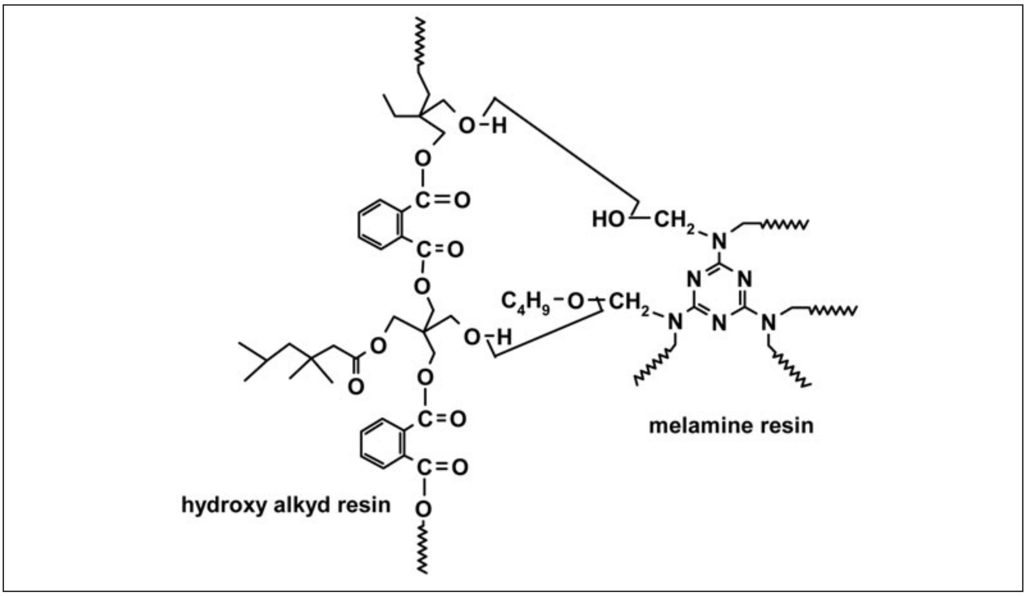


Figure II-2.8: Principles behind co-crosslinking of alkyd resin and melamine resin

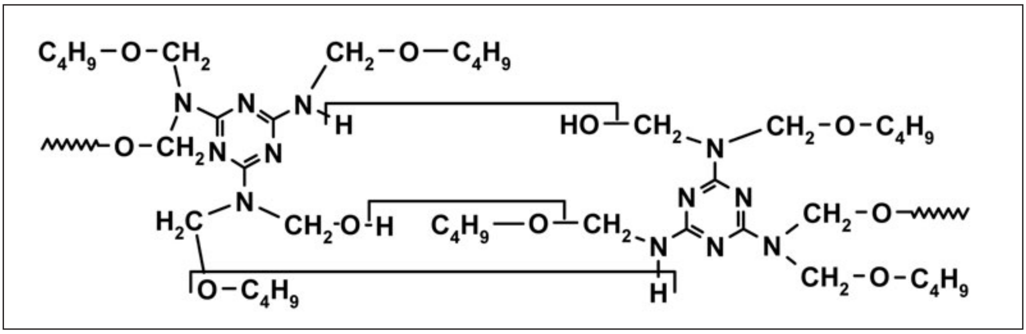


Figure II-2.9: Self-crosslinking of melamine resins

The reactions of self-crosslinking amino resins are shown in Figure II-2.9. Self-crosslinking of amino resins is basically the continuation of the molecular growing process. Free NH groups react with methylol groups, with cleavage of water, to form methylene groups. If they react with methylol ethers, monoalcohol is cleaved. Methylol groups react with themselves to form dimethylene ether bridges, with cleavage of monoalcohol. If the stoving temperatures are high or a higher amount of acid catalysts is added, cleavage of formaldehyde from methylol and methylol ether groups may occur, followed by other reactions.

The various reactions have different reaction rates. Table II-2.1 shows the order of reactivity for the various crosslinking mechanisms, starting with the fastest.

One of the particular advantages of crosslinking with amino resins is the relatively heavy dependence of the reaction rate on the temperature (*Arrhenius* equation), relative to other crosslinking mechanisms. This opens up the possibility of selecting the specific melamine resins on the basis of their characteristics (molar mass, content of imino groups, methylol groups, and methylol ether groups) with a view to meeting the required application conditions (time and temperature). And it also guarantees good storage stability at ambient temperatures (room temperature). Additionally, the storage stability is supported by the usual monoalcohols and glycol monoethers as solvents. In these cases, the equilibrium for the reaction is shifted to the side of the reactants because the hydroxyl groups of the solvents are in competition with the hydroxyl groups of the resins.

Co-crosslinking and self-crosslinking of amino resins and resins containing hydroxyl groups produce different film properties. Co-crosslinking promotes flexibility, chemical resistance and weatherability. Self-crosslinking supports hardness and solvent resistance. The amount of co-crosslinking can be controlled relative to self-crosslinking to meet different application requirements. Co-crosslinking is favoured if the hydroxyl number of the

Table II-2.1: Order of crosslinking reactions of amino resins and hydroxy groups in relation of reaction rate

1. NH-groups with methylol groups forming methylene bridges, splitting of water
2. NH-groups with methylol ether groups forming methylene bridges, splitting off alcohol
3. Methylol groups with hydroxy groups, splitting off water
4. Two methylol groups, forming dimethylene ether groups, splitting off water
5. Etherified methylol groups with hydroxy groups, splitting off water
6. Etherified methylol groups with methylol groups , forming dimethylene ether groups, splitting off alcohol
7. Splitting off formaldehyde of dimethylene ether groups and methylol groups, followed by further reactions

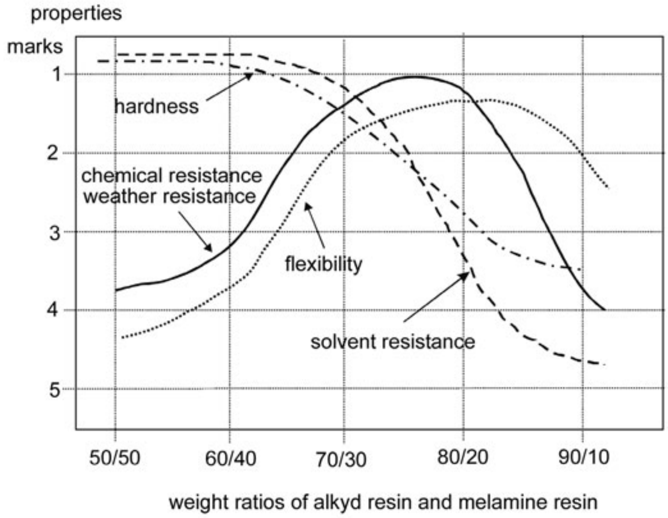


Figure II-2.10: Film properties as a function of the ratio of alkyd resin to melamine resin

co-resin is high, the hydroxyl groups are reactive, and the reactivity of the amino resin is relatively low. Lower stoving temperatures and lower amounts of catalysts tend to have an effect in the same direction. In contrast, self-crosslinking occurs if the hydroxyl numbers of co-resins are low, the hydroxyl groups are less reactive, the amino resins are highly reactive, the catalysts are strong acids and their addition levels are high, and if the stoving temperatures are also high. Given these different tendencies, there is no way of calculating the mixing ratios of co-resins and amino resin stoichiometrically. However, experience does provide extensive clues.

One example is the classic combination of a short oil alkyd resin containing a saturated synthetic fatty acid with a partly butanol-etherified melamine resin. Such combinations are preferred for the formulation of high-quality stoving topcoats.

Figure II-2.10 shows the various film properties as a function of different mixing ratios.

An optimum combination is 65 to 75 wt.% alkyd resin and 25 to 35 wt.% melamine resin. Higher amounts of melamine resin increase the hardness and solvent resistance, but decrease the flexibility, chemical resistance, and weatherability. Higher contents of alkyds improve flexibility but finally lead to a gradual deterioration in all properties (sub-crosslinking).

Experience gained with different types of melamine resins leads to different optimum mixing ratios. Low-molecular melamine resins require higher amounts of hydroxyl resin. The optimum proportion is about 70 to 80 wt.% of hydroxyl resin and 20 to 30 wt.% of melamine resins, which contain free imino groups. In the case of HMMM resin, the optimum ratios are 75 to 85 wt.% hydroxyl resin and 15 to 25 wt.% HMMM resin. But, of course, the specific application requirements have to be considered in all cases.

2.2.5 *Catalysis of crosslinking reactions*

The reactivity of methylol and methylol ether groups of melamine resins is readily increased by mobile hydrogen ions (protons). Protons are generated mainly by acid solutions in water. They are also generated in organic solvents, albeit in lower quantities. Together with the

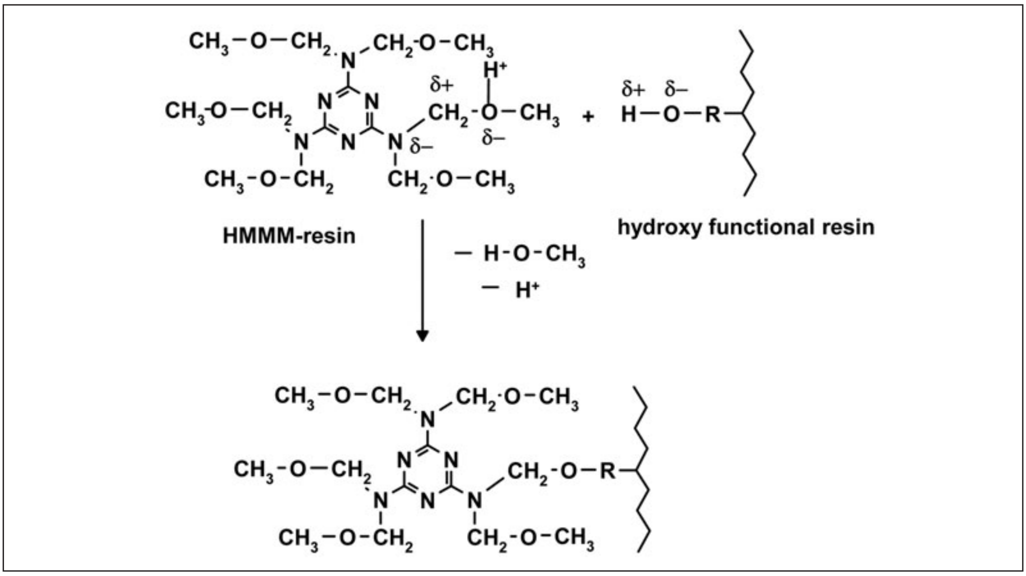


Figure II-2.11: Influence of an acid catalyst on the reaction of methylol ether groups

directing effect of the amide nitrogen, protons polarize the methylol and methylol ether groups of amino resins. This effect of protons and the subsequent start of the crosslinking reaction are presented in Figure II-2.11.

In particular, the relatively slow reactions between methylol ether groups and hydroxyl groups can be accelerated by protons in the presence of acid catalysts. Since the effective crosslinking temperature for HMMM resins without catalysts is about 180 °C, the addition of acid catalysts allows the crosslinking temperature to be lowered to 120 to 140 °C.

Catalytic effects are also attributed to carboxyl groups (acid number) of alkyd, polyester, and acrylic resins. For most combinations with amino resins, this effect is adequate.

For the separate addition of acid catalysts, a series of compounds is available. The most important selection criterion for the acids is their compatibility with resins in organic solutions and during film formation. Like the case for dissociation reactions in water, the various acid catalysts exhibit different efficiencies when it comes to proton formation (different acidic strength). In practice, the types of acid catalysts are chosen on the basis of type of amino resin and the film forming conditions (temperature and stoving time). The use of high amounts of relatively strong acids may shorten the storage time of the paints. But a shorter paint pot-life is usually acceptable if it means a much lower stoving temperature (e.g. for repair coatings).

Since acid catalysts remain in the film, other influences exerted by them have to be considered. These include hydrophilic effects, which may restrict humidity resistance. Since acid catalysts increase the reaction rate of self-crosslinking more than of co-crosslinking, the equilibrium of the crosslinking mechanism is shifted towards self-crosslinking. This may lead to lower flexibility and restricted weatherability of coating films formed with the aid of acid catalysts. In some cases, intercoat adhesion of repair finish topcoats may be adversely affected.

The following acids are used for acid catalysis, in order of decreasing acidic strength.

- p-Toluenesulphonic acid
- Dodecylbenzenesulphonic acid

- Dinonylnapthalenedisulphonic acid
- Dinonylnapthalenesulphonic acid
- Phosphoric acid
- Phenyl phosphoric acid
- Butyl phosphoric acid
- Dibutyl phosphoric acid
- Maleic acid
- Maleic monobutyl ester

To increase the storage stability of paints containing relatively strong acids (sulphonic acids, phosphoric acids), so-called blocked acid catalysts are available. Blocking is based on neutralization of the acid catalysts with amines to form amine salts of the acids. Several amines are suitable, e.g. dimethylethanolamine, triethylamine, diisopropanolamine, N-alkyl morpholines, AMP (2-amino-2-methyl propanol), dimethyl AMP, and oxazolidines prepared from AMP and formaldehyde. Since most of the amine salts of acid catalysts are water-soluble, these blocked catalysts are suitable for water-borne paint systems too. At ambient temperatures, the blocked acid catalysts do not act as strong acids. The salts will decompose at specific temperatures to an extent depending on the type of acids and amines. At the specific elevated temperature, the amine evaporates, the acid is released and is able to provide catalysis. The time and temperature at which the amine evaporates not only influence the crosslinking reaction, but also are important for levelling and sagging resistance.

Alternative blocking agents exist. Instead of amines, the acids may be blocked with monoepoxies, with the formation of ß-hydroxyl esters.

Examples of commercial products are [8]:
Cycat 296, 500, 600, 4040 (Cytec); Nacure 155, 1051, 4054, 5076, X49-110, 5225, 2500, 2558 (King Industries); Dynapol catalyst 1203 (Evonik Degussa)

2.2.6 Formulation of stoving enamels based on amino resins

The following examples of stoving paint systems are presented and described below:

1. Primer surfacer
2. Automotive topcoat
3. Automotive basecoat
4. Automotive clear coat
5. Coil coating topcoat

1. Formulation of a primer surfacer for industrial use that also may serve as primer [11]
The requirements are adequate adhesion and flexibility, and corrosion resistance. The stoving temperature is to be 170 °C.

The resins chosen consist of a combination of a saturated polyester and a highly reactive melamine resin (imino type) and a specific amount of epoxy resin, which improves adhesion and corrosion resistance. The pigment is titanium dioxide, the extender is barium sulphate. A small amount of yellow iron oxide [10] provides colouration. The wetting agent for the pigments is an organic salt of calcium. For improved levelling, a small amount of silicone oil is used. If the primer surfacer is stoved at higher temperatures, nonpolar and polar solvents with longer evaporation times are used. The formulation is presented in Table II-2.2.

The ingredients (items 01 to 08) are dispersed on a sand mill, followed by items 09 to 14. Finally, the viscosity is adjusted.

Table II-2.2: Primer surfacer for industrial use

pos.	raw material	solids [wt.%]	density [g/cm³]	formulation [wt.%]
pigment dispersion				
01	saturated, branched polyester (60% in xylene)	8.04	1.2	13.40
02	titanium dioxide	12.90	4.1	12.90
03	yellow iron oxide	0.20	4.0	0.20
04	barium sulfate	19.40	4.2	19.40
05	wetting agent (5% Ca)			0.40
06	butyl glycol			0.70
07	xylene			6.70
08	methoxy propyl glycol			1.70
completion				
09	saturated, branched polyester (60% in xylene)	12.90	1.2	21.50
10	imino melamine resin (70% in butanol)	8.05	1.5	11.50
11	epoxy resin (50% in MPA/MIBK)	3.25	1.2	6.50
12	butyl glycol			1.60
13	terpene hydrocarbon			2.50
14	silicone oil (1% in xylene)			0.01
sum		64.74		100.00

pos. 01, 09: Setal 183 (Nuplex)
pos. 02: Titanium dioxide 11 P (Titafrance)
pos. 03: Bayferrox 316 (Bayer)
pos. 04: Blanc fixe F (Sachtleben)
pos. 10: Setamine US 138 (Nuplex)
pos. 11: Epikote 1001 (Hexion)
pos. 13: Depanol J (Clariant)
pos. 14: Baysilon paint-additive OL 31 (Borchers)

Weight ratios of resins: polyester/melamine resin/epoxy resin = 65 : 25 : 10

P/B = 1 : 1

$$\text{PVC} = \frac{12.90 / 4.1 + 0.20 / 4.0 + 19.4 / 4.2}{12.90 / 4.1 + 0.20 / 4.0 + 19.4 / 4.2 + 20.94 / 1.2 + 8.05 / 1.5 + 3.25 / 1.2} \cdot 100\%$$

PVC = 23%

Thinning solvents: Aromatic 100/methoxypropyl acetate = 75 : 25
Application viscosity: 30 s (DIN 53211 flow cup 4/23 °C)
Stoving conditions: 20 min 170 °C
Film thickness (dry): 35 µm

2. Formulation of a high gloss, weatherable, white automotive topcoat, for stoving at 130 to 140 °C

The resin base for the topcoat is an alkyd resin, modified with a low amount of saturated fatty acid (short oil type) containing adequate hydroxyl groups, and a reactive melamine resin, partly etherified by butanol containing free methylol groups. The pigment is titanium dioxide. The wetting additive is chosen to support dispersion of the pigment [10]. Modified silicone oil is added for levelling and appearance. The solvents have medium evaporation rates. Details of the formulation are presented in Table II-2.3.

Table II-2.3: High gloss, white, automotive stoving topcoat

pos.	raw material	solids [wt.%]	density [g/cm³]	formulation [wt.%]
pigment dispersion				
01	short-oil alkyd, with saturated fatty acids (70% in aromatic 100/xylene 93/7)	11.34	1.2	16.20
02	titanium dioxide rutile	32.40	4.1	32.40
03	dispersing agent			0.40
completion				
04	short-oil alkyd, with saturated fatty acids (70% in aromatic 100/xylene 93/7)	19.04	1.2	27.20
05	partly etherified melamine resin (70% in butanol)	10.15	1.5	14.50
06	butyl glycol			4.10
07	terpene hydrocarbon			4.00
08	silicone oil (1% in xylene)			1.20
sum		72.90		100.00

pos. 01, 04: Setal 84 (Nuplex)
pos. 02: Kronos 2310 (Kronos)
pos. 03: SER-AD FA 196 (Condea Servo)
pos. 05: Setamine US 132 (Nuplex)
pos. 07: Depanol J (Clariant)
pos. 08: Baysilon paint-additive OL 17 (Borchers)

The first three components are dispersed on a grinding mill with stirring. Then items 04 to 08 are added. The paint is adjusted to the application viscosity.

Binder composition: alkyd resin/melamine resin = 75 : 25

P/B = 0.8 : 1

$$\text{PVC} = \frac{32.4 / 4.1}{32.4 / 4.1 + 30.38 / 1.2 + 10.15 / 1.5} \cdot 100\% = 20\%$$

Thinning solvents: Aromatic 100/xylene/butanol = 75 : 20 : 5
Application viscosity: 20 s (DIN 53211 flow cup 4/23 °C)
Stoving conditions: 30 min at 135 °C
Film thickness (dry): 45 µm

3. Formulation of a silver metallic basecoat for automotive OEM, applied wet-on-wet with clear coat

The choice of resins yields a combination of cellulose acetate butyrate, a modified saturated polyester, and a highly reactive melamine resin [14]. Cellulose acetate butyrate ensures physical drying of the basecoat, which is necessary for the wet-on-wet application. Due to its excellent weather resistance, cellulose acetate butyrate is preferred to other polymers that also dry rapidly. Moreover, this polymer confers optimum application properties. The degree of esterification and the molar mass of cellulose acetate butyrate determine the compatibility with other resins. Both parameters also determine the application solids and workability in the wet-on-wet process. Grades with high molar masses are optimal for the application process; no re-dissolving of the physically dried basecoat by the clear

Table II-2.4: Metallic basecoat, silver, for automotive OEM

pos.	raw material	solids [wt.%]	density [g/cm³]	formulation [wt.%]
01	saturated polyester, modified with urea (50% in aromatic 100/xylene/MPA)	19.65	1.2	39.30
02	polyethylene copolymer dispersion (4.7% in xylene/butyl acetate, butanol)	0.74	1.0	15.70
03	imino melamine resin (70% in butanol)	7.63	1.5	10.90
04	butyl acetate			1.50
05	aluminium pigment (65% in solvent)	4.81		7.40
06	butyl acetate			5.90
07	xylene			1.50
08	cellulose butyrate acetate (25% in butyl acetate)	4.45	1.2	17.80
sum		37.28		100.00

pos. 01: Setal 90173 (Nuplex)
pos. 02: Ceratix 8461 (Byk Cera)
pos. 03: Setamin US 138 (Nuplex)
pos. 05: Stapa Metallux R 9755 (Eckardt)
pos. 08: CAB 381-0.5 (Eastman)

coat occurs. But their use leads to less compatibility and low application solids. Cellulose acetate butyrates with low molar masses are more compatible with other resins, are more soluble, support levelling, and yield higher application solids. But they offer less resistance to redissolving. Basecoat formulations exist which consist of mixtures of high-molecular and low-molecular types.

The combination resins for cellulose acetate butyrate have to fulfil two basic requirements. First, they effect plasticization of the physically drying component. Secondly, due to crosslinking during stoving with the clear coat, they have a beneficial effect on the mechanical properties and durability of the finished coating system (including weather resistance).

The metallic effect is achieved with lamellar aluminium pigments (flakes). Optimum effects are supported by means of rheology additives. There are different types of such additives: polyethylene copolymer dispersions (“waxes”), low-molecular crystalline ureas (for example, prepared from benzyl amine and hexamethylene diisocyanate), as well as crystalline polyamides and bentonites. A typical formulation is presented in Table II-2.4.

Items 01 to 04 are mixed intimately. Items 05 to 07 are carefully premixed separately, and then added to the first mixture and homogenized. Finally, the solution of CAB is added. The viscosity of the resulting basecoat is adjusted for application by adding butyl acetate.

Binder ratios: cellulose acetate/polyester/melamine resin = 14 : 62 : 24

P/B = 0.15 : 1

Thinning solvent: Butyl acetate

Application viscosity: 15 s (DIN cup 4/23 °C)
Application solids: 23 to 25 wt.%
Film thickness (dry): 15 µm

After spray application of the basecoat, there is a short drying time (e.g. 5 min at 80 °C). Then the clear coat is applied. After a second short flash-off, both coats are stoved for 20 min at 140 °C (so-called wet-on-wet process).

Table II-2.5: Automotive OEM-clear coat

pos.	raw material	solids [wt.%]	density [g/cm^3]	formulation [wt.%]
01	acrylic resins, containing hydroxyl groups (65% in aromatic 100/butanol 97/3)	27.87	1.2	42.88
02	acrylic resins, containing hydroxyl groups, modified with SCA (60% in aromatic 100/butanol 97/3)	8.73 0.62	1.2	15.59
03	imino melamine resin (70% in butanol)	15.61	1.5	22.30
04	silicone oil, polyether modified (2% in xylene)	0.05		2.60
05	radical scavenger, derivate of (N-methyl-2,2,6,6-tetramethylpiperidine)	0.52		0.52
06	UV-absorber (hydroxyphenyl benzotriazole, subst.)	0.49		0.52
07	butyl diglycol			0.52
08	aromatic solvent (boiling range 180 to 210 °C)			0.36
09	xylene			5.71
sum		53.89		100.00

pos. 01: Setal 1761 (Nuplex)
pos. 02: Setal 71761 (Nuplex)
pos. 03: Setamine US 138 (Nuplex)
pos. 04: Baysilon paint additive OL 17 (Borchers)
pos. 05: Tinuvin 292 (BASF Swiss, Ciba)
pos. 06: Tinuvin 384 (BASF Swiss, Ciba)
pos. 08: Solvesso 150 (Exxon)

4. Formulation of an automotive OEM clear coat compatible with solvent-borne basecoats for wet-on-wet application, for stoving at 130 to 140 °C

The clear coat [15] consists of a combination of an acrylic resin containing hydroxyl groups (the monomer composition has been selected specifically for clear coats (weather resistance, scratch resistance) and a reactive melamine resin. The weather resistance is improved by adding an UV absorber (substituted hydroxyphenyl benzotriazole) and a sterically hindered amine as free-radical scavenger (derivative of N-methyl-2,2,6,6-tetramethyl piperidine). The use of such additive combinations is common in automotive clear coats.

A portion of the acrylic resin is modified by a crystalline urea dispersion prepared from benzyl amine and hexamethylene diisocyanate to prevent sagging if the clear coat is applied in relatively thick layers. The urea acts as the sag control agent (SCA). The amount is 1.15 wt.%, calculated on clear coat solids. The levelling agent is a polyether-modified silicone oil. The free solvents are chosen for optimum wet-on-wet application. Besides a relatively fast-evaporating aromatic solvent (xylene), only a small amount of a polar high-boiling solvent is present (butyl diglycol). Details of the formulation are presented in Table II-2.5

The ingredients are added in the given order and stirred intimately.
Acrylic resin/melamine resin = 70 : 30
Thinning solvent: Aromatic 100
Application viscosity: 28 s (DIN 53211 flow cup 4/23 °C)
Stoving conditions: 24 min at 140 °C
Film thickness (dry): Approx. 40 µm

5. Formulation of a highly flexible, glossy, white coil coating topcoat

This formulation [16] consists of two different polyester resins (in the ratio 70 : 30) and an HMMM resin. The pigment is titanium dioxide (rutile [10]), and the PVC is 23 vol.%. The catalyst is a mixture of an amine salt of a sulphonic acid and a free sulphonic acid. In view of the

Table II-2.6: Coil coating topcoat, white, high glos

pos.	raw material	solids [wt.%]	density [g/cm^3]	formulation [wt.%]
solution of polyesters				
01	saturated polyester (100%)	42.30	1.20	42.30
02	saturated polyester, flexible OH-no. 65 to 80 mg KOH/g (75% in aromatic solvents)	17.70	1.20	23.60
03	aromatic solvent			24.10
04	dibasic ester			10.00
sum		60.00		100.00
pigment dispersion				
05	polyesters solution (pos. 01 to 04)	10.82	1.20	18.04
06	titanium dioxide rutile	32.36	4.10	32.36
07	aromatic solvent			6.77
08	butyl glycol			2.25
09	levelling agent acrylic resin (50% in aromatic solvent)			0.65
completion				
10	polyesters solution (pos. 01 to 04)	16.30	1.20	27.17
11	HMMM resin (100%)	4.85	1.50	4.85
12	nonionic blocked PTSA (50% in xylene)	0.90		1.80
13	PTSA- solution (40% in isobutanol)	0.26		0.65
14	aromatic solvent			4.23
15	butyl glycol			1.41
sum		45.49		100.00

pos. 01: Uralac XP 907 SN (DSM)
pos. 02: Uralac 866 SN (DSM)
pos. 03, 07, 14: Solvesso 150 (Exxon)
pos. 04: dimethyl ester of dicarboxylic acids (DuPont)
pos. 06: Kronos 2160 (Kronos)
pos. 09: Disparlon L 1984 (Kusumoto Chem.)
pos. 11: Cymel 303 (Cytec)
pos. 12: Dynapol catalyst 1203 (Evonik Degussa)
pos. 13: K-Cure 1040 (King Ind.)

application conditions, an aromatic high-boiling solvent is combined with a medium-boiling glycol ether and a very high-boiling ester solvent. An aromatic solvent and ester solvent are selected for dissolving the polyester. To optimize levelling, a special acrylic polymer (polar type) is added to the mill base. The formulation and the various production steps are presented in Table II-2.6.

First, a polyester solution is prepared by mixing the solid polyester with the already dissolved polyester, and then adding two solvents (items 01 to 04). The mill base consists of this solution (item 05), the pigment, some additional solvent, and the levelling agent (items 06 to 09). After pre-dispersing on a dissolver the mill base is ground in a pearl mill to the required fineness (particle size below 7 µm). Finally, more polyester solution, melamine resin, two catalysts, and the residual amounts of solvents are added (items 10 to 15).

P/B = 1 : 1

$$\text{PVC} = \frac{32.36 / 4.1}{32.36 / 4.1 + 27.12 / 1.2 + 4.85 / 1.5} \cdot 100\% = 23\%$$

Application viscosity: 90 s (DIN cup 4/23 °C)
Substrate: Chromated aluminium
Application process: Roller coating
Application conditions: Recirculated-air oven, air temperature 300 °C, metal temperature 232 °C (i.e. the panels are stoved until the surface temperature reaches 232 °C)

Properties:
Gloss (20°): 83%
MEK double rubs: >100
Pencil hardness: H
T-bend test: 1

2.3 Stoving enamels based on thermosetting phenolic resins (resols)

Phenolic resins are synthesized from phenol and formaldehyde. The reaction conditions and the molar ratios determine whether novolak or resol resins (Figure II-2.12 und 13) are obtained. A disadvantage of all phenolic resins is their more or less pronounced inherent colour; consequently, phenolic resins are not used for decorative applications. Novolak resins (Figure II-2.12) are not self-curing and are physically drying binders; they are used, e.g., in insulating varnishes. This chapter will deal with self-curing resols and not novolaks (Figure II-2.13).

Formaldehyde can react with phenol in ortho- or para-position to the hydroxyl group. In the synthesis of resols (Figure II-2.13) phenol can be replaced by other phenol derivatives, such as alkylphenols or resorcinol.

As a rule, the adhesion of resol coatings on metals is excellent, a fact which may be explained by the formation of surface chelates of the ortho-hydroxybenzyl alcohol moiety (see Figure II-2.13) [24]. One possible structure of such a complex is presented in Figure II-2.14 (6-ring chelate). Recent molecular calculations allow of the possibility of a second resol-metal chelate (8-ring chelate in Figure II-2.14); see also Chapter I-1.6.2. As a rule, 8-ring chelates are less stable than 6-ring chelates but may also be considered here.

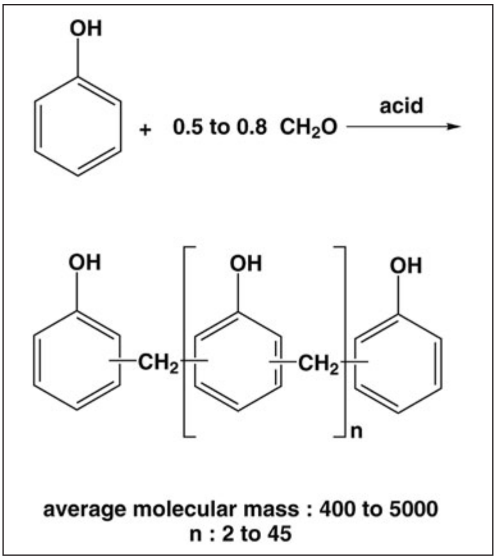


Figure II-2.12: Simplified diagram of novolak resins

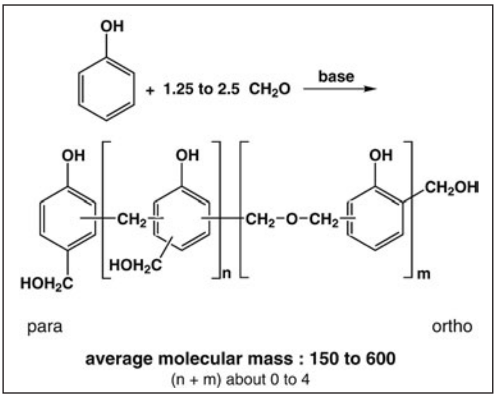


Figure II-2.13: Simplified diagram of resol resins

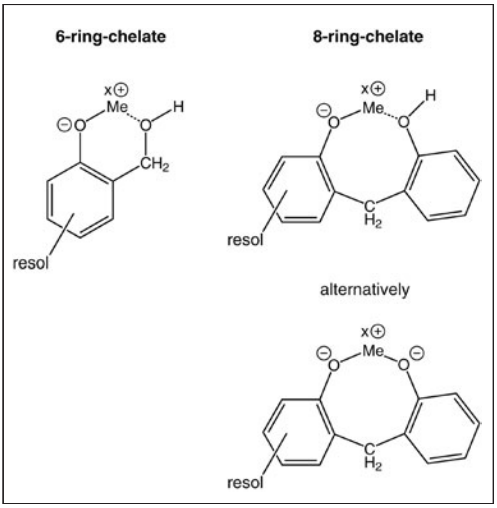


Figure II-2.14: Possible chelate formation of resols on a metal (oxide) surface

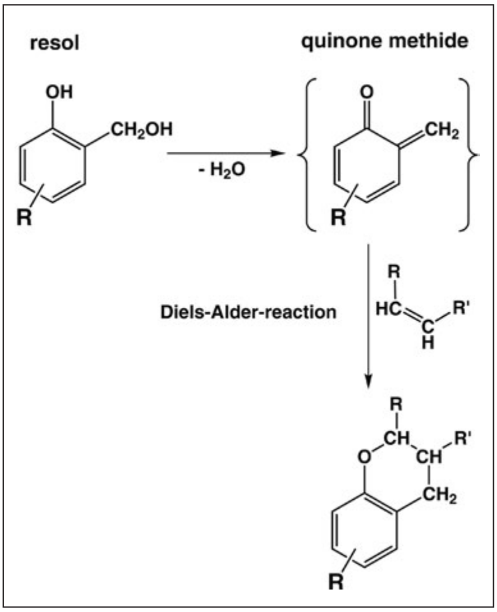


Figure II-2.15: Reaction of resols with unsaturated resins or oils (simplified diagram)

The etherification of methylol groups, e.g. with 1-butanol, yields resols which can be diluted with aromatic hydrocarbon solvents. Resols cure by polycondensation, either acid-catalyzed or at elevated temperatures; this reaction produces brittle thermosets (resite, “bakelite”). As resols lead to brittle coatings, they are plasticized with certain resins (e.g. epoxy resins) or oils (vegetable oils or poly-butadiene oil; see Figure II-2.15).

Curing of resols takes place by one of two reactions:

- Self-curing (homocondensation) via methylol or methylol ether groups (see melamine resins)
- Curing with other resins (cocondensation)

a) of the methylol or methylol ether groups with suitable functional groups of compatible resins (e.g. -OH)
b) with unsaturated resins or oils (Figure II-2.15)

Table II-2.7 presents a starting formulation for a stoving primer based on epoxy and resol resin [25]. The stoving conditions (uncatalyzed) are 30 to 50 min at 180 °C or 15 to 30 min at 205 °C. If a stoving topcoat is applied, the primer should be cured incompletely in order that interlayer adhesion may be improved, e.g. 10 to 20 min at 175 °C or 7 to 12 min at 190 °C. Complete crosslinking of the primer should take place when the topcoat is being cured.

If the formulations are catalyzed, the stoving temperatures are 10 to 20 °C lower. Note that understoving produces brittle coatings with inadequate chemical and solvent resistance. The surprising brittleness of understoved coatings (little or no crosslinking) may be caused by the relatively high glass temperature of epoxy resin type 7 (T_g = 67 °C, see Table II-1.22) [30]. Stoving enamels based on epoxy and resol resins are relatively insensitive to overstoving (with the exception of yellowing).

For the analysis of the formulation (Table II-2.7), let us calculate the characteristic data:

EP : PF = 70 : 30 (solid/solid)

Pigment/binder ratio
P/B = (12.5 + 8.5 + 4):(12.4 + 5.3) = 1.4 : 1

$$\text{PVC} = \frac{12.5 / 5 + 8.5 / 4.3 + 4 / 2.7}{12.5 / 5 + 8.5 / 4.3 + 4 / 2.7 + 17.7 / 1.2} \cdot 100\% = 29\%$$

To make the stoving primer (Table II-2.7), first dissolve the solid epoxy resin. Then disperse the pigment and fillers as well as the organoclay paste in the epoxy resin solution. Let down with resol and solvents (if necessary, with a catalyst as well).

Properties of coatings based on epoxy and resol resins:

- Excellent resistance to chemicals and solvents
- High hardness and abrasion resistance
- Very good flexibility and adhesion
- High impact resistance
- Excellent resistance to temperature cycles and sterilizing

Applications for coatings based on epoxy and resol resins:

- Tube lacquers and interior can-coatings
- Interior coatings for tanks and containers
- Interior coatings for equipment in chemical industry
- Coatings for laboratory and hospital equipment
- Wire and insulating enamels
- Primers for household appliances and machines

Table II-2.7: Formulation for a stoving primer based on epoxy and resol resin

pos.	raw material	parts by weight	solids	density [g/cm³]
01	epoxy resin type 7	12.4	12.4	1.2
02	resol (65% in 1-butanol)	8.2	5.3	1.2
03	iron oxide red	12.5	12.5	5.0
04	baryte filler ($BaSO_4$)	8.5	8.5	4.3
05	talc	4.0	4.0	2.7
06	organoclay (10% in xylene)	1.0	0,1	
07	isopropyl glycol	23.8		
08	aromatic solvent	17.5		
09	methoxypropyl acetate	8.5		
10	1-butanol	3.6		
sum		100.0	42.8	

pos. 01: epoxy equivalent mass about 1875, epoxy value about 0.053, hydroxy value about 0.37; e.g. Epikote 1007. By addition of epoxy resin type 9 the coating can be flexibilized.
pos. 02: thermosetting, non-plasticized phenolic resin (resol), 65% in 1-butanol; e.g. Phenodur PR 217
pos. 06: organoclay as rheology modifier; e.g. Bentone 34
pos. 08: boiling range 165 to 185 °C, evaporation number (to diethyl ether = 1) 46; e.g. Shellsol A
pos. 07: boiling point 143 °C, evaporation number 65 (one could try also butyl glycol)
Optional addition of a catalyst: Morpholine salt of 4-toluenesulfonic acid, addition 0.5 – 2% (salt to solid binder)

2.4 Stoving enamels based on blocked polyisocyanates

2.4.1 Structure and properties of blocked polyisocyanates

The products of the reactions of polyisocyanates and compounds which contain mobile hydrogen atoms may decompose at higher temperatures to form their educts products [4, 6, 7]. The reason is that the accumulated double bonds of the isocyanate group are stable at higher temperatures. This insight underlay the production of so-called blocked polyisocyanates.

Combinations of blocked polyisocyanates and resins containing hydroxyl groups react at higher temperatures by cleavage of the first reaction partner, the blocking agent. The result-

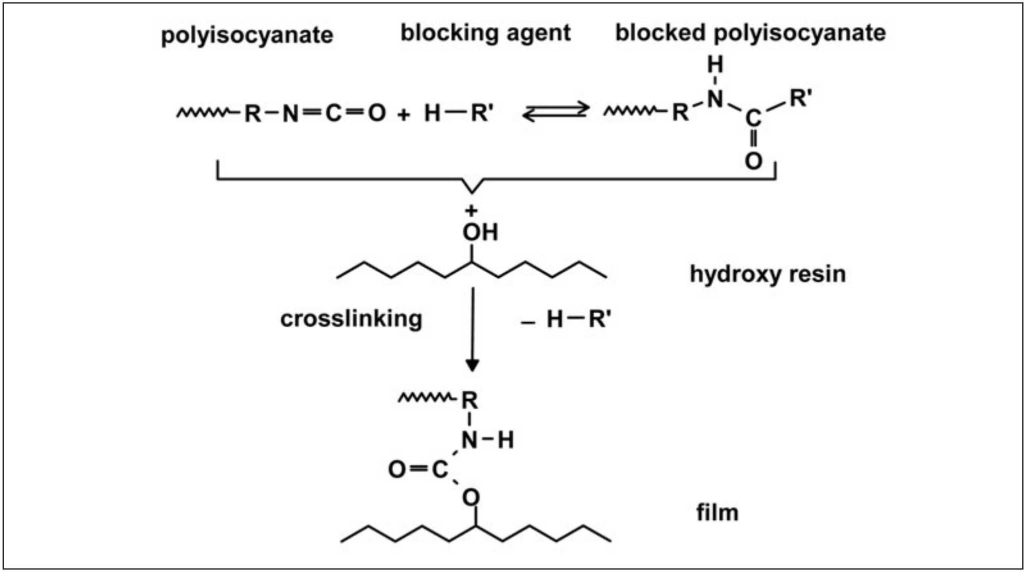


Figure II-2.16: Principle behind the reactions of blocked polyisocyanates

ant films consist of molecular networks that are comparable to those generated by the reaction of free polyisocyanates. Combinations of blocked polyisocyanates and resins containing hydroxyl groups exhibit adequate stability at ambient temperatures. These formulations are one-component paints. Such combinations confer the advantages of films with urethane networks, but without a pot-life effect, which is the disadvantage of two-component paints.

Analyses have shown that the reactions of blocked isocyanates with partners containing hydroxyl groups are substitutions, and comparable to trans-esterification reactions [18 to 20]. The reaction is shown in Figure II-2.16.

The efficiency of these reactions is influenced by the reactivity of both compounds. Influences include the type of polyisocyanate (aromatic isocyanates are much more reactive than aliphatic or cycloaliphatic) and the type and reactivity of partner groups (primary hydroxyl groups are more reactive than secondary). But the type of blocking agent significantly determines the reactivity and the required stoving temperature. Suitable blocking agent are phenols, ε-caprolactam, ketoximes (methyl ethyl ketoxime), 3,5-dimethyl pyrazole, acetoacetates (e.g. ethyl acetoacetate), malonates (diethyl malonate). The reactivity of blocked polyisocyanates increases in the order given above. If an aliphatic polyisocyanate is blocked with these blocking agents and then combined with a polyester containing hydroxyl groups, the effective stoving temperatures are between 120 and 180 °C (given a stoving time of 20 to 30 min).

Figure II-2.17 shows the various effective temperatures as a function of blocking agent.

Phenols are generally suitable for blocking aromatic polyisocyanates, but due to their toxicity and the tendency to discolour, their use is mostly restricted to primers and electrical insulation enamels. The blocking agent 1,2,4-triazole confers a high glass transition temperature and restricted solubility. For this reason, it is used primarily in powder coatings. Although methyl ethyl ketoxime is now defined as toxic, its blocked polyisocyanates are still standard products for stoving enamels (primer surfacers, topcoats). Blocked polyisocyanates with 3,5-dimethyl pyrazole are more reactive and offer better yellowing resistance. Although the products are relatively expensive, they are used for high-quality topcoats and clear coats featuring outstanding weatherability. Blocked polyisocyanates with ethyl acetoa-

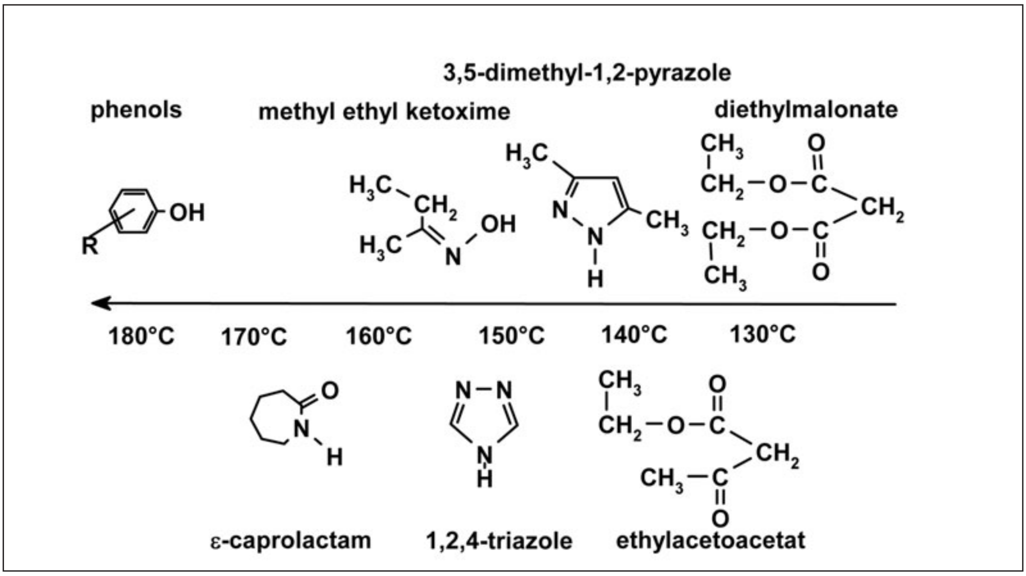


Figure II-2.17: Effective stoving temperatures of blocked polyisocyanates with different blocking agents during crosslinking of hydroxyl polyesters

cetate and diethyl malonate react at significantly lower temperatures than those with other blocking agents. The reaction with hydroxyl groups takes the form of a trans-esterification, the cleavage product being ethanol. The reaction is supported by the directing influence of the β-diketo groups. In the case of diethyl malonate, this reaction is much more pronounced. GC analysis reveals little cleavage of β-diketo blocking agents until much higher temperatures are reached. The reaction of β-diketo blocking agents is presented in Figure II-2.18.

It is also possible to use cyclopentanone-2-carboxylic ester as a blocking agent; it also contains β-diketo structures. At high temperatures, reaction with hydroxyl groups leads to ring opening and possibly crosslinked structures, without cleavage of any low-molecular products [31].

Since the effective stoving temperatures of paints containing polyisocyanates blocked with 3,5-dimethyl pyrazole and the β-diketo blocking agents are relatively low, the products meet the application requirements of automotive OEM (20 to 30 min at 130 to 145 °C). As the films offer excellent weather resistant, the products are suitable for topcoats and clear coats. Ethyl acetoacetate causes some yellowing. Blocking with diethyl malonate requires special measures to improve the solubility of the products.

If the stoving temperatures are higher than 200 °C, secondary and tertiary alcohols and glycol monoethers may also be used as blocking agents.

Resins containing free amino groups react much faster with blocked isocyanates than those containing hydroxyl groups. There are two-component formulations with partners, which are of very low viscosity and reactive at room temperature (see Part IV: Solvent-free paints).

Like free polyisocyanates, blocked aromatic polyisocyanates also react much faster than blocked aliphatic or cycloaliphatic polyisocyanates. Therefore, for cationic electrodeposition paints (ED coats), the crosslinkers are aromatic and the blocking agents are sterically hindered alcohols (e.g. 2-ethyl hexanol) or glycol monoethers (e.g. propyl glycol). These blocked polyisocyanates react with hydroxyl groups, or more particularly with amino groups, of the modified epoxy resin, which is the main binder component of the ED coat. The crosslinking

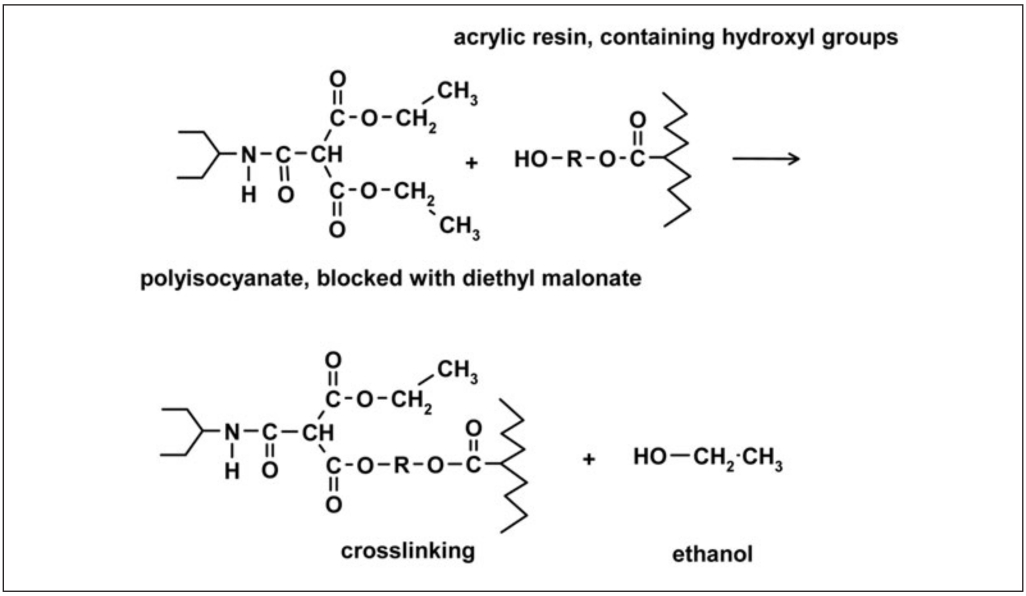


Figure II-2.18: Reaction between polyisocyanate blocked with diethyl malonate and acrylic resin containing hydroxyl groups

takes place at 160 to 180 °C, but an addition of catalyst is required (see Part III: Water-borne paints).

The production of blocked polyisocyanates is based on the same polyisocyanate starter products used as crosslinkers in two-component paints containing resins bearing hydroxyl groups. These include urethane oligomers, such as the product of the reaction between trimethylol propane and three molecules of toluene diisocyanate (TDI); the isocyanurate trimers of TDI, hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI); and finally the biuret of HDI.

A special group are the uretdiones, which contain little or no blocking agent. Uretdiones can decompose at higher temperatures to generate free isocyanate groups that are ready for crosslinking. As the polymer uretdiones are solids with relatively high melting temperatures, the products are mainly used for powder coatings (see Part IV).

The reaction rate of blocked isocyanates may be accelerated by the same catalysts which are used for the reaction of free isocyanates. Dibutyltin catalysts are preferred. These catalysts do not accelerate the trans-esterification reaction of polyisocyanate blocked with ß-diketo compounds.

2.4.2 Combination partners for blocked polyisocyanates

The combination partners for blocked polyisocyanates are the same resins that are suitable for the crosslinking with amino resins and free polyisocyanates. The preferred resins are alkyds that contain hydroxyl groups, saturated polyesters, acrylic resins [1, 2, 4, 6, 7]. Additionally epoxy resins, epoxy ester resins, and polyvinyl polymers containing hydroxyl groups could be used for specialty applications.

Unlike crosslinking with amino resins and like crosslinking with free polyisocyanates, the reactions of blocked polyisocyanates are relatively clear. Only co-crosslinking occurs. Thus, it is possible to calculate the ratios of resin combinations stoichiometrically from the hydroxyl number of the co-resin and the potential NCO values of the blocked polyisocyanate.

Mostly, formulation consists of resins in balanced stoichiometric ratios ($n_{NCO} = n_{OH}$). For a high crosslinking density, co-resins with high hydroxyl numbers are preferred. The films exhibit optimum chemical resistance, weather resistance, and flexibility. Carboxyl groups of co-resins are usually indifferent to crosslinking. They can form amides by reaction with isocyanates only at relatively high temperatures, which may cause yellowing. Thus, most of the co-resins for crosslinking by blocked polyisocyanates have low acid numbers.

The principles for selecting co-resins for blocked polyisocyanates are the same as those for selecting co-resins for crosslinking by amino resins. Due to the effective availability of hydroxyl groups, saturated polyesters confer optimum durability and flexibility. The effect of modifying alkyd resins with fatty acids is optimum wetting, levelling, and appearance. Acrylic resins feature, on account of their coiled molecular structure, good physical drying and chemical resistance. If suitable blocked polyisocyanates are chosen, the combinations have excellent colourfastness and weather resistance. Crosslinking of epoxy resins, epoxy ester resins, or polyvinyl polymers with blocked polyisocyanates produces films that exhibit good adhesion and good resistance against mechanical impacts.

2.4.3 Comparison of blocked polyisocyanates and amino resins in stoving enamels

Molecular networks formed by crosslinking with blocked polyisocyanates have nearly the same structure as those formed by free polyisocyanates. In contrast to crosslinking by amino resins, the reaction is well defined. The resultant molecular networks are homogeneous and probably more extended than those of crosslinked amino resins. But, due to the structural elements, the networks are more widely meshed. The reaction rate of blocked polyisocyanates as a function of reaction temperature is less steep than that of amino resins. Thus, raising the temperature causes amino acceleration of the crosslinking rate. The networks containing urethane groups are much more resistant to acidic agents than the methylol ether groups in networks formed from melamine resins.

Generally, films formed by crosslinking with blocked polyisocyanates are resistant to chemicals and are weather resistance (if the base polyisocyanates are aliphatic or cycloaliphatic). Additionally, they are more flexible (due to higher levels of the elastic component of flexibility) and more resistant to mechanical impact (stone-chip resistance). But there are also some disadvantages relative to amino resin crosslinking. Due to their structure, the films formed by the use of blocked polyisocyanates are less solvent-resistant and therefore swellable by solvents. Depending on the types of polyisocyanate and blocking agent, the films tend to become yellow, particularly in the event of overstoving. Some types may cause problems with intercoat adhesion (e.g. repair coatings).

On the basis of the properties described above, blocked polyisocyanates are preferred for the formulation of highly flexible and chemically resistant stoving enamels for industrial use and for coil coating and can coating enamels.

Stoving enamels containing saturated polyesters and aromatic blocked polyisocyanates are used for electrical insulation coatings (wire enamels) that are solderable directly (in a bath of molten tin).

To fulfil all the requirements on coating films, blocked polyisocyanate are often combined with amino resins acting as crosslinkers. To an extent depending on the ratios of the combinations and the different types of both crosslinkers, a balance of all properties (hardness, flexibility, solvent resistance, chemical resistance, weather resistance, refinish ability) will be achieved. In most cases, the reaction rates of the two crosslinker types are different, but that may be an advantage for film properties. Where the two crosslinker types are mixed, it makes sense to first calculate the combination ratio for the polyisocyanate and then, for the residual content of co-resin, to select the content of amino resin from established empirical ratios [17]. A combination of blocked polyisocyanates and melamine resins may be used to formulate highly flexible primer surfacers and clear coats which are chemically resistant and weatherable and which may serve in automotive OEM applications.

Examples of commercial products are [8]: Desmodur BL 1265, BL 3165, BL 3175, BL 4265 (Bayer); Vestanat B 1370, B 1358 (Evonik Degussa); Tolonate D 2 (Rhodia)

2.4.4 Formulation of stoving enamels based on blocked polyisocyanates

The following examples of stoving enamels based on blocked polyisocyanates are presented below:

1. Topcoat for general industrial use
2. Automotive OEM primer surfacer
3. Wire enamel, solderable directly

1. Formulation of a highly chemically resistant, glossy, white stoving topcoat for general industrial use

The chosen resin combination [21] consists of a saturated polyester and a HDI isocyanurate trimer, blocked with methyl ethyl ketoxime. The crosslinking ratio of hydroxyl and isocyanate groups is 0.7 to 1.0. The reaction catalyst is a solution of dibutyltin dilaurate. Levelling is supported by adding a polyether-modified silicone oil. The free solvents consist of a mixture of glycol ether acetate and an aromatic hydrocarbon. The formulation details are presented in Table II-2.8.

P/B = 0,8 : 1

Table II-2.8: Topcoat for general industry

pos.	raw material	solids [wt.%]	density [g/cm^3]	formulation [wt.%]
pigment dispersion				
01	saturated polyester, OH-number 132 mg KOH/g (65% in aromatic 100/isobutanol 31.5/3.5)	7.90	1.2	12.15
02	xylene			7.39
03	titanium dioxide	28.84	4.1	28.84
completion				
04	saturated polyester, OH-number 132 mg KOH/g (65% in aromatic 100/isobutanol 31.5/3.5)	16.76	1.2	25.79
05	blocked HDI-trimer, with MEK-oxime (pot. NCO-content: 14.8%)	11.39	1.2	15.18
06	silicone oil, polyether modified (10% in xylene)	0.02		0.20
07	dibutyl tin dilaurate (50% in aromatic solvent)	0.36		0.72
08	butyl glycol acetate			1.93
09	xylene			7.26
sum		65.27		100.00

pos. 01, 04: Desmophen T 1665 (Bayer)
pos. 03: Crenox R-KB-4 (Crenox)
pos. 05: Desmodur BL 3175 (Bayer)
pos. 06: Basilon paint additive OL 17 (Borchers)

$$\mathrm{PVC} = \frac{28.84 / 4{,}1}{28.84 / 4.1 + 24.66 / 1.2 + 11.39 / 1.2} \cdot 100\% = 19\%$$

Thinner: Xylene/butyl glycol acetate = 8 : 2
Application viscosity: 30 s (DIN 53211 flow cup 4/23 °C)
Stoving conditions: 20 min at 150 °C
Film thickness (dry): 35 µm

2. Formulation of a highly flexible, grey OEM primer surfacer, for stoving at 160 °C

The chosen resin combination [22] consists of a saturated hydroxyl polyester, an amino resin containing imino groups, and a blocked polyisocyanate based on an HDI isocyanurate trimer blocked with methyl ethyl ketoxime. The pigments and extenders are titanium dioxide and barium sulphate. The grey colour is generated by adding small amounts of carbon black. Pyrogenic silicon dioxide is added to prevent pigment settling [10]. The levelling agent is an acrylic polymer (without additional functional groups). The solvent mixture consists

Table II-2.9: Primer surfacer, highly flexible, for OEM application

pos.	raw material	solids [wt.%]	density [g/cm³]	formulation [wt.%]
pigment dispersion				
01	saturated hydroxyl polyester (62% in xylene/butanol 85/15)	10.03	1.2	16.17
02	barium sulphate	21.86	4.4	21.86
03	titanium dioxide	14.56	4.1	14.56
04	carbon black	0.07	1.0	0.07
05	pyrogene silicium dioxide	0.22	2.1	0.22
06	methoxy propyl acetate			1.75
07	butanol			5.68
completion				
08	saturated hydroxy polyester (62% in xylene/butanol 85/15)	11.14	1.2	17.97
09	imino melamine resin (70% in butanol)	4.56	1.5	6.52
10	MEK-oxime blocked polyisocyanate (70% in aromatic 100)	4.26	1.2	6.08
11	acrylic polymer levelling agent (25% in xylene)	0.06	1.2	0.24
12	butyl glycol acetate			2.80
13	terpene hydrocarbon			0.88
14	butanol			3.00
15	xylene			2.20
sum		66.76		100.00

pos. 01, 08: Setal 1600 (Nuplex)
pos. 02: Blanc fixe micro (Sachtleben)
pos. 03: Kronos 2059 (Kronos Titan)
pos. 04: Printex 200 (Evonik Degussa)
pos. 05: Aerosil 200 (Evonik Degussa)
pos. 09: Setamine US 138 (Nuplex)
pos. 10: Desmodur BL 3175 SN (Bayer)
pos. 11: Modaflow (Cytes Surface Specialties, Monsanto)

of butanol, glycol ether acetate, terpene hydrocarbon, and xylene. Details of the formulation are presented in Table II-2.9.

The components of the mill base (items 01 to 07) are mixed, pre-dispersed in a dissolver, and dispersed with stirring in a mill to a maximum fineness of 10 µm. The mill base is completed by admixing items 08 to 15 stepwise. Aromatic 100 is used to adjust the application viscosity.

P/B = 1,2 : 1

$$\text{PVC} = \frac{21.86 / 4.4 + 14.56 / 4.1 + 0.07 / 1.6 + 0.22 / 2.1}{21.86/4.4 + 14.56/4.1 + 0.07/1.6 + 0.22/2.1 + 21.17/1.2 + 4.65/1.5 + 4.26/1.2} \cdot 100\%$$

PVC = 23%

Thinner: Aromatic 100
Application viscosity: 23 s (DIN 53211 flow cup 4/23 °C)
Stoving conditions: 20 min at 160 °C
Film thickness (dry): 35 µm

3. Formulation of a wire enamel for electrical insulation, solderable directly

The resin combination [23] consists of a hydroxyl polyester modified with diimide dicarboxylic acid and an aromatic isocyanate adduct (product of the reaction of trimethylol propane and TDI) blocked with phenol. The crosslinking catalyst is dibutyltin dilaurate and the levelling agent is a silicone oil. The solvent is the typical mixture for electrical insulation enamels and consists of cresol and Aromatic 100. Details of the formulation are presented in Table II-2.10.

The resin and crosslinker solutions (items 01 and 02) are mixed by stirring intimately for some hours. The other components (items 03 to 06) are admixed step by step.

Application: Recirculated-air oven, air temperature 330 to 380 °C
Copper wire, diameter: 0.15 mm
Passage speed: 60 m/min

Table II-2.10: Wire enamel, solderable directly

pos.	raw material	solids [wt.%]	density [g/cm³]	formulation [wt.%]
01	saturated, branched polyester (OH-EW: 289 g/mol; 50% in cresol)	15.83	1.2	31.66
02	TDI-adduct with TMP; blocked with phenol (pot. NCO-EW: 350 g/mol, 50% in cresol/aromatic 100)	19.17	1.2	38.34
03	dibutyl tin dilaurate (10% in aromatic 100)			0.20
04	cresol			14.60
05	silicone oil, polyether modified (10% in aromatic 100)			0.20
06	aromatic 100			15.00
sum		35.00		100.00

pos. 01: polyester of 1.0 mol diimid dicarboxylic acid, formed of 4,4'-diamino diphenyl methan and trimellitic anhydride, 2.0 mol dimethyl terephthalate, 2.0 mol ethylene glycol, 1.9 mol glycerol
pos. 02: Desmodur AP-Stabil (Bayer)
pos. 05: Baysilon OL 14 (Bayer)
pos. 06: Solvesso 100 (Exxon)

Method of application: 6 dips, and levelled off with felt blocks
Total film thickness (dry): 25 to 30 µm.

The insulated wire is solderable directly in 0.4 s. The heat-shock test temperature is as high as 180 °C.

2.5 Other solvent-borne stoving enamels

2.5.1 Self-crosslinking acrylic resins

If acrylic copolymers consist partly of acrylic amide or methacrylic amide as monomers, they can add formaldehyde to form methylol groups and additionally methylol ethers by reaction with monoalcohols. The process affords acrylic resins containing methylol ether groups and is comparable to that for amino resins. The second method for preparing such resins is a co-polymerization process in which the monomers are etherified methylol acryl amide or methacrylic amide. The resultant resins can self-crosslink at elevated temperatures or under the influence of acid catalysts [1, 2, 4]. The preferred self-crosslinking reaction is condensation between residual free NH groups and methylol ethers, with cleavage of monoalcohols, to form methylene bridges. The reaction is described in Figure II-2.19.

The resins are suitable for the formulation of stoving enamels. The paints are similar to those containing hydroxyl acrylic resins and amino resins, but they need only one resin component and no additional crosslinker. When stoving primers are prepared from this class of resin, often low amounts of aromatic epoxy resins are added to improve adhesion and support corrosion resistance. The crosslinking reaction requires stoving temperatures of 160 to 180 °C. The reaction may be accelerated by adding acid catalysts. The resultant films are much more chemically resistant than films formed by the crosslinking of hydroxyl acrylic resin and amino resins. Therefore, their main use lies in industrial applications which require adequate chemical resistance. The resins are used for the formulation of domestic appliance paints (refrigerator enamels, washing machine coatings). But coil coating enamels and powder paints (see Part IV) are currently being used more and more in this application field to simplify the application process and to avoid solvent pollution.

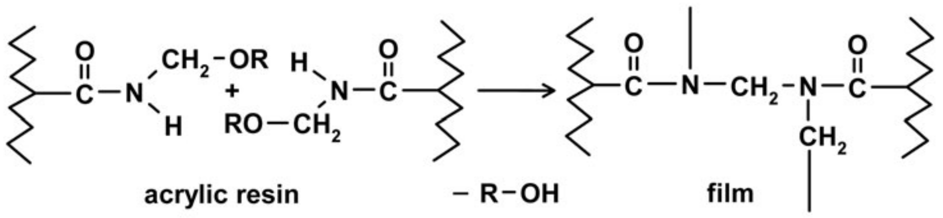


Figure II-2.19: Reaction of self-crosslinking acrylic resins

2.5.2 Self-crosslinking polyesters

Self-crosslinking polyesters are mainly used for electrical insulation enamels (wire enamels). Special low-molecular, branched polyesters can self-crosslink at high stoving temperatures by means of trans-esterification. This is accompanied by cleavage of relatively low-boiling diols (e.g. ethylene glycol). Optimum conditions are needed for applying paint to wire. The air temperature in the oven ranges from 350 to 420 °C. The maximum film thickness for one layer of the multicoating process is much less than 8 µm (varies according to the wire diameter). The crosslinking reaction is very effective and the molecular networks can have a high density and be highly extensive. This network structure yields an optimum balance of hardness and resistance as opposed to flexibility (including high levels of elasticity). The coatings fulfil the requirements for wire enamels perfectly (resistance to refrigerants, stability for winding the wires). Additionally, the polyesters mainly comprise structural elements which confer stability to elevated temperatures. The simplest types consist of terephthalic acid, trishydroxy ethyl isocyanurate, and ethylene glycol. Due to the high excess of polyols, the molar masses of the polyesters are relatively low. During the crosslinking process, the ethylene glycol is cleaved and the polyester forms molecular networks efficiently. The crosslinking reaction is accelerated by alkyl or aryl titanium ester catalysts. To improve the heat resistance, some structural elements containing heterocyclic compounds are used instead of terephthalic acid. Thus diimide dicarboxylic acids are formed by reaction between primary aromatic diamines and trimellitic anhydride. Other polycarboxylic acids may consists of hydantoin rings. The polyesters are sparingly soluble and for application purposes are dissolved in cresols, xylenols and N-methyl pyrrolidone.

2.5.3 Reactions between epoxy groups and acid derivatives

Usually, the reaction between aliphatic or cycloaliphatic epoxy groups and carboxyl groups requires elevated temperatures. Combinations of resins containing these groups are used for weather resistance powder coatings (see Part IV). But such combinations are also reported as alternatives for the most common combinations of hydroxyl acrylic resins and melamine resins in solvent-borne paints. These are acrylic resins containing epoxy groups, combined with resins containing carboxyl groups, e.g. polyesters consisting of cycloaliphatic and aliphatic structural elements. These combinations are suitable for weather resistance automotive clear coats. Storage stability is limited. They can also be formulated as two-component systems.

2.5.4 Siloxanes in stoving enamels

Silicone resins are prepared by partial hydrolysis of di- and tri-functional alkoxyalkyl (or aryl) silanes. These resins have low molar masses and their functional groups are residual alkoxy groups (methoxy groups) [1, 2, 4]. The resins can self-crosslink by further hydrolysis to yield relatively brittle films. For optimum flexibility, the pure silicone resins are combined with hydroxyl resins, especially with saturated hydroxyl polyesters. If the compatibility of the two ingredients is poor, they have to be “hot blended” at temperatures up to 180 °C to yield so-called precondensates.

Crosslinking takes place by reaction between the hydroxyl groups of the polyester and the methoxy groups of the silicone resin part, with cleavage of methanol. The required stoving temperatures are 180 to 200 °C. Even then, catalysts are required; these are Lewis acids (e.g. butyl titanate). The resultant films are eminently weatherable and particularly resistant to high temperatures. Thus, the binders are suitable for weatherable coil coatings (front panel coatings), for painting motor parts (exhaust pipes), for heat exchangers and others.

A second way of incorporating siloxanes into resin molecules is to make trimethoxy alkylsilane react with functional groups of other resin components. For example, 3-isocyanatopropyl trimethoxy silane can be added to hydroxyl groups of polyesters or acrylic resins. The product of the reaction can crosslink at temperatures of 150 to 170 °C, under the influence of Lewis acid catalysts, to form molecular networks containing Si-O-Si bridges that are very resistant to all chemicals. The films also feature excellent weather resistance. The systems are relatively expensive and used for special high-quality topcoats.

2.6 Fastness to re-coating

When the organic pigments used are slightly soluble in paint media, bleeding may occur, especially in the case of stoving enamels [26, 27]. But bleeding can also happen at room temperature, e.g. in paints based on cellulose nitrate.

Pigment red 3 (toluidine red; Figure II-2.20), whose favourable price makes it one of the 20 most commonly used organic pigments, may lead to bleeding. Pigment red 3 is (sparingly) soluble in some organic solvents. Other pigments, e.g. pigment yellow 1 (Figure II-2.20), bleed as well.

Moreover, coatings containing pigment red 3 and pigment yellow 1 show inadequate fastness to re-coating. This defect can be seen when a coloured primer is coated with a white topcoat (Figure II-2.21). The organic pigment migrates into the white topcoat, where it causes pronounced discolouration (bleeding), the extent of which can be evaluated visually.

When comparative tests (Figure II-2.1) are carried a non-bleeding organic pigment (e.g. pigment red 178), it can be demonstrated that the discolouration of the white topcoat is not due to inadequate hiding power of the white coating [28].

The question now arises as to whether the inadequate fastness to re-coating of coatings containing pigment red 3 or pigment yellow 1 is caused only by the poor solvent resistance of these pigments [28]. Accordingly, the amount of bleeding of pigment red 3 was tested qualitatively with reference to

- Type of solvent (organic solvent or water)
- Type of binder system
  - – Physically drying systems, e.g. primary dispersions
  - – chemically curing systems, e.g. oxidatively curing alkyd resins, two-components polyurethane and epoxy systems as well as stoving enamels (e.g. AK/MF and AY/MF)
- Temperature

Many tests showed that the organic pigments should be blended with titanium dioxide in the primer. The ratio of pigment red 3 to titanium dioxide should be 1 : 12 to 1 : 15, and the P/B should be 0.7 : 1. For pigment yellow 1, the P/B should be 0.7 : 1 again and the ratio pigment yellow

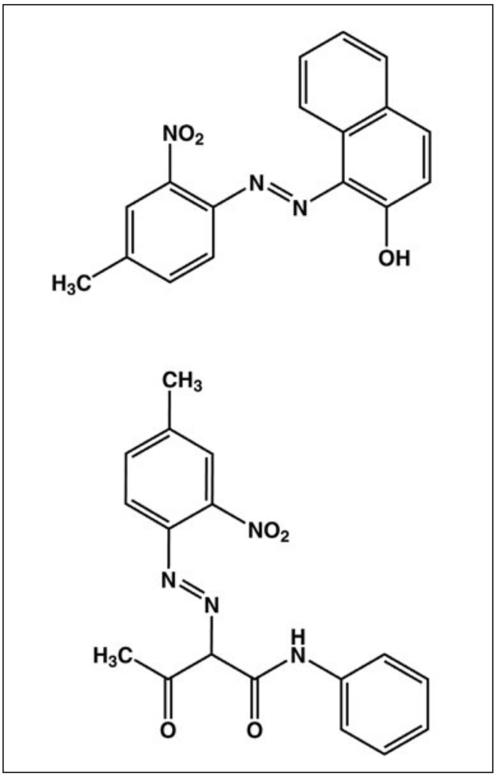


Figure II-2.20: Structural formulas of pigment red 3 (toluidine red, above) and pigment yellow 1 (below)

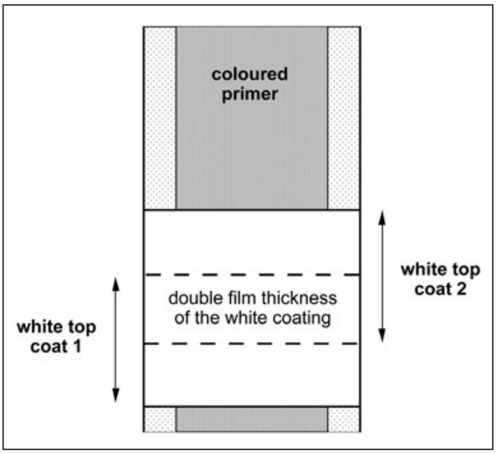


Figure II-2.21: Multi-coat system of test panels

1 : titanium dioxide should be 1 : 1. The pigment/binder ratio of the white topcoat is preferably 1 : 1 (titanium dioxide only).

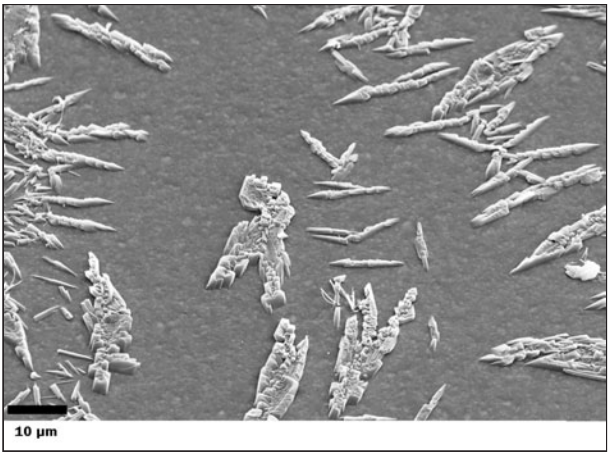


Figure II-2.22: Blooming of pigment red 3 on the surface of a white solvent-borne two-components polyurethane coating (below CPVC) after exposure for 60 min to 150 °C (scanning electron micrograph)

Figure II-2.23: Blooming of pigment yellow 1 on the surface of a white water-borne stoving coating (above CPVC) after exposure for 5 h to 150 °C (scanning electron micrograph)

Many tests surprisingly revealed that the solvents have no significant influence on re-coating fastness. Comparable solvent-borne and water-borne paint systems produced similar results. The most important factor is the temperature at which the white topcoat is dried or cured. For example, if a completely cured (and, therefore, crosslinked and solvent-free) two-components polyurethane primer containing pigment red 3 or pigment yellow 1 is re-coated with a white two-components polyurethane topcoat, little bleeding of pigment red 3 or pigment yellow 1 occurs after curing at room temperature; the choice of solvent in the topcoat does not make any appreciable difference. If this cured (and solvent-free) white topcoat is then heated in an oven, bleeding of pigment red 3 or pigment yellow 1 into the white topcoat increases significantly with increase in temperature. Sometimes, especially at high temperatures, blooming of pigment red 3 or pigment yellow 1 can be observed (recrystallisation on the surface of the white topcoat). Figures II-2.22 (pigment red 3) and II-2.23 (pigment yellow 1) show scanning electron micrographs of the blooming of organic pigments on the surfaces of white topcoats [29].

Besides recrystallised pigment yellow 1, Figure II-2.23 reveals the titanium dioxide particles in the white coating because the PVC of the white topcoat is above the CPVC.

A possible explanation of these results is that pigment red 3 and pigment yellow 1 dissolve in the binder of the white topcoat at elevated temperatures and recrystallise upon cooling. But blooming may also occur on surfaces of non-recoated coloured coatings (with pigment red 3 and pigment yellow 1). Pigment red 3 and pigment yellow 1 should therefore only be used in air-drying paint systems (drying or curing at ambient temperature) [28].

2.7 References

[1] H. Wagner, H. F. Sarx: Lackkunstharze, Publisher Carl Hanser, Munich 1971
[2] D. Stoye, W. Freitag (editor): Lackharze, Publisher Carl Hanser, Munich 1996
[3] H. van Dijk: The Chemistry and Application of Amino Crosslinking Agents or Aminoplasts, J. Wiley and Sons, London etc. 1998
[4] W. Krauß (editor): Kittel, Lehrbuch der Lacke und Beschichtungen Vol. 2: Bindemittel für lösemittelhaltige und lösemittelfreie Systeme, Publisher S. Hirzel Stuttgart Leipzig 1998
[5] A. Valet (editor U. Zorll): Lichtschutzmittel für Lacke, Publisher Vincentz Network, Hannover, 1996
[6] P. Thomas (editor): Polyurethanes, J. Wiley and Sons, London etc. 1998
[7] M. Bock (editor U. Zorll): Polyurethane für Lacke und Beschichtungen, Publisher Vincentz Network, Hannover, 1999
[8] O. Lückert: Karsten – Lackrohstofftabellen, 10. Edition Publisher Vincentz Network, Hannover, 1996
[9] U. Poth, R. Schwalm, M. Schwartz: Acrylic Resins; Publisher Vincentz Network, Hannover, 2011
[10] O. Lückert: Pigment und Füllstoff Tabellen, Publisher Vincentz Network, Hannover, 2001
[11] W. J. Blank et al (King Industries): Catalysis of Blocked Isocyanates with Non-Tin Catalysts
[12] Nuplex, Specialty Resins, (2001) REC 96049
[13] Nuplex, Specialty Resins, (2001) REC 96062
[14] Nuplex, Specialty Resins, (2001) REC 98072
[15] Nuplex, Specialty Resins, (2001) REC 97049
[16] Datasheets and formulations of DSM: 011262/2
[17] U. Röckrath, K. Brockkötter, Th. Frey, U. Poth, G. Wigger (BASF Coatings): Investigations of Crosslinking Mechanism of Etch Resistant Clear coats, 22nd Int. Conference of Water-borne, High-Solids and Powder Coatings Science and Technology, A. V. Patsis, Athen, 1996
[18] V. Mirgel, K. Nachtkamp (Bayer): Chemische Aspekte vernetzender Einbrennurethanharze, Farbe + Lack 89, 12 (1983) p. 928-934
[19] S. P. Pappas, E. H. Urruti (North Dakota State Univ.) Kinetics of oxime blocked aromatic and aliphatic isocyanates with amines and alcohols, 13th Intern. Conference of Water-borne and Higher Solids Coatings, Science and Technology. A. V. Patsis, Athen, 1986
[20] C. Kuo, T. Provder (Glidden Co.) Development of FTIR methodology for envolved gas analysis: Crosslinking of MEK-oxime blocked polyisocyanates Polym. Mat. Sci. Eng., 59 (1988), p. 474-479
[21] Datasheets and formulations of Bayer: NOE 5505/0
[22] Nuplex, Specialty Resins, (2001) REC 99032
[23] Example 1 of patent DE 19 67 171 (Herberts GmbH)
[24] B, Müller, Adhäsion, 46 (2002) No. 6, p. 34-38 and Suf. Coat. Int., Vol. 85, B2 (2002) p. 111-114
[25] Booklet “Epikote” of Shell (now Hexion)
[26] W. Herbst, K. Hunger, Industrial Organic Pigments, 2nd ed., Wiley-VCH (2004)
[27] D. Wang, T. Schauer, M. Entenmann, Europ. Coat. Journ., No. 5 (2000) p. 52-58
[28] B. Müller, Welt der Farben, No. 10 (2000) p. 12-13
[29] S. Ljesic, Diploma Thesis, University of Applied Science, Esslingen (2005)
[30] B. Müller, Welt der Farben, No. 5 (2003), p. 14-17
[31] A. Gürtler, Farbe + Lack, 110 (2004) 12, p. 34-37; 111 (2005) 11, p. 22-25

Part III Water-borne paints

Part III Water-borne paints

1 Solubility and dispersibility of paint resins in water

This chapter will discuss fundamental correlations between the chemical structure of organic paint resins, and the nature of their distribution in water. Without this information, the properties of water-borne paints cannot be understood.

Water-borne paints are increasingly being used for two reasons:

- Ecology: Reduction in levels of emissions of organic solvents to the atmosphere
- Economy: Water is much less expensive than organic solvents and is available nearly everywhere

The replacement of organic solvents by water causes problems because the physical and chemical properties of water are totally different from those of organic solvents – this needs to be discussed below.

1.1 Exceptional position of water as a paint solvent

The physical data for water and some common organic solvents are compared in Table III-1.1 [1, 2].

Table III-1.1: Comparison of physical data for water and organic solvents

	water	**1-butanol**	**butyl glycol**	**m-xylene**	**benzin 100/140**	**Solvesso* 150**
boiling point resp. range [°C, 1 bar]	100	116 to 118	167 to 173	136 to 139	110 to 140	177 to 206
evaporation number (diethyl ether = 1)	80	33	160	13.5	7.6	115
heat of evaporation [kJ/kg at b.p.]	2258	599	368	344	322	305
density [g/ml]	1.00	0.81	0.90	0.86	0.74	0.89
surface tension [mN/m, 20 °C]	72.2	25.5	27.8	29.5	25.2	33.7
electrical resistance [kΩ/cm]	10	50	100	$>10^6$	$>10^6$	$>10^6$
carbon content [mg/g]	0	648	610	906	842	900

** trade name for alkylaromatic solvents*

Bodo Müller, Ulrich Poth: Coatings Formulation

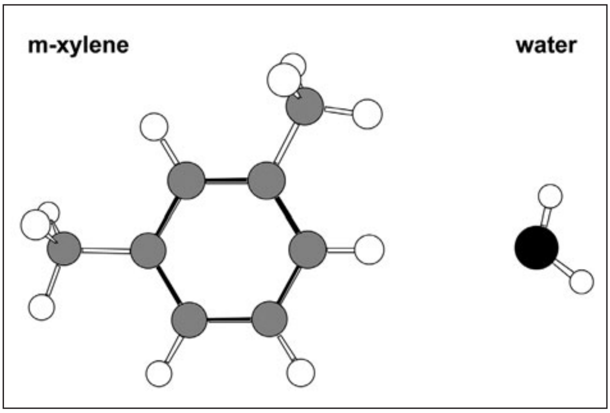


Figure III-1.1: Molecular models of meta-xylene and water

Figure III-1.1 shows that the polar properties (Table III-1.1) of the very small water molecule are caused by its angular structure. Moreover, the strength of the hydrogen bonds is of great importance. The high values for surface tension, boiling point, heat of evaporation and evaporation number are caused by the hydrogen bonds of water. The high surface tension (poor wetting of nonpolar substrates) and the high evaporation number (long flash-off times) are not conducive to use of water as a paint solvent. Water dissolves salts excellently but the relatively nonpolar (hydrophobic) paint resins are solvated either poorly or not at all. The advantages of water over organic solvents are its non-flammability and its non-toxicity, which is in distinct contrast to many harmful organic solvents. But water is chemically highly reactive, especially as regards hydrolysis and corrosion. This fact is not widely recognized in everyday life because water is essential for every kind of organism. This high reactivity of water militates against its use as paint solvent. For example, water-borne paints can only be produced or applied in (expensive) stainless steel devices because otherwise corrosion would take place.

1.2 Distributions of polymers in water

Organic paint resins (oligomers or polymers) are mostly hydrophobic and cannot be dissolved in water direct. Some water-soluble paint resins exist which have the disadvantage of being water-sensitive (swellable) after film formation. They are therefore only used as co-binders or additive binders in relatively small amounts. The hydrophobicity of the common paint resins is an advantage for use as water-resistant coatings.

Special production methods are needed for making paint resins for water-borne paints. The water-solubility of such paint resins can be achieved by a higher acid number (see Chapter III-1.4); the carboxylic groups are converted with the help of amines to hydrophilic carboxylate groups during dissolution (salt formation, Equation 1).

$$\text{Pol-COOH} + \text{NR}_3 \rightarrow \text{Pol-COO}^{\ominus} + \text{HNR}_3^{\oplus} \qquad \textit{Equation 1}$$

Another type of water-borne paint resin is that of polymer dispersions. These are disperse two-phase systems containing more or less hydrophobic polymers as the disperse phase and water as the dispersion medium (see Chapter III-1.3.1).

Between the two limiting cases of the (colloidally) dissolved and the completely dispersed paint resin, all intermediate states are possible, and are caused, e.g., by the acid number or the molar mass of paint resins. The distribution of a paint resin in water can be characterized via the particle size of the dissolved or dispersed polymer (Table III-1.2).

The appearance of polymer distributions described in Table III-1.2 may be roughly explained as follows. When light interacts with particles which are small in comparison to its wavelength λ, light will be scattered according to the Rayleigh principle (opalescence or Tyndall effect) [3]. Accordingly the scattering coefficient is proportional to λ^{-4}; i.e., short-wave, blue light is scattered ten times as strongly as long-wave, red light. This explains why fine (col-

Table III-1.2: Distribution of organic binders (paint resins) in water

particle size [nm]	appearance*	type
above 1000	milky white	coarse polymer dispersions coarse emulsions
1000 to 100	white to bluish	fine polymer dispersions
100 to 50	bluish semitransparent	very fine polymer dispersions dissolved high polymers ** microemulsions
50 to 10	increasing transparency	hydrosols dissolved high polymers **
10 to 1	transparent (Tyndall-effect)	molecular solutions ***

** with significant difference of the refractive indices of water and binder.*
*** molecular colloids*
**** paint resins with low molecular masses (e.g. melamine resins)*

ourless) polymer dispersions have a bluish shimmer when observed from the side but are reddish in transmitted light.

Conversely, if this "colour effect" is observed, the particle size of the polymer dispersion is smaller than the wavelength of visible light. Dispersed particles larger than the wavelength of visible light also scatter light (Mie scattering); such dispersions are colourless and milky turbid (e.g. coarse polymer dispersions).

When the appearance of dispersions is being evaluated, it should be remembered that disperse systems mostly have a more or less broad particle size distribution; a few large particles at the limits of the particle size distribution can significantly increase the turbidity of the dispersion. Moreover, dispersions may appear clear and transparent if there is no significant difference between the refractive indices of the dispersion medium (water) and the disperse phase (polymer).

Dispersions with particle sizes ranging from 5 to 1000 nm are called colloids or colloidal dispersions (Chapter I-2.1). Consequently, most distributions of organic paint resins in water are in the colloidal state. Only very coarse polymer dispersions (Ø > 1000 nm) and molecular solutions of low-molecular paint resins (Ø < 5 nm, e.g., HMMM resins) are not colloids.

Molecular solutions of water-soluble, high polymers (such as certain polysaccharides and proteins) may have particle sizes up to 100nm and are therefore called molecular colloids (Table III-1.2). One example of a molecular colloid that is important in paint technology is the water-soluble polysaccharide xanthen (molar mass $2 \cdot 10^6$), which is used as a rheology modifier [4].

1.3 Dispersions and emulsions of paint resins and polymers

Aqueous polymer dispersions are thermodynamically metastable two-phase systems containing a solid disperse phase (paint resin) and water as dispersion medium.

1.3.1 Primary dispersions

Primary dispersions (latices) are manufactured by emulsion polymerization [5]; they have a discrete disperse phase and a distinct phase boundary between the disperse phase (polymer) and the dispersion medium (water). Primary dispersions are mostly dispersion colloids.

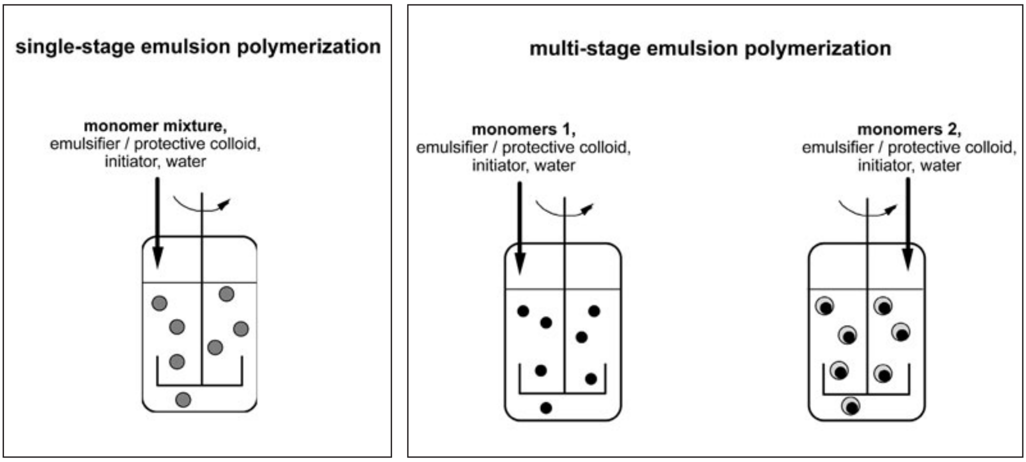


Figure III-1.2: Simplified diagram of the single-stage and multi-stage emulsion polymerization techniques

The properties of primary dispersion particles are determined principally by the colloid properties (e.g. stabilization system; see below), the particle properties (e.g. particle size, particle size distribution and morphology of the particles) and the polymer properties (e.g. molar mass, type and amount of monomers employed) [6]. Furthermore, the properties of films made from primary dispersions are influenced by the particle and polymer properties.

As a rule, during single-stage emulsion polymerization, a homogeneous dispersion containing a more or less random copolymer is formed from the monomer mixture (Figure III-1.2). Multi-stage emulsion polymerization is frequently employed to meet the demands imposed on superior latex gloss enamels [5], namely easy film formation at ambient temperature coupled with high hardness [6, 7]. In multi-stage emulsion polymerization, two different monomer mixtures are added one after the other (Figure III-1.2).

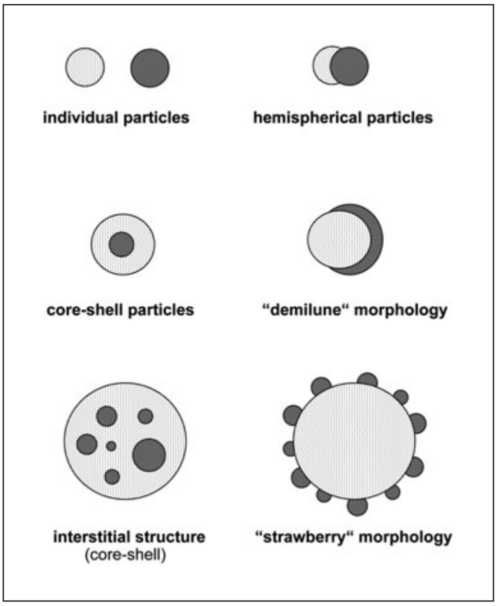


Figure III-1.3: Possible structures (cross-sections) of particles of primary dispersions obtained by multi-stage emulsion polymerization of at least two monomers (heterogeneous dispersions)

The result is heterogeneous polymer dispersions having structured polymer particles whose particle morphology (a particle property) can vary over a wide range in accordance with the type of polymer and the polymerizations process (Figure III-1.3). Commercial dispersions for latex gloss enamels frequently contain complex particle structures, e.g. hemispherical particles or "strawberry" morphology [6]. The two polymer phases mostly consist of a hard polymer (high glass temperature) and a soft polymer (low glass temperature).

As a rule, primary dispersions are thermodynamically unstable as regards coagulation (colloid property). They therefore have to be stabilized electrostatically or sterically, i.e., a thermodynamically metastable state has to be attained.

Emulsifiers (low-molecular, usually anionic surfactants) provide electrostatic stabilization and will produce fine dispersions during emulsion polymerization. It should be noted that fine dispersions have a large phase boundary and so a great deal of emulsifier is needed.

Protective colloids (high-molecular, water-soluble polymers such as polyvinyl alcohol and cellulose ethers) provide steric stabilization and mostly yield coarse dispersions during emulsion polymerization. The finer the polymer dispersion particles, the higher is their pigment binding power (CPVC), penetration into porous substrates, homogeneity and gloss of the resultant film.

The emulsifiers or protective colloids added during emulsion polymerization can be grafted onto the polymer by chain-transfer reactions; they are located as hydrophilic groups on the surface of the dispersion particles. Furthermore, the monomer mixtures frequently contain polar monomers, such as acrylic acid and maleic acid, which will be also located on the surface of the dispersion particles; in alkaline paint media, these carboxylic groups form salts, thereby generating stabilizing charges. Additionally, charged functional groups may originate from initiators, such as peroxodisulphate (Equation 2).

$$^{\ominus}O_3S - O - O - SO_3^{\ominus} \longrightarrow \text{polymer} - O - SO_3^{\ominus}$$ *Equation 2*

The metastability of primary dispersions leads to the following technological properties:

- Film formation (coagulation on the substrates) of primary dispersions is thermodynamically favoured.
- High shear (e.g. dissolver, pumps) may lead to coagulation.
- Increases in temperature may cause coagulation of sterically stabilized dispersions.
- Freezing may also lead to coagulation.
- Salts (especially multivalent cations, such as Ca^{2+}, Fe^{3+} or Al^{3+}) can coagulate electrostatically stabilized dispersions; sterically stabilized dispersions are less sensitive to salts.
- Lowering the pH (decreasing the number of stabilizing charges) may effect coagulation of electrostatically stabilized dispersions.

A relatively modern type of primary dispersion is that of aqueous microgels. These are produced by crosslinking emulsion polymerization, which leads to intraparticularly crosslinked primary dispersions. During crosslinking emulsion polymerization, several wt.% (sometimes up to 20 wt.%) of bifunctional monomers (e.g. allyl acrylate, divinyl benzene, hexanediol diacrylate) are added. Like primary dispersions, suitably formulated microgels are able to form films and can be used as paint resins [8].

The dependence of the viscosity on the nonvolatiles content of two poly-mer solutions and two polymer dispersions is shown in Figure III-1.4. The polymer solutions have higher viscosities, which increase

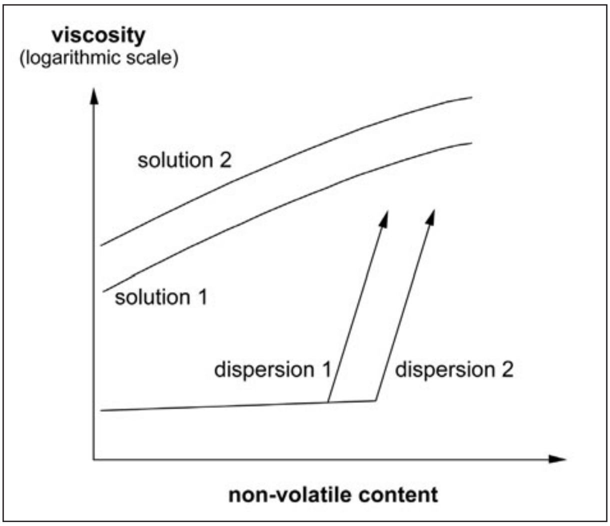


Figure III-1.4: Simplified diagram of the viscosity versus nonvolatile content of two polymer solutions and two polymer dispersions. Molar mass of dissolved polymer 1 < molar mass of polymer 2. Particle size of polymer dispersion 1 < particle size of dispersion 2. OR, given identical average particle size of polymer dispersions 1 and 2: Particle size distribution of polymer dispersion 1 is narrower than that of dispersion 2 with increase in molar mass. The completely different shape of the viscosity curve of the polymer dispersions (Figure III-1.4) is due to the fact that the spheres of activity of the polymer particles do not influence each other at low or medium nonvolatiles content. Moreover, the viscosity of a polymer dispersion is more or less independent of the molar mass of the dispersed polymer (polymer property). With increase in nonvolatiles content, the distance between the polymer particles decreases. These can interact with each other and so the viscosity increases rapidly [9].

But the size of the dispersed polymer particles (particle property) influences the shape of the viscosity curve; the finer the particles, the more the viscosity increases at low polymer content (Figure III-1.4). Also important is the particle size distribution (particle property) – the wider the distribution, the more closely the polymer particles can be packed together.

First and foremost, then, the viscosity of polymer solutions is governed by polymer properties whereas the viscosity of polymer dispersions is governed by particle properties. The most important technological advantage of many polymer dispersions, and especially of primary dispersions, over polymer solutions is that the viscosity of a dispersion is largely independent of the molar mass of the dispersed polymer. This means that polymers with very high molar masses (10^6 and higher) are easy to apply; these high polymers yield high-quality coatings without crosslinking.

Technologically, the most important types of primary dispersions are acrylate dispersions (copolymers of different esters of methacrylic/acrylic acid) and styrene-acrylate dispersions (copolymers of styrene and esters of acrylic acid) [10]. As a rule, these macromolecules are produced by free-radical copolymerization. Their polymer backbone consists only of nonsaponifiable C-C bonds and of difficult-to-saponify ester groups in the methacrylate/acrylate side chains; the resultant coatings are highly resistant. The more inexpensive vinyl ester dispersions are mostly easier to saponify and are less suitable for high-performance coatings.

Primary dispersions are used mainly as binders for architectural coatings, especially for physically drying latex paints. Moreover, heterogeneous primary dispersions produced by multi-stage emulsion polymerization can be used as binders for latex gloss enamels (e.g. for wood) [6, 7]. The main difference between latex paints and latex gloss enamels is the pigment/binder ratio and, hence, the different pigment volume concentration (PVC). As a rule, latex paints have PVCs ranging from 40 to 90 vol.%, while latex gloss enamels have PVCs below 25 vol.%. Latex gloss enamels are able to form dense, more or less glossy films because of the heterogeneous structure of the particles (core shell structure, shell polymer with low glass temperature) and low PVC.

Film formation by primary dispersions (physical drying) is described in detail in Chapter III-2.1.1. For the moment, it should just be noted that, in a film prepared from a primary dispersion, each polymer particle retains its own identity [11].

The term “emulsion paint” is often used for latex paints. However, it is a misnomer that should be avoided because an emulsion consists of two liquid phases (Chapter III-1.3.2), whereas a latex is a dispersion of a solid polymer in water (liquid medium) [5].

1.3.2 Emulsions of liquid paint resins

Emulsions are thermodynamically metastable two-phase systems of a liquid disperse phase (liquid paint resin) in a water dispersion medium (particle size often 1μm or larger). The disperse phase has a distinct phase boundary, rather like that of primary dispersions, and that is why emulsions are described in this chapter. Examples are emulsions of silicone resins or of long-oil alkyd resins and oxidatively drying oils. There are also liquid epoxy resins (with emulsifiers) that form emulsions in water. Binder emulsions are of minor importance relative to other types of water-borne paint resins.

1.3.3 Secondary dispersions

Secondary dispersions are formed from polymers which first are synthesized in solution or in melt and then are transformed into an aqueous dispersion. Consequently, the very high molar masses observed for primary dispersions are not feasible in this case. As a rule, after film formation of secondary dispersions by physical drying, discrete dispersion particles are no longer detectable, in contrast to the case for primary dispersions (see Figure III-2.2 later). Secondary dispersions are disperse two-phase systems but, unlike the case for primary dispersions and emulsions, there is no distinct phase boundary between the disperse phase (paint resin) and the dispersion medium (water). Solvated polymer loops bearing hydrophilic groups (e.g. carboxylate groups) can project from the particle surface into the water phase [12, 13].

Secondary dispersions rank between molecularly dissolved polymers and primary dispersions. Both thermodynamically stable secondary dispersions (emulsifier-free, "self dispersing") and metastable secondary dispersions exist.

1.3.3.1 Acrylate secondary dispersions

Figure III-1.5 shows the differences in the production processes for emulsifier-free acrylate secondary dispersions and acrylate primary dispersions (with emulsifiers) [14]. An acrylate solution of appropriate acid number (neutralized at least partially with amines) spontaneously forms a secondary dispersion on dilution with water (self-dispersing effect); the particle size is 20 to 200 nm [14]. Usually, a water-soluble organic solvent is added to lower the viscosity of the acrylate polymer; after formation of the acrylate secondary dispersion, the solvent can be distilled off. The molar masses of acrylate secondary dispersions are 50,000 to 150,000 and thus significantly lower than those of acrylate primary dispersions (about 10^6).

Acrylate secondary dispersions are used as binders for anticorrosion paints [14], in water-borne stoving enamels for industrial applications and for automotive coatings [15].

1.3.3.2 Polyurethane secondary dispersions

The general properties of secondary dispersions were first elucidated by studying the long-established emulsifier-free polyurethane (ionomer) dispersions [16, 17]. Polyurethane dispersions serve as binders for various water-borne paint systems, e.g. primer surfacers and basecoats for automobiles. Two different processes for manufacturing polyurethane dispersions are explained below.

The ketone process is shown in Figure III-1.6. The first step is polyaddition of diol (mostly polyester diol), diisocyanate and dimethylol

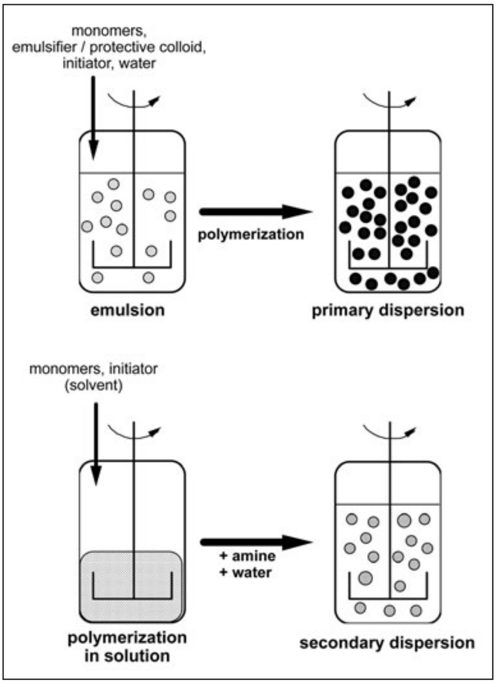


Figure III-1.5: Simplified diagram of the manufacturing process for acrylate primary and acrylate secondary dispersions

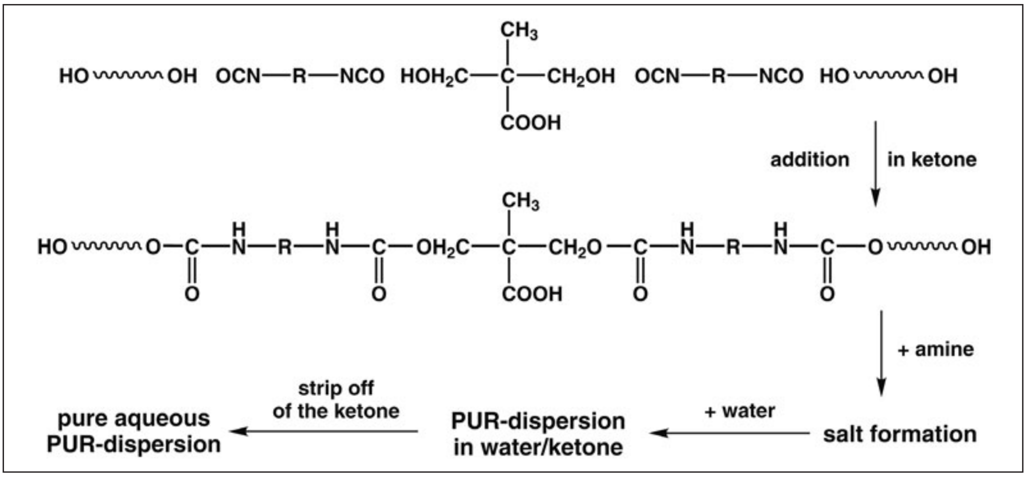


Figure III-1.6: Simplified diagram of the ketone process for the production of polyurethane (PUR) secondary dispersions

propionic acid to form a linear polyurethane polymer (NCO/OH ≈ 1). Because the viscosity rises during polyaddition (increase in molar mass), a ketone has to be added (e.g. acetone, MEK or MIBK). Nevertheless, the maximum molar mass is approx. 50,000. Then, an amine is added to neutralize the carboxylic groups (salt formation). Water is added, whereupon a polyurethane ionomer dispersion forms spontaneously; an appropriate acid number is needed for the dispersion to be spontaneous. Finally, the ketone is distilled off to leave a purely aqueous polyurethane dispersion (Figure III-1.6). The polyurethane dispersion may have other functional groups (hydroxyl groups) which are capable of crosslinking with, e.g., melamine resins.

The prepolymer process is shown in Figure III-1.7. Again, the first step is polyaddition of diol (mostly polyester diol), diisocyanate and dimethylol propionic acid to form a linear isocyanate-terminated prepolymer (NCO/OH > 1). Because this process is solvent-free, the liquid prepolymer has a relatively low molar mass (low viscosity). Then, concurrently, a tertiary amine bearing no other functional groups (e.g. triethylamine) is added along with water for dilution (Figure III-1.7). A prepolymer emulsion forms spontaneously; this isocyanate-terminated prepolymer emulsion is stable in water for a short time.

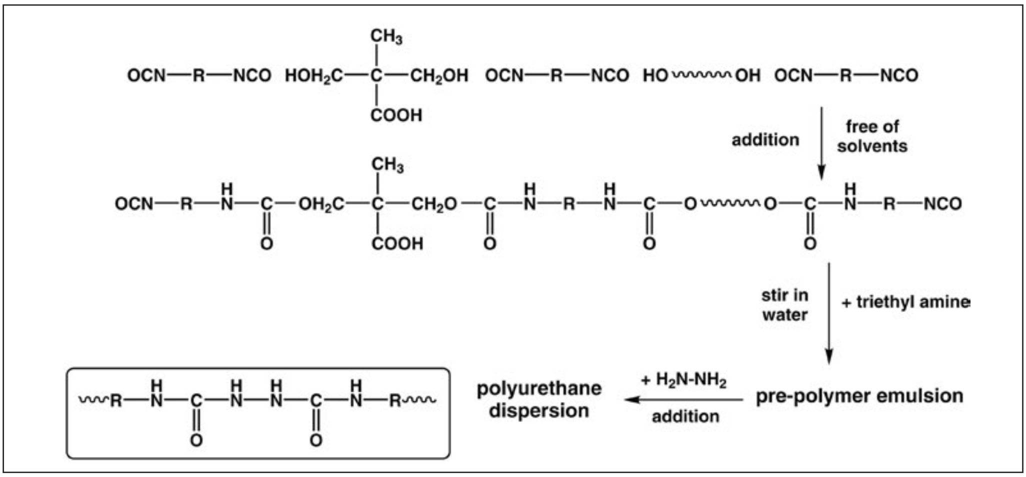


Figure III-1.7: Simplified diagram of polyurethane secondary dispersions made by the prepolymer process

Finally, hydrazine is added; this reacts very rapidly with isocyanate-terminated prepolymer and leads to chain extension. As chain extension (increase in molar mass) is carried out in the disperse phase, high molar masses are attainable. Polyurethane dispersions that have been chain-extended with hydrazine exhibit very good physical drying and yield films with excellent cohesion (many hydrogen bonds).

Alternatively, chain extension may be performed without the hydrazine, which is toxic, by the slower reaction with water, which reacts with the isocyanate groups to form urea linkages. This process may also be performed in the presence of the solvents used, preferably those which do not have to be distilled off, such as N-methyl pyrrolidone (NMP) or its substitute NEP (Figure III-1.10 later). Possible health risks of NMP should be borne in mind.

Polyurethane dispersions have average particle sizes of 10 to 500 nm, and a mostly wide particle size distribution. As the hydrophilicity increases (e.g. with increase in acid number), the particle size decreases and the viscosity increases; i.e. the dispersions become more stable [18].

The spontaneous formation of a dispersion (self-dispersing effect) admits of the assumption that the acrylate and polyurethane secondary dispersions described here are thermodynamically stable. In contrast, primary dispersions exhibit thermodynamic metastability only (given appropriate stabilization, see Chapter III-1.3.1).

1.4 Aqueous solutions of paint resins

1.4.1 Water-solubility of paint resins

There are only a few paint resins which are water-soluble. They are polar (hydrophilic) and solvated by water. Examples are non-etherified amino resins and most of their methanol-etherified counterparts, some resols (thermosetting phenolic resins), polyethylene glycols and low-molecular polypropylene glycols.

As most paint resins usually contain hydrophobic units, certain steps are taken to render them water-soluble. The most common is to incorporate hydrophilic groups that are solvated by water. Such groups could be hydrophilic polyethers, which are usually incorporated as side-chains. More common is the use of ionic groups (cations and especially anions) that are also solvated by water and thereby increase the water-solubility of the paint resins. The most important ionic groups are functional groups that are able to form ions on addition of a neutralizing agent.

Anionic water-borne paint resins contain a certain number of carboxylic, sulphonic, phosphonic or phosphoric acid groups. They are rendered water-soluble by neutralization with bases, preferably with (volatile) amines or ammonia (e.g. Equation 3).

$$\text{Pol-COOH} + \text{NR}_3 \longrightarrow \text{Pol-COO}^{\ominus} + \text{HNR}_3^{\oplus} \qquad \textit{Equation 3}$$

Cationic water-borne paint resins (Chapter III-4.4.3) contain amino groups which can be protonated by low-molecular carboxylic acids (Equation 4). The sulphonium and phosphonium derivatives also mentioned play a minor role.

$$\text{Pol-NR}_2 + \text{R'-COOH} \longrightarrow \text{Pol-}\overset{\oplus}{\text{N}}\text{HR}_2 + \text{R'-COO}^{\ominus} \qquad \textit{Equation 4}$$

The advantage of ionically dissolved paint resins is that, during film formation, the salt forming agents (volatile amines or low-molecular carboxylic acids) evaporate and so the number of ionic hydrophilic groups in the film decreases dramatically.

This improves the water resistance of coatings made from such paint resins. The water resistance of coatings made from paint resins which are water-soluble without the need for neutralization, e.g. methanol-etherified amino resins, must be developed by a crosslinking reaction. Coatings made from water-soluble polyethers and polyether-stabilized paint resins remain somewhat hydrophilic and may be swellable by water.

Neutralizing agents for anionic paint resins are amines and ammonia because they evaporate during film formation; it is possible to formulate water-borne paints which dry at ambient temperature and which solidify at elevated temperatures (60 to 180 °C).

In contrast, the acids used for neutralizing cationic binder systems are less volatile. These systems therefore require relatively high stoving temperatures (above 160 °C) for effective curing. Cationic water-borne paint resins are mostly used in electrodeposition primers, which are cured at high temperatures (Chapter III-4.4.3).

Ionic water-borne paint resins form colloidal aqueous solutions. The transition to electrostatically stabilized secondary dispersions is a fluid one. Paint resins are more likely to be in an aqueous state if the molar masses and the glass temperatures are low, and the acid number and the content of cosolvent (Chapter III-1.4.3) are high.

Water-borne paint resins are offered in different forms:

- Solid resins (mostly binders for printing inks, e.g. maleic resins, styrene-maleic acid anhydride copolymers)
- Solutions (60 to 90% solids) in water-miscible organic solvents (e.g. butyl glycol) non-neutralized (e.g. AK, SP, AY, MF)
- Neutralized solutions in a solvent mixture (predominantly water) which can be directly diluted with water (e.g. AK, SP, AY).
- Aqueous solutions without neutralizing agent (certain MFs)

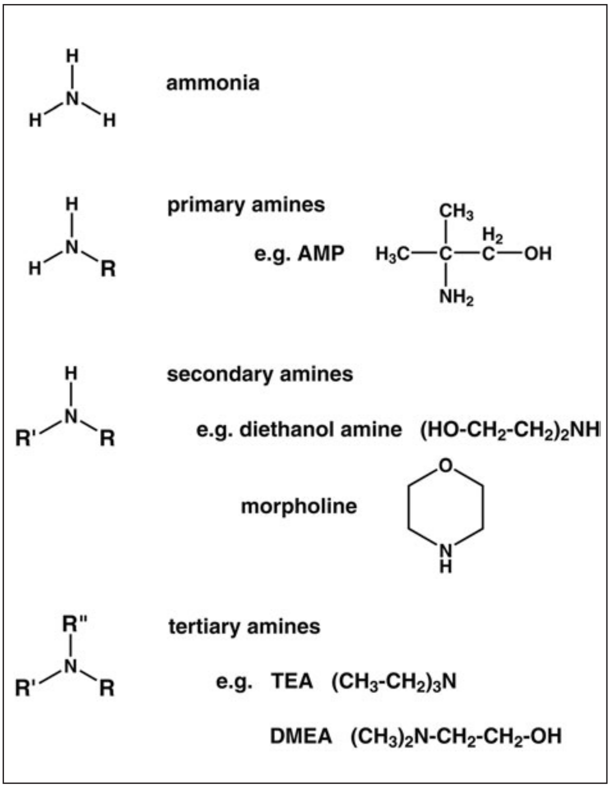


Figure III-1.8: Amines as neutralizing agents

1.4.2 Neutralizing agents

Paint resins containing carboxylic groups are the most important water-borne binders. Amines serve as neutralizing agents (Figure III-1.8). These amines should be volatile upon drying or curing in order that the hydrophilicity of the coatings may be lowered (Equation 5).

$$\text{Pol-COO}^{\ominus}\ \text{HNR}_3^{\oplus} \longrightarrow \text{Pol-COOH} + \text{NR}_3\uparrow \qquad \textit{Equation 5}$$

For stoving enamels, DMEA and, to a lesser extent, AMP, are the most important neutralizing agenta. For air-drying paints, the more volatile amines are used, e.g. ammonia or triethylamine (TEA). In special cases, other amines are also used. All amines have a strong and unpleasant odour. For latex paints, the non-volatile and odour-free potassium hydroxide (KOH) may be used.

Amines also influence the solubility of paint resins. In this case, their basicity is of lesser importance than their solubilising properties. In the series DMEA > TEA > ammonia, the solubility of paint resins decreases or the turbidity of (colloidal) aqueous resin solutions increases.

The amount of an amine (mass: m_{amine}; molar mass: M_{amine}) for complete neutralization of a paint resin (mass: m_{resin}) can be calculated from the acid number (AN, mg KOH/g) of the paint resin:

$$m_{amine} = \frac{M_{amine} \cdot AN \cdot m_{resin}}{56100}$$

As a rule, the pH of an anionic water-borne paint should be about 8. It should be noted that amines are adsorbed on the surfaces of pigments and fillers (especially on post-oxidized acidic carbon blacks). With pigmented paints, the amount of amine for adjusting the pH to 8 may be much higher than calculated. When water-borne paints are being produced, the pH value should be checked at every step so that unpleasant surprises such as coagulation of the paint resin may be avoided.

When neutralized paint resins containing carboxyl groups (e.g. AK, SP, AY) are diluted with water, abnormal viscosity behaviour is often observed [19, 20]. This viscosity anomaly is caused by two opposing effects (Figure III-1.9):

- The diluting effect of water lowers the viscosity.
- Water is a poor solvent for organic paint resins (exceptions are certain melamine and urea resins). Thus, the solvent power of the medium decreases on dilution with water; this leads to increasing association of resin molecules (similar to the case for secondary dispersions) and a rise in “viscosity peak”.

1.4.3 Cosolvents

Addition of organic water-miscible cosolvents improves the solubilising power of the medium and decreases the formation of viscosity-increasing resin associates (Table III-1.3, Figure III-1.10).

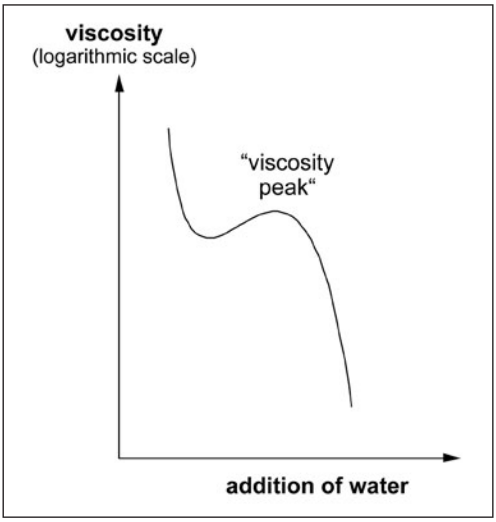


Figure III-1.9: Simplified diagram of the change in viscosity of a neutralized water-borne paint resin during dilution with water

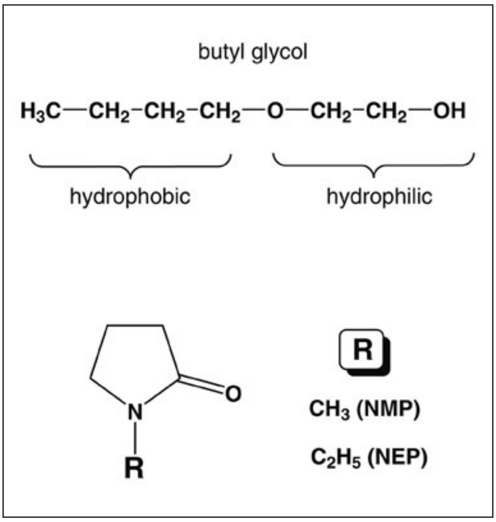


Figure III-1.10: Formulas of butyl glycol and N-alkyl-2-pyrrolidone

Table III-1.3: Important cosolvents for water-borne paints

solvents	solubility in water at 20 °C
1. protic cosolvents	
1-butanol	8 wt.%
butyl glycol	unlimited
butyl diglycol	unlimited
2. dipolar aprotic cosolvent	
N-methyl-2-pyrrolidone (NMP)	unlimited
N-ethyl-2-pyrrolidone (NEP)	unlimited

The best cosolvent for normal viscosity behaviour on dilution with water is undoubtedly butyl glycol (Figure III-1.10). The hydrophobic n-butyl group associates with the organic hydrophobic paint resin. This lowers the tendency of the resin molecules to associate with each other, as a result of which the rise in viscosity on dilution with water is less pronounced and may even be zero. It should be noted that many mixtures of water and butyl glycol exhibit an upper miscibility gap at temperatures exceeding 50 to 55 °C. Effective cosolvents do not have to be totally miscible with water (e.g. 1-butanol; see Table III-1.3).

In a hydrosol, a secondary dispersion or a primary dispersion, the concentration of the usual protic cosolvents is higher in the dispersed resin particle than in the aqueous phase. Disperse resins are also able to absorb small amounts of solvents that are totally immiscible with water, e.g. white spirit. This may lead to swelling of the disperse polymer particles and to a rise in viscosity. In contrast, dipolar aprotic solvents, such as N-methyl-2-pyrrolidone (NMP, Figure III-1.10), may become enriched in the aqueous phase. Some water-borne polyurethane secondary dispersions contain a few wt.% NMP. Furthermore, NMP is added to water-borne plastics paints to improve their adhesion. It should be noted that NMP is nowadays considered to be toxicologically harmful; N-ethyl-2-pyrrolidone (NEP; Figure III-1.10) has recently been proposed as a substitute [21].

For ecological reasons, the amount of organic cosolvents in water-borne paint systems should be as low as possible. The ideal situation of totally solvent-free water-borne paints can only be reached step by step. Many resins for water-borne paints dissolved in organic cosolvents are now being changed to more or less aqueous dilution forms. This causes difficulties because water, a chemically aggressive solvent (Chapter III-1.1), is able to hydrolyze certain paint resins (especially polycondensates such as alkyd resins and saturated polyesters). Hydrolysis (saponification) starts as soon as the water is added. In other words, an aqueous resin solution prolongs the hydrolysis time by the length of time the resin solution is stored prior to production of the water-borne paint. Nowadays, most producers of paint resins have solved this problem and mostly specify a shelf life for water-borne paints of 6 to 12 months.

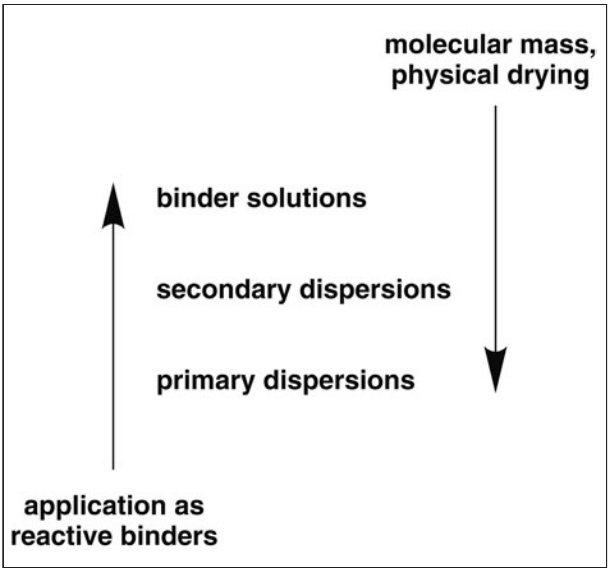


Figure III-1.11: Very simplified diagram of the properties of various distributions of organic paint resins in water

Summary

It should be noted that only a small proportion of paint resins dissolve to form clear (i.e., molecular) solutions in water (colloidal solutions may also sometimes appear clear). Most aqueous resin solutions are more or less turbid; i.e., associates or secondary dispersions (Chapter III-1.3.3) are formed by hydrophobic interactions. The one and the same paint resin may be molecularly dissolved, associated or at least in the form of a secondary dispersion, depending on the paint formulation (pH, amine, cosolvent). Therefore, the term "water-soluble paint resin" is not always totally correct. For this reason, they are often referred to as "water-thinnable paint resins", which also is not precise enough since primary dispersions (Chapter III-1.3.1) are water-thinnable too.

Paint resins dissolved in water are predominantly used in chemically curing paint systems as these do not tend to dry physically on account of their relatively low molar masses (Figure III-1.11). These may be paints which cure at ambient temperature (e.g. two-components polyurethanes) or water-borne stoving enamels (e.g. MF-crosslinked AK, SP or AY). Particularly interesting are the so-called hybrid systems, which are a combination of reactive water-borne resins and primary as well as secondary dispersions. They make for rapid physical drying and, thanks to downstream crosslinking, yield typical thermoset properties (e.g. solvent resistance and infusibility).

1.5 References

[1] Data sheets of BASF SE, Shell, Exxon
[2] Ullmann's Encyclopedia of Industrial Chemistry, Vol. 18, Chapter 3.3 "Water-borne Paints", p. 434, VCH Weinheim (1991)
[3] Wo. Ostwald, Licht und Farbe in Kolloiden, first part, Verlag Th. Steinkopff (1924)
[4] B. Müller, Understanding Additives, Vincentz Network (2010)
[5] Z. W. Wicks, F. N. Jones, S. P. Pappas, Organic Coatings - Science and Technology, 2nd ed., Wiley-Interscience (1999), Chapter 8 and 31
[6] U. Désor, S. Krieger, Welt der Farben, 7+8/1997, p. 6-12
[7] R. Baumstark et al., Farbe & Lack, 106 (2000) No. 11, p. 125-147
[8] Z. Vachlas, Journ. Oil Color Chem. Assoc., 72 (1989) p. 139-144
[9] D. Stoye (ed.), Lacke und Lösemittel, Verlag Chemie (1979), p. 23
[10] U. Poth, R. Schwalm, M. Schwartz, Acrylic Resins, Vincentz Network (2011)
[11] D. Distler, G. Kanig, Colloid & Polym. Sci., 256 (1978) p. 1052-1060
[12] D. Dieterich, Angew. Chem. 82 (1970) p. 53 ff
[13] O. Lorenz et al., Angew. Makromol. Chem. 172 (1989) p. 113 ff;
[14] B. Schlarb, M. Gyopar Rau, S. Haremza, Progr. Org. Coat. 26 (1995) p. 207-215
[15] U. Kubillus, H. Oswald, Kunstharz-Nachrichten 29 (1993) p. 43-47
[16] D. Dieterich, Progr. Org. Coat. 9 (1981) p. 281 ff
[17] D. Dieterich, Angew. Makromol. Chem. 98 (1981) p. 133 ff
[18] M. Bock et al., Polyurethanes for Coatings, Vincentz Network (2001)
[19] J. Dörffel, Farbe & Lack 81 (1975) p. 10-15
[20] H. J. Luthardt, Farbe & Lack 87 (1981) p. 456-460
[21] https://www.basf.de/en/intermed/news/publications/assets-download.htm?getasset=file1&name=Broschuere_NEP_en.pdf&docid=40867

2 Water-borne paints and coatings that dry/cure at ambient temperatures

2.1 Physically drying paints

Latex paint is a generic term for physically drying paints based on aqueous polymer dispersions, pigments and fillers. The frequently encountered term “emulsion paint” is misleading [1]; see also Chapter III-1.3.1. For the purposes of this book, latex paints are characterized by a PVC > 40% and latex gloss enamels, by a PVC < 40% (Table III-2.1).

Table III-2.1: Classification of latex gloss enamels and latex paints

paint type	PVC [vol.%]	content of binder [wt.%]
1. latex gloss enamels		
glossy	10 to 15	70 to 65
semi-glossy	15 to 30	65 to 38
satin	30 to 40	38 to 33
2. latex paints (flat)		
exterior (facades)	40 to 60	33 to 21
interior	60 to 80	21 to 10
cheap interior version	80 to 90	10 to 5

The components of latex gloss enamels and latex paints are listed in Table III-2.2. The binders are mostly primary dispersions (e.g. pure acrylate or styrene-acrylate). For weatherable latex gloss enamels, pure acrylates are preferred [2].

2.1.1 Film formation by primary dispersions

As the water evaporates, the polymer particles come closer and closer to each other until spherical

Table III-2.2: Components of latex gloss enamels and latex paints

dispersion medium	water
pigment	titanium dioxide rutile*
fillers	e.g. chalk [3]
binder	polymer dispersions (mostly primary dispersions)
rheology modifiers	polymers like ASE, HASE, HEUR, cellulose ethers and inorganic clays [4]
dispersing agents	polyanions like polyacrylates, polyphosphates [4]
defoamers	hydrocarbon or silicone defoamers [4]
preservatives	fungicides, biocides [4]
coalescing agents	low-volatile organic solvents (see below)
pH stabilizers	bases like ammonia, sodium hydroxide
anti-corrosion additives	only in latex gloss enamels for metals [4]

** By producing latex paints only titanium dioxide and fillers are dispersed. Other (pastel) colours are made by addition of tinting base (water-borne pigment preparations). By producing latex gloss enamels also other pigments may be dispersed.*

packing takes place (Figure III-2.1). Further evaporation of water causes capillary forces of the very thin water lamellas to deform the spherical polymer particles, yielding rhombic dodecahedrons (Figure III-2.2). These fuse together (coalesce) at the particle boundaries. Interdiffusion of polymer chains across the particle boundaries may occur. Primary dispersions are thermodynamically unstable with regard to coagulation; i.e. film formation leads to a thermodynamically irreversible, stable state. In coatings yielded by primary dispersions, the individual polymer particles are still identifiable (Figure III-2.2). Figure III-2.2 shows a transmission electron micrograph of a contrasted thin-section of a film obtained from a pure acrylic primary dispersion; the two-dimensional diagram of the rhombic dodecahedra looks like honeycomb (Figure III-2.2).

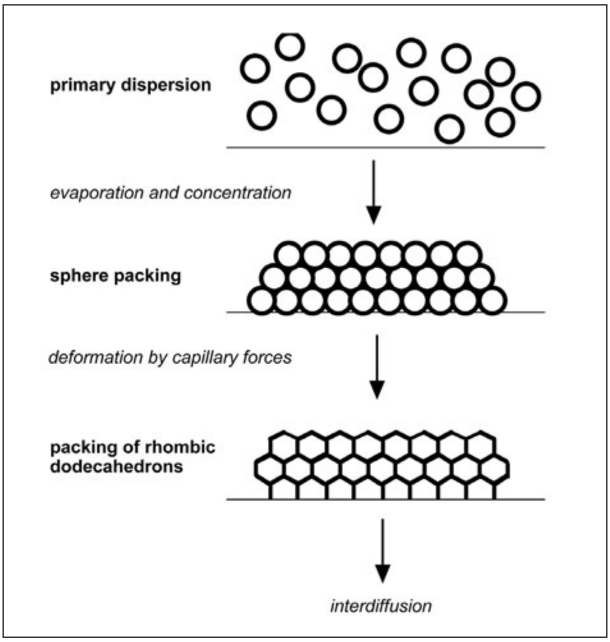


Figure III-2.1: Film formation by primary dispersions

All coatings of primary dispersions are non-crosslinked films and thus are thermoplastic and swellable by solvents.

The coalescence (film formation) of primary dispersion particles only takes place above the minimum film forming temperature (MFFT). Below the MFFT, the poly-mer is in the glassy state and unable to form a film. The MFFT of polymer dispersions is often between -5 and 25 °C; in special applications (latex gloss enamels for industrial uses), the MFFT can be much higher. A low MFFT means that the polymer is soft, and that can lead to poor mechanical film properties. Mostly, the MFFT is slightly lower than the glass temperature (T_g; polymer property) of the disperse polymers [2].

Primary dispersions with an MFFT above 5 °C require external plasticization by adding permanent plasticizers (e.g. phthalates); even better is the addition of coalescing agents (low-volatility organic solvents) as temporary plasticizers. In contrast to permanent plasticizers, coalescing agents leave the film after a certain time and do not cause continuous plasticization.

The requirements for coalescing agents are:

- Optimal dissolving or swelling of the polymer particles
- No influence on the stability of the polymer dispersion

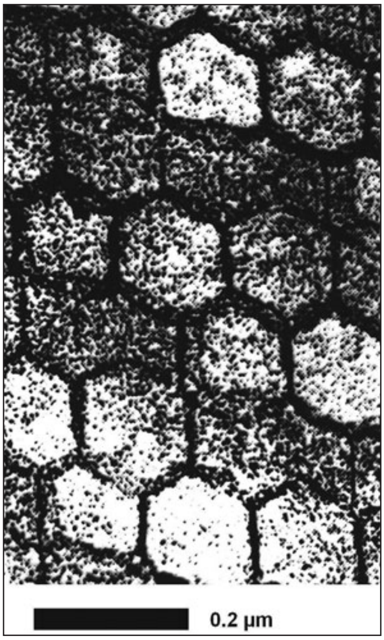


Figure III-2.2: Transmission electron micrograph of a contrasted thin-section of a film obtained from a pure acrylic primary dispersion

Table III-2.3: Examples of important coalescing agents and cosolvents

substance	evaporation number*	solubility in water (rt)
1. coalecing agents		
2,2,4-trimethyl-1,3-pentandiol-1-isobutyrate (Texanol)	5000	0.05 wt.%
butyl glycol acetate	137	1.5 wt.%
butyl diglycol acetate	> 3000	6.5 wt.%
2. cosolvents		
butyl glycol	119	unlimited
butyl diglycol	1200	unlimited
3. others		
1,2-propylene glycol**	1000	unlimited

* diethyl ether = 1

** 1,2-propylene glycol is neither a cosolvent nor a coalescing agent. In latex paints it is used as water retention agent; i.e., it prolongs the "open time". Moreover, it has antifreeze properties.

- Very low solubility in water; i.e. solution in the polymer
- Fast evaporation after film formation
- Odour-free
- Ecologically safe

The difference between cosolvents (Chapter III-1.4.3) and coalescing agents is blurred (Table III-2.3). For example, butyl glycol can act as both cosolvent and coalescing agent.

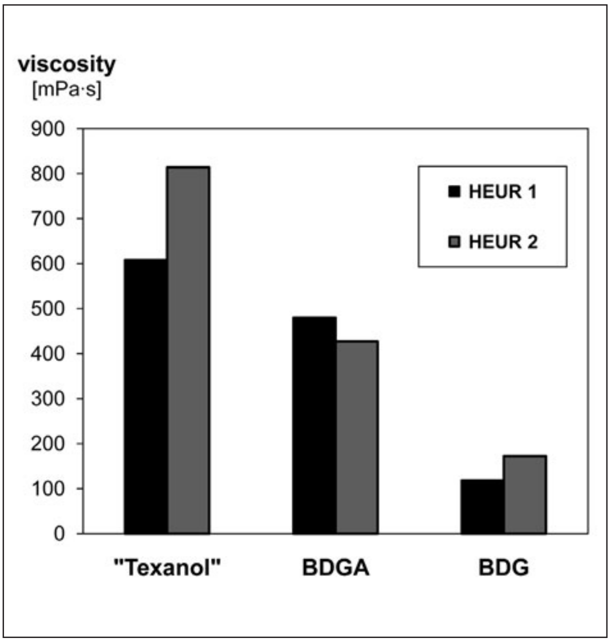


Figure III-2.3: Influence of coalescing agents on the viscosity of latex paints with HEUR additives. Texanol = 2,2,4-trimethyl-1,3-pentanediol-1-isobutyrate (Table III-2.3), BDGA = butyl diglycol acetate (Table III-2.3), BDG = butyl diglycol (Table III-2.3)

White spirit is totally immiscible with water but it can act as coalescing agent, alone or in combination with other solvents (e.g. 1:1 mixture with Texanol).

It should be noted that coalescing agents and cosolvents may affect the viscosity:

- By swelling the polymer particles
- By interacting with rheology modifiers, especially HEUR additives (hydrophobically modified ethylene oxide urethanes) [4, 5]

This influence on the viscosity will now be explained with the aid of some simplified latex paint formulations (Figure III-2.3). The formulation parameters of these white latex paints (all with an equal amount of water) are:

Pigment/binder ratio P/B = 4 : 1

Binder: Fine styrene-acrylate dispersion (Acronal 290 D)
Addition of coalescing agent: 4.0 parts by weight

Rheology modifiers based on polyether-urea-polyurethane (addition: each 1.0 part by weight, 25 wt.% in water/butyl diglycol = 8/2): HEUR 1 and HEUR 2 (Rheolate 255 and 278).

Measurement of the viscosity of the latex paints at low shear shows that the extremely sparingly water-soluble Texanol (Table III-2.3) yields the highest viscosity because it causes extensive swelling of the polymer particles and the HEUR micelles (see [4], Figure III-2.3). The completely water-miscible butyl diglycol (BDG, Table III-2.3) leads to the lowest viscosity because it causes the least swelling of the polymer particles and the HEUR micelles; butyl diglycol is mostly dissolved in the water phase and dilutes the paint. Furthermore, water-miscible cosolvents, such as butyl diglycol, lower the surface tension of water and disturb the micelle (associate) formation of HEUR additives, a fact which also leads to a lowering of viscosity. As expected, the partly water-miscible butyl diglycol acetate (BDGA, Table III-2.3) has a neutral effect (Figure III-2.3).

2.1.2 Latex gloss enamels

As already explained, latex gloss enamels are paints based on polymer dispersions. In contrast to latex paints, latex gloss enamels yield coatings with relatively high gloss. Latex gloss enamels owe their glossiness essentially to three formulation parameters:

Table III-2.4: Formulation of a white latex gloss enamel

pos.	raw material	parts by weight	solids	density [g/cm^3]
01	water	12.8		
02	dispersing agents	0.8		
03	defoamer	0.2		
04	preservative	0.2		
05	AMP-90	0.2		
06	1,2-propylene glycol	4.0		
07	HEUR	2.5		
08	ammonia	0.3		
09	titanium dioxide rutile	21	21.0	4,1
dispersion by dissolver				
10	primary dispersion (47 wt.%)	53	24.9	about 1.2
11	butyl glycol	2.0		
12	methoxy butanol	2.0		
13	HASE	1.0		
sum		100.0	45.9	

pos. 02: dispersing agent based on sodium polyacrylate, e.g. Lopon 890 (45% in water)
pos. 03:defoamer based on hydrocarbons and hydrophobic pyrogenic silica, e.g. Agitan 295 (100 wt.%)
pos. 05 and 08: 2-Amino-2-methyl-1-propanol (AMP-90) and ammonia, amines for adjusting the pH value
pos. 06: water retention agent
pos. 07: hydrophobic modified ethylene oxide urethane, associative rheology modifier, e.g. Borchigel VP 97105 - NT 40 (40% in water)
pos. 10: styrene-acrylate dispersion, 47% in water, particle size about 0.12 µm, MFFT about 11 °C, e.g. Mowilith LDM 7450
pos. 11 und 12: coalescing agents respectively cosolvents
pos. 13: Hydrophobic modified anionic Isoluble/swellable emulsion, associative rheology modifier, e.g. Mowilith VDM 7000, 30% in water, pH 3,0

- The PVC should be as low as possible – for glossy latex gloss enamels, it should be less than 20%.
- The polymer dispersion (mostly pure acrylate) should have a particle size of 0.1 çμm or less.
- Appropriate rheology modifiers for latex gloss enamels should be used, e.g. based on HEUR [4, 5]. HEUR additives have the advantage of not affecting levelling; unlike clays, HEUR additives do not cause matting.

Table III-2.4 shows a formulation for a white latex gloss enamel [9]. As a rule, when latex gloss enamels and latex paints are being produced, the polymer dispersion is added after grinding of the pigment because otherwise coagulation by shear forces may occur during dispersion of the pigment. Pigments and fillers are mostly dispersed with a dissolver.

The characteristic values of the latex gloss enamels are calculated as follows.

Pigment/binder ratio $P/B = 21 : 24.9 = 0.84 : 1$
$PVC = [(21/4.1) : (21/4.1 + 24.9/1.2)] \cdot 100\% = 20\%$

The pigment/binder ratio and the PVC are calculated roughly, without allowance for the additives. As HEUR and HASE additives are polymers, they may be calculated as additional binders.

2.2 Façade coatings

Water is the most important factor in the degradation and corrosion of mineral-based building materials. The water balance (water absorption and desorption) is an important criterion for all building materials. Moreover, water transports harmful salts. Thus, the absorption of moisture is a determinant of the lifetime of construction materials. This means that architectural coatings for exterior façades should have a high water vapour transmission rate as well as low capillary water absorption (resistance to driving rain).

Architectural coatings on façades are attacked chemically, mechanically and biologically from the outside. They are also attacked from the inside by bases, salts and moisture, which come from within the construction material itself. Most problematic of all is an accumulation of moisture in the coating/substrate interface, which is the weak point of the multi-coat system. Therefore, not only is the type of coating important for the protective effect, but also the priming of the substrate.

The main objective of priming is to form a hydrophobic, water-repellent, dry area directly beneath the coating. This lowers absorption by the substrate so much that moisture cannot accumulate in the coating/substrate interface. Furthermore, it stops ingress of driving rain through fine cracks and other damage in the coating, and deactivates cracks in the substrate. For an adequately deep hydrophobic zone in the substrate, it is necessary to use impregnants of sufficient penetrating power.

Impregnants (sealing primers) are low-viscosity, capillary-active formulations for priming absorbent substrates (e.g. concrete, plaster, wood), the purpose being to reduce the absorption of the substrates and to increase their hydrophobicity. A further goal is to strengthen the substrates. Silicone-based impregnants for mineral substrates are also called “hydrophobing agents” [6].

The ecological benefits of aqueous silicone micro-emulsions as hydrophobing impregnants merits special attention [7]. In the past, solvent-borne primers accounted for more than 95% of organic solvents emitted during façade coating.

2.2.1 Latex paints

Low-cost latex paints for interior walls have a PVC > CPVC (sometimes PVC >> CPVC), which leads to porous coatings with a (desirably) high water vapour diffusion (Figure III-2.4); capillary water absorption is also high, but that is not critical for indoor use. Figure III-2.4 shows the typically totally porous structure of a coating in which the PVC >> CPVC (low-cost, indoor latex paint). In high-quality latex paints for façades, by contrast, the PVC < CPVC and that leads to virtually non-porous coatings with low water absorption [8].

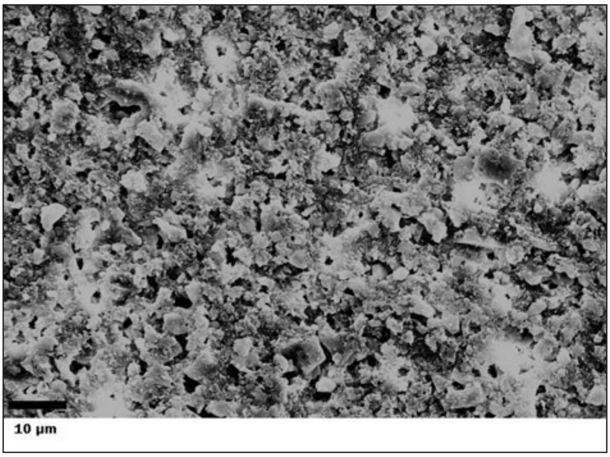


Figure III-2.4: Scanning electron micrograph of the surface of an interior wall coated with a low-cost latex paint

Besides titanium dioxide as white pigment, latex paints contain large amounts of (inexpensive) fillers (Table III-2.5), which are a key factor in the price of latex paints. Colourless solid inorganic substances with refractive indices of less than 1.7 are generally called fillers (extenders), and those with refractive indices greater than 1.7 are said to be white pigments (Table III-2.5).

The hiding power of a white coating is determined by the magnitude of the difference between the refractive indices of binder and pigment or filler; the greater this difference, the greater is the hiding power. Large differences always result in air, which is why colourless fillers (extenders) appear white in powder form. If the PVC is greater than the CPVC, filler/air interfaces form in the coating. For this reason, fillers (extenders) can influence hiding power above the CPVC ("dry-hiding" effect).

Table III-2.5: Refractive indices of some raw materials for paints

substance	refractive index
paint resins (solid)	1.47 to 1.68
fillers (extenders)	1.55 to 1.64
white pigments	
zinc oxide	2.00
zinc sulfide	2.34
zirkonium dioxide	2.40
diamond (for comparison)	2.42
titanium dioxide anatase	2.55
titanium dioxide rutile	2.70
others	
vacuum	1.0000
air	1.0003
water	1.3300

$$\text{refractive index} = \frac{\text{light velocity in vacuum}}{\text{light velocity in the medium}}$$

The ratio of titanium dioxide : filler (extender) is generally:

10 : 90 for interior latex paints (above the CPVC)
40 : 60 for high-quality latex paints for façades (below the CPVC)

Formulations

Two formulations are described below that differ enormously in their PVCs. One is an interior latex paint (PVC >> CPVC) and the other a façade paint (PVC < CPVC). Table III-2.6 shows the formulation for the interior latex paint [9]. A typical feature of highly loaded latex paints is the very different particle sizes of the white pigment (0.25 – 0.3 µm)

Table III-2.6: Formulation of a highly loaded latex paint for interior walls

pos.	raw material	parts by weight	solids	density [g/cm³]
01	water	26.9		
02	dispersing agent	0.7		
03	HEUR (50 wt.%)	0.2	0.1	
04	MHEC	0.3	0.3	
05	defoamer	0.1		
06	NaOH (25 wt.%)	0.1		
07	dipropylene glycol-n-butylether	0.5		
08	preservative	0.2		
09	titanium dioxide rutile	5.7	5.7	4.1
10	calcite	29.7	29.7	2.7
11	chalk	12.5	12.5	2.7
12	PCC	8.0	8.0	2.7
13	talc	9.1	9.1	2.8
14	primary dispersion (53 wt.%)	6.0	3.2	1.2
sum		100.0	68.2	

pos. 02: one may use a combination of two different types, e.g. polyphosphate and polycarboxylate
pos. 03: hydrophobically modified ethylene oxide-urethane, rheology modifier, e.g. Borchigel WN 50 S (50% in water)
pos. 04: methylhydroxyethyl cellulose, rheology modifier, e.g. Walocel XM 30000 PV
pos. 05: for example Nopco 8034 E
pos. 06: for adjusting the pH value
pos. 07: coalescing agent, evaporation number 900
pos. 10: crystalline calcium carbonate, e.g. Omyacarb 5 GU, average particle diameter 5 µm
pos. 11: calcium carbonate, e.g. Omyalite 90, average particle diameter 1 µm
pos. 12: precipitated calcium carbonate, e.g. Socal P2, average particle diameter 0.28 µm
pos. 13: lamellar magnesium silicate hydrate
pos. 14: vinylacetate-ethylene-copolymer, 53% in water, MFFT about 0 °C, T_g about 12 °C, particle size 0.1 bis 0.45 µm, e.g. Mowilith LDM 1871

and of the fillers (Table III-2.6); this “mix” of particle sizes leads to a high packing density and a high CPVC (Chapter I-3.2).

Let us now roughly calculate the characteristic values of this latex paint, excluding the additives.

Pigment/binder ratio P/B = (5.7 + 29.7 + 12.5 + 8 + 9.1) : 3.2 = 65 : 3.2 ≈ 20 : 1

$$\text{PVC} = \frac{5.7 / 4.1 + 29.7 / 2.7 + 12.5 / 2.7 + 8 / 2.7 + 9.1 / 2.8}{5.7 / 4.1 + 29.7 / 2.7 + 12.5 / 2.7 + 8 / 2.7 + 9.1 / 2.8 + 3.2 / 1.2} \cdot 100\% \approx 90\%$$

Titanium dioxide : fillers = 5.7 : 59.3 = 8.8 : 91.2

The low concentration of titanium dioxide is characteristic of inexpensive indoor latex paints having a PVC >> CPVC (“dry-hiding” effect; see above).

Table III-2.7 shows a formulation for a high-quality latex paint for facades [2].

Again, let us now roughly calculate the characteristic values of this latex paint.

Pigment/binder ratio P/B = (15.5 + 17.5 + 5.5) : 18.5 = 38.5 : 18.5 = 2.1 : 1

Table III-2.7: Starting formulation of a high-quality latex paint for façades

pos.	raw material	parts by weight	solids	density [g/cm³]
01	water	13.7		
02	dispersing agent	0.6		
03	ammonia (conc.)	0.2		
04	preservative	0.3		
05	HEC (2% in water)	5.0		
06	HEUR	0.4		
07	defoamer	0.3		
08	white spirit	1.2		
09	butyl diglycol	1.2		
10	propylene glycol	1.6		
11	titanium dioxide rutile	15.5	15.5	4.1
12	calcit	17.5	17.5	2.7
13	talc	5.5	5.5	2.8
14	primary dispersion (50 wt.%)	37.0	18.5	1.2
sum		100.0	57.0	

pos. 02: combination of polyacrylate and polyphosphate
pos. 05: hydroxyethyl cellulose, rheology modifier, e.g. Natrosol 250 HHR
pos. 06: hydrophobically modified ethylene oxide-urethane, rheology modifier, e.g. Collacral PU 85 (24 to 28% in water/butyl diglycol = 4 : 1)
pos. 07: defoamer based on hydrocarbons and hydrophobic pyrogenic silica, e.g. Agitan 280 (100%)
pos. 12: crystalline calcium carbonate, e.g. Omyacarb 5-BG average particle size 5 µm
pos. 13: lamellar magnesium silicate hydrate, average particle size 5 µm
pos. 14: 50% in water, e.g. Acronal 18 D (pure acrylate) particle size about 0.1 µm, MFFT 13 °C

$$\text{PVC} = \frac{15.5 / 4.1 + 17.5 / 2.7 + 5.5 / 2.8}{15.5 / 4.1 + 17.5 / 2.7 + 5.5 / 2.8 + 18.5 / 1.2} \cdot 100\% = 44\%$$

Titanium dioxide : fillers = 15.5 : 23 = 40 : 60

2.2.2 Silicone resin paints

The goal of developing silicone resin paints for façades is to produce coatings that offer a high water vapour transmission rate as well as low capillary water absorption (resistance to driving rain).

The binder for silicone resin paints is an “standard” primary polymer dispersion; a silicone resin emulsion is added to serve as internal hydrophobing agent. As the mixing ratio is not fixed, there are silicone resin paints on the market which contain only a little amount of (expensive) silicone resin. A better name for this type of paint would be ”silicone-modified latex paints”. But the polymer dispersion does have advantages because its pigment binding power is superior to that of silicone resins.

Two parameters have to be taken into account when silicone resin paints are being formulated:

- PVC
  The higher the PVC is above the CPVC, the larger is the volume of the pores in the coating and the higher is the water vapour transmission rate (desirable) and the higher is the capillary water absorption (undesirable).
- Ratio of polymer dispersion : silicone resin emulsion
  The more silicone resin emulsion there is, the lower the level of capillary water absorption and the more expensive is the formulation.

Table III-2.8 shows a starting formulation for a silicone resin paint for façades [5]. Again, typical of highly loaded latex paints is the very different particle sizes of the white pigment (0.25 – 0.3 µm) and of the fillers (Table III-2.8), which gives rise to a high packing density.

Let us now roughly calculate the characteristic values of the silicone resin paint. The silicone resin is not usually calculated as binder.

Pigment/binder ratio P/B = (12.5 + 2 + 10 + 10 +15 + 3) : 6 = 8.8 : 1

$$\text{PVC} = \frac{12.5 / 4.1 + 2 / 2.1 + 10 / 2.7 + 10 / 2.7 + 15 / 2.7 + 3 / 2.8}{12.5 / 4.1 + 2 / 2.1 + 10 / 2.7 + 10 / 2.7 + 15 / 2.7 + 3 / 2.8 + 6 / 1.2} \cdot 100\% = 78\%$$

Table III-2.8: Formulation of silicone resin paint for façades

pos.	raw material	parts by weight	solids	density [g/cm^3]
01	water	25.40		
02	clay	0.30	0.3	
03	defoamer	0.20		
04	preservative	0.15		
05	dispersing agents	0.45		
06	AMP 90	0.10		
07	titanium dioxide rutile (0.25 to 0.3 µm)	12.50	12.5	4.1
08	aluminium silicate (0.035 µm)	2.00	2.0	2.1
09	PCC (0.3 µm)	10.00	10.0	2.7
10	calcit (2.7 µm)	10.00	10.0	2.7
11	calcit (7 µm)	15.00	15.0	2.7
12	mica (27 µm)	3.00	3.0	2.8
dispersion				
13	coalescenting agent	1.00		
14	silicone resin emulsion	7.20	3.6	
15	primary dispersion	12.00	6.0	1.2
16	HEUR	0.70		
sum		100.00	62.4	

Average particle sizes of the fillers in round brackets.
pos. 02: rheology modifier, e.g. Bentone LT
pos. 05: combination of polyphosphate (e.g. Calgon N) and ammonium polyacrylate (e.g. Lopon 886)
pos. 13: Texanol (Table III-2.3)
pos. 14: 50% in water/xylene = 4 : 1, e.g. Tego Phobe 1000
pos. 15: 50% in water, e.g. Acronal 290 D (styrene-acrylate) particle size about 0.1 µm, MFFT 20 °C
pos. 16: hydrophobically modified ethylene oxide-urethane, rheology modifier, e.g. Rheolate 278

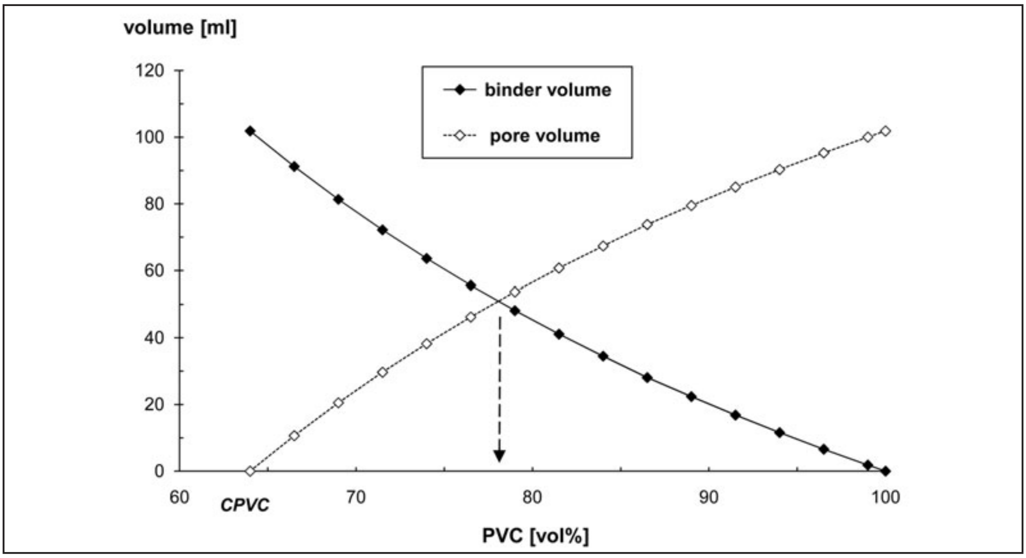


Figure III-2.5: Binder and pore volume of silicone resin paints

In reference [5], a figure of 77% is calculated for the PVC (CPVC = 64%); this comparison shows that the rough PVC calculations used in this book yield adequate results.

Polymer dispersion : silicone resin emulsion = 1 : 0.6 (solids)

Titanium dioxide: fillers = 12.5 : 40 = 24 : 76

Figure III-2.5 explains the porosity of such systems. The optimum PVC for silicone resin paints is determined from the intersection of the curves for the binder and the pore volume [5]. At the intersection, the binder and pore volume are present in equal proportions (each 50 vol.%). This is the optimum PVC. In other words, silicone resin paint coatings are highly porous and allow water vapour to permeate easily. Capillary water absorption is low because of the hydrophobicity of the silicone resin [8]. The scanning electron micrograph in Figure III-2.6 shows the porosity of a façade coating based on silicone resin.

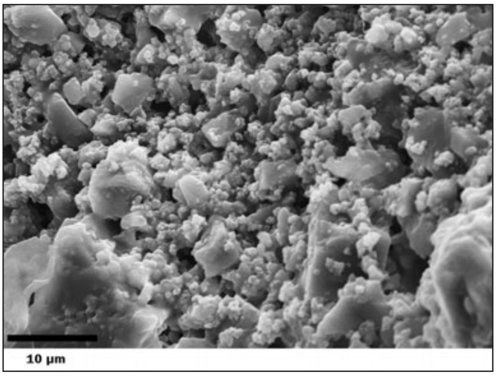


Figure III-2.6: Scanning electron micrograph of a façade coating based on silicone resin paint

2.2.3 Silicate paints (two-components)

Silicate paints (two-components silicate paints, pure silicate paints) are prepared on the building site by stirring together a liquid waterglass solution (fixative) and a ready-made powdery mixture of pigments and fillers (containing powdery additives if necessary). The mixture needs to stand for several hours prior to application. This type of paint was developed by Adolf Keim in 1879; coatings obtained from silicate paints are nothing other than an early type of sol-gel coating.

Because inorganic binders such as waterglass are completely different from organic paint resins, they will now be briefly explained. Waterglasses (alkali silicates) are prepared by baking a mixture of quartz sand (SiO_2) and alkali carbonates (Me_2CO_3) at 1400 - 1500 °C:

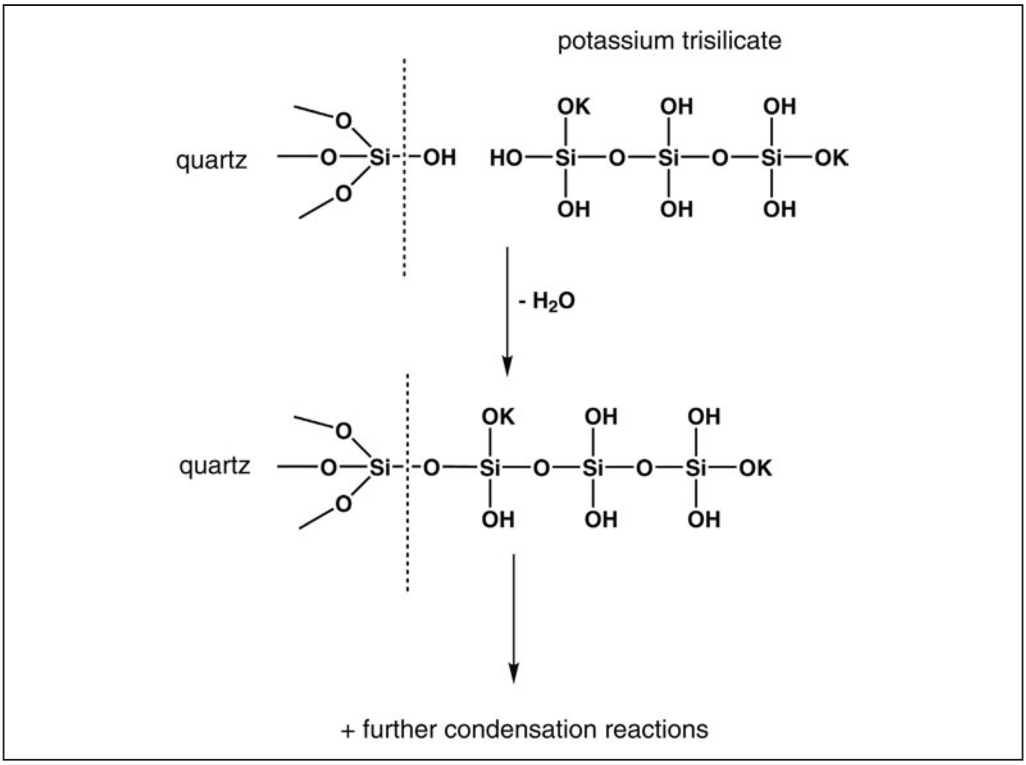


Figure III-2.7: Reaction between potassium trisilicate and quartz (silicification)

$Me_2CO_3 + x\ SiO_2 \rightarrow [Me_2O \cdot x\ SiO_2] + CO_2$

Afterwards, the alkali silicates are dissolved in water at elevated temperatures (sometimes under pressure). The pH of aqueous waterglass solutions is between 10.5 and 13.5, the exact figure depending on the type of waterglass.

Alkali silicates are characterized by

- The ratio $Me_2O : SiO_2$ (see factor x in the equation above)
- The type of alkali metal (Me: Li, Na, K)
- The viscosity of the aqueous solution (the more SiO_2, the higher the molar mass and the higher the viscosity).

Potassium silicate solutions are often used for silicate paints. Aqueous solutions of potassium trisilicate can be described in simple terms by $[K_2O \cdot 3\ SiO_2 \cdot 3\ H_2O]$ (Figure III-2.7). It should be noted that, in aqueous waterglass solutions, there is a dynamic equilibrium between monomeric silicate ions, polysilicate ions and colloidal silica sol.

After the application of silicate paints (and latex silicate paints, see below), chemical curing takes place. All other paints in this chapter (latex gloss enamels, latex paints and silicone resin paints) only dry physically, i.e., without chemical reaction.

The chemical reaction between waterglass and mineral substrates is called silicification and leads to excellent adhesion (Figure III-2.7).

Curing reactions of waterglass (e.g. potassium trisilicate):

a) With carbon dioxide (atmosphere)
$n\ [K_2O \cdot 3\ SiO_2 \cdot 3\ H_2O] + n\ CO_2 \rightarrow [K_2CO_3 \cdot 3\ SiO_2]_n + 3n\ H_2O$ (polycondensation)

b) With green concrete (silicification)
$Ca(OH)_2 + [K_2O \cdot 3\ SiO_2 \cdot 3\ H_2O] + CO_2 \rightarrow [CaO \cdot K_2CO_3 \cdot 3\ SiO_2] + 4\ H_2O$

c) With mineral building materials, inorganic pigments or fillers (silicification); for example, quartz (see also Figure III-2.7)
$SiO_2 + [K_2O \cdot 3\ SiO_2 \cdot 3\ H_2O] + CO_2 \rightarrow [K_2CO_3 \cdot 4\ SiO_2] + 3\ H_2O$
This type of reaction can take place with any solid inorganic substance which has surface hydroxyl groups.

d) Thermosetting (in special industrial coatings)
$n\ [K_2O \cdot 3\ SiO_2 \cdot 3\ H_2O] \rightarrow [K_2CO_3 \cdot 3\ SiO_2]_n + 3n\ H_2O$ (polycondensation)
Polycondensation of waterglass can be catalyzed by acids (e.g. phosphoric acid: H_3PO_4); this leads to two-components or three-components systems.

Waterglass is not film-forming; its coatings are therefore highly porous [8], a fact which promotes water vapour transmission and, unfortunately, capillary water absorption. Silicate coatings are often aftertreated with hydrophobing agents ("external hydrophobising") to reduce their capillary water absorption.

Advantages of silicate paints
+ Adhesion (silicification)
+ Weatherability (light fast)
+ Resistance to chemicals
+ Water vapour transmission
+ Non-flammability
+ Freedom from cosolvents

Disadvantages of silicate paints
- Difficult application
- Two-components system (pot-life must be considered)
- Limited number of shades (only inorganic pigments)
- High capillary water absorption (external hydrophobising necessary)
- Low flexibility

Two-components silicate paints are used especially in the protection of monuments.

2.2.4 Latex silicate paints (one-component)

One-component silicate paints are rendered stable for storage by adding nonsaponifiable polymer dispersions (mostly styrene-acrylate) and a quaternary ammonium compound not specified in detail. Only paints containing less than 5% organic compounds can be called latex silicate paints. By organic compounds is meant the polymer dispersion and all organic additives. As in the case of silicate paints, chemical curing combined with silicification takes place.

Internal hydrophobising of latex silicate paints can be effected by adding hydrophobing agents, e.g. silicone resin emulsions or paraffin waxes.

Table III-2.9 shows a starting formulation for a latex silicate paint [5].

Let us roughly calculate the characteristic values of the latex silicate paint. The binder is an inorganic silicate and an organic styrene-acrylate dispersion.

Pigment/binder ratio P/B = (10 +7.5 +22.5) : (0.15 + 3.25 + 8) = 40 : 11.4 = 3.5 : 1

$$\text{PVC} = \frac{10 / 4.1 + 7.5 / 2.7 + 22.5 / 2.7}{10 / 4.1 + 7.5 / 2.7 + 22.5 / 2.7 + 8.15 / 2 + 3.25 / 1.2} \cdot 100\% = 67\%$$

Titanium dioxide : filler = 10 : 30 = 25 : 75

Figure III-2.8 shows two scanning electron micrographs of a latex silicate coating (for interior use); the microporosity throughout this coating can be seen clearly. This porosity

Table III-2.9: Starting formulation for a latex silicate paint

pos.	raw material	parts by weight	solids	density [g/cm^3]
01	water	15.8		
02	dispersing agent	0.2		
03	clay	0.15	0.15	
04	xanthen	0.15	0.15	
05	potassium silicate-solution (29 wt.%)	0.5	0.15	about 2*
06	titanium dioxide rutile	10.0	10.00	4.1
07	calcit (0.7 µm)	7.5	7.50	2.7
08	dolomite (5 µm)	22.5	22.50	2.7
09	defoamer	0.4		
10	white spirit	1.5		
11	primary dispersion (50 wt.%)	6.5	3.25	1.2*
12	silicate stabilizer	0.5		
13	potassium silicate-solution (29 wt.%)	27.5	8.00	about 2*
14	water	6.8		
sum		100.0	51.70	

** approximate values for dry film densities*
average particle sizes of the fillers in round brackets
pos. 02: combination of tetrapotassium diphosphate (e.g. Calgon TK) and ammonium polyacrylate (e.g. Lopon 886)
pos. 03: rheology modifier, e.g. Bentone LT
pos. 04: polysaccharide, polymeric rheology modifier, e.g. Rhodopol 50 MD
pos. 05 and 13: stabilized potassium silicate solution, 29% in water, e.g. Betolin P 35
pos. 11: Acronal 290 D, Mowilith DM 765 or Acronal DS 6105
pos. 13: 17.5 wt.% in water, e.g. Betolin Quart 15

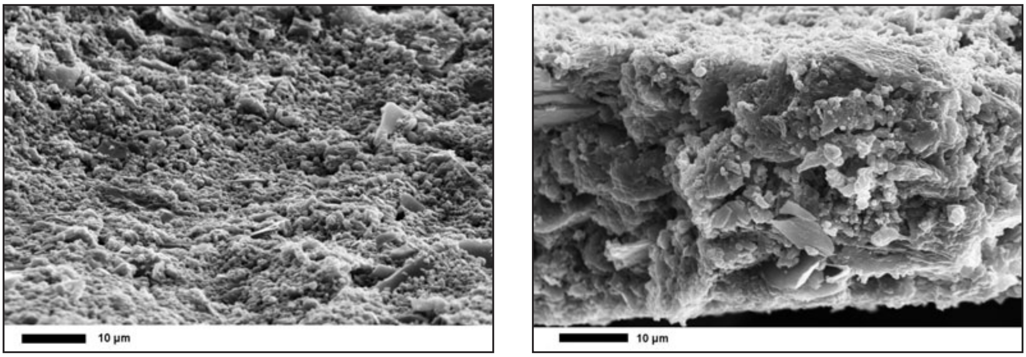


Figure III-2.8: Scanning electron micrographs of a latex silicate coating: left: surface (oblique top view) right: cross-section (fracture) confers a very high water vapour permeability (diffusion-equivalent air layer thickness sd of less than 0.02 metres), which is preferred for interior coatings.

The dependence of the water vapour transmission rate as well as the capillary water absorption on the micro-structure of different types of coatings for façades is detailed in an excellent publication [8], which contains an impressive series of scanning electron micrographs of the various micro-structures.

2.3 References

[1] Z. W. Wicks, F. N. Jones, S. P. Pappas, Organic Coatings – Science and Technology, 2nd ed, Wiley (1999) p. 467
[2] R. Baumstark, M. Schwartz, Water-borne Acrylates, Vincentz Network, 2001
[3] H. Kittel (ed.) Lehrbuch der Lacke and Beschichtungen, Band 2, Pigmente Füllstoffe, Farbstoffe, Verlag W. A. Colomb, 1974
[4] B. Müller, Understanding Additives, Vincentz Network, 2010
[5] H. Dörr, F. Holzinger, Kronos Titandioxid in Dispersionsfarben, 1989
[6] DIN-Term, Beschichtungsstoffe, Vincentz Network, 1st ed., 2001
[7] H. Mayer, Farbe & Lack, 97 (1991) p. 867 ff
[8] P. Grochal, Farbe & Lack 97 (1991) p. 670-675
[9] Starting formulation of Borchers GmbH

3 Water-borne paints that cure at ambient temperatures

3.1 Water-borne paints that cure oxidatively

3.1.1 Water-borne paints based on alkyd resins

As already mentioned in Chapter II-2.1, oxidative-cure requires resins that contain adequate amounts of fatty acids with two or more double bonds. These ingredients are, of course, also necessary for water-borne paints that cure oxidatively. The most important resin group for such paints is that of alkyd resins. There are water-soluble alkyd resins (water-thinnable) and alkyd resin emulsions [1].

A combination of resins that consists of significant amounts of renewable raw materials and water as solvent or dispersing agent is highly appealing from the point of view of environmental protection. But, unfortunately, there are some problems.

Water-soluble or water-thinnable alkyd resins are stabilized by anions. Mostly, these anions are generated by adequate amounts of carboxylic groups from the alkyd resin that are neutralized by amines or ammonia. Since carboxylic groups are only weak bases, the pH values of the neutralized solutions are about 7.5 to 8.2. That is the reason why the ester groups of the alkyd resin can be saponified relatively easily. Paint systems containing such solutions have only limited storage times.

Alkyd resins for solvent-borne paints usually consist of ortho-phthalic esters. But due to the steric effect of the ortho-position of both carboxylic groups, these esters are highly sensitive to saponification. In particular, if phthalic acid in an alkyd resin molecule forms a free carboxylic group at the end of a chain, saponification can take place rapidly. In this case, phthalic acid is cleaved, and the resin molecules lose their anionic stabilization and solubility. Furthermore, other terminal anhydrides on alkyd resin molecules may be cleaved by saponification.

The most important way of avoiding or at least minimising this effect is to select molecular structural elements that are more resistant to saponification. For example, when isophthalic acid is used instead of ortho-phthalic anhydride for the formation of alkyd resins, the solutions of the resins in aqueous phase are much more resistant to saponification [2]. A more specific method is to use trimellitic anhydride and to randomly esterify two of the three potential carboxylic groups to form only one free carboxylic group in a side-chain for neutralization [3]. The resultant water-borne resin solutions are much more resistant to saponification than resins which simply contain added anhydrides.

Furthermore, the use of co-solvents can support stability to saponification. In particular, butyl glycol, due to its molecular structure (see Chapter III-1.4.3), forms solvated alkyd resins in the aqueous phase; more solvent and less water is then present in the colloidal particles. Then, of course, saponification reaction takes place less often. But if the goal of using water-borne paints is to reduce the levels of volatile organic compounds (VOCs), the amount of co-solvents in such systems is limited, too.

Another way of effecting anionic stabilization is to use sulphonic isophthalic acid or its salts. In this case, solubility in water is achieved with smaller amounts of anions of sulphonic groups than of carboxylic groups.

Polyunsaturated fatty acids can undergo addition reactions with maleic anhydride. On addition of polyols or water, these adducts form free carboxylic groups, which may be neutralized with amines or ammonia. Water-borne solutions of resins (alkyd resins, oils) containing such modified adducts are relatively resistant to saponification. The reason is that the carboxylic groups of these adducts are connected via C-C bonds to the polymer chain of the resin molecule. But, commensurate with the amount of added maleic anhydride, there is a loss of double bonds capable of serving as reactive groups for oxidative-cure. Therefore, the resins prepared by this process are preferred for other crosslinking reactions (stoving enamels based on, e.g., maleinised oil; see Chapter III-4.3).

Dispersing heated resins or solution of resins in water by stabilizing them with emulsifiers yields emulsions of oxidative-cure alkyd resins [6]. As there is virtually no water in the dispersed particles, the emulsions are relatively resistant to saponification. The best emulsifiers are those which take part in the crosslinking reaction with oxygen.

There are other resins containing polyunsaturated fatty acid which are relatively resistant to saponification. First, there are polyurethanes prepared from soft segments containing fatty acids (these are basically low-molecular alkyd resins), diisocyanates, and, e.g., dimethylol propionic acid for generating carboxylic groups in a side-chain (see Chapter III-1.3.3.2 and [7]). Second, there are epoxy esters, which contain polyunsaturated fatty acids and also carboxylic groups [8, 9].

As already mentioned in the description of solvent-borne paints (see Chapter II-1.2.3) the oxidative-cure process is accelerated by siccatives. Siccatives are also necessary for optimum formulations of water-borne resins that cure oxidatively. It is important to ensure that the siccatives are mixed effectively and stably with the resins in aqueous phase. The same siccatives can be used as for solvent-borne systems (e.g. metal octoates). These products may be mixed with the resins in organic phase. Some suppliers of water-borne resins suggest adding the siccatives already to the mill base formulation. However, the metal salts might conceivably diffuse from the aqueous phase into the colloidal particles of resins, where they can additionally react with carboxylic groups. But the suppliers of siccatives also offer grades specifically intended for water-borne systems [10]. These products are mainly complex salts of mixed metals (e.g. mixtures of cobalt, zinc and barium or of cobalt, zirconium and calcium). Special siccatives are also commercially available for alkyd emulsions. But also for water-borne coating systems, the cobalt siccatives are going to become replaced by alternatives (e.g. manganese salts, iron complex compounds).

For water-borne systems, it is not normally necessary to use anti-skinning agents.

Co-solvents for oxidative-cure paints are butyl glycol, methoxy propanol, ethoxy propanol, butoxy propanol, and secondary butanol.

Neutralization agents are ammonia (e.g. 25 wt.% solution in water), dimethyl ethanolamine (DMEA), triethyl amine (TEA), and dimethyl amino methylpropanol (DMAMP). Some commercial resins are already neutralized. The addition of amines to resins that are not neutralized has to be calculated stoichiometrically. The method of calculation is presented in Chapter III-1.4. The amines may inhibit the oxidative curing process by reduction effect. Effective drying may take place not only before evaporation of amines.

For water-borne paints, special levelling agents are available. Those preferred are polyether-modified silicone oils and acrylic polymers containing free carboxylic groups.

The water used in the preparation of water-borne paint systems is either distilled or passed through an ion exchanger to be rendered virtually free of electrolytes.

Water-borne alkyd resins are eminently suitable for the preparation of pigment dispersions. The unusual viscosity behaviour of aqueous alkyd resin solutions resins has to be taken into consideration. The viscosity of the mill base has a crucial bearing on the grinding efficiency of pigments as it is influenced not only by the ratio of pigment, resin, and the amount of water, but also by the amount of co-solvent and degree of neutralization. The viscosity may vary during the process. Pigments which are basic may react with the carboxylic groups of resins to form coagulates. Pigments which react as acids require the addition of neutralization agents.

Water-borne paints based on alkyd resins are preferred for corrosion protection primers, for primer surfacers and topcoats in industrial coating systems. They are also suitable for wood and house paints. They emit much lower quantities of organic compounds than conventional solvent-borne paint systems. This reduction is evident from the following example.

Formulation of a water-borne white topcoat

For the white topcoat, a short oil alkyd containing 37 wt.% of a special, polyunsaturated fatty acid is chosen [11]. The delivery form of the alkyd is 75 wt.% in a co-solvent. The acid number of the alkyd resin is 35 to 45 mg KOH/g. For the mill base, the alkyd resin is neutralized with triethyl amine. Besides the alkyd resin and the neutralization agent, the mill base contains titanium dioxide, butyl glycol and ethoxy propanol as additional co-solvents, and deionized water. Siccatives may be added to the mill base. The mill base is ground for 20 minutes on

Table III-3.1: Water-borne white topcoat

pos.	raw material	solids [wt.%]	density [g/cm³]	formulation [wt.%]
pigment dispersion				
01	water thinnable alkyd resin (37% special fatty acids) AN: 35–45, 75% in cosolv.	9.00	1.20	12.00
02	triethyl amine			0.70
03	butyl glycol			1.10
04	ethoxy propanol			1.30
05	deionized water			10.60
06	titanium dioxide, rutil type	26.00	4.10	26.00
07	cobalt siccative (water syst.)			0.10
08	zinc siccative (water syst.)			0.20
completion				
09	water thinnable alkyd resin (37% special fatty acids) AN: 35–45, 75% in cosolv.	12.90	1.20	17.20
10	ammonia (25% in water)			0.50
11	deionized water			30.10
12	levelling additives			0.20
sum		47.90		100.00

pos. 01, 09: Worléesol 07 A, 75% in butyl glycol / sec. Butanol (Worlée)
pos. 04: Ektasolve EP (Eastman)
pos. 06: Tioxide TR 92 (Tioxide)
pos. 07: Servosyn WEB Co 8% (Servo)
pos. 08: Servosyn WEB Zr 10% (Servo)
pos. 12: Worlée Add 327 (Worlée)

a pearl mill. It is then let down by adding the same alkyd resin, but now neutralized with ammonia (25 wt.% in water). A levelling agent is added and the batch is diluted with deionized water. The formulation is presented in Table III-3.1.

The solids content of the water-borne white topcoat is 47.9 wt.%. The paint consists of 9.7 wt.% co-solvents, 0.8 wt.% amines, 0.5 wt.% additives, and 41.1 wt.% water. This composition yields a VOC value of 115 g/l.

$$P/B = 26.0 : 21.9 = 1.2 : 1.0$$

$$PVC = \frac{26.0 / 4.1}{26.0 / 4.1 + 21.9 / 1.2} \cdot 100\% = 26\%$$

The viscosity of the paint is 80 to 90 s (DIN 53211 flow cup 4/20 °C) and the pH value is 8.2 to 8.5.

After application, the white topcoat is initially dried in 45 minutes, while the film is touch-dry after 4 hours and fully dry after 16 hours.

3.1.2 Hybrid systems

So-called hybrid systems for water-borne paints are a combination of primary dispersion and a water-soluble resin. The primary dispersion forms films by physical drying, while the water-soluble resins cure chemically. The combination of the two confers optimum properties on the films. The primary dispersion supports fast initial drying and good stability of films. Co-solvents are not generally needed. Primary dispersions are less suitable for the preparation of pigment dispersions. They do not form dense, glossy films. In contrast, water-soluble resins form dense films of good appearance and gloss. Additionally, they are highly suitable for the production of pigment dispersions. Curing reactions occur much more easily in films made from water-soluble resins than in films formed from primary dispersions. One such curing reaction is the oxidative-cure of water-borne alkyd resins. Film formation by a combination of a water-borne alkyd resin and a primary dispersion can be conceived of as the alkyd resin's filling the spaces between the spherical particles of the primary dispersion. Drying and curing yield a dense film that is relatively resistant to diffusion. Furthermore, the pigments, ground first in the water-soluble resins, are effectively embedded in the film matrix. It is important that the emulsifier of the primary dispersion be compatible with the water-soluble resin, as otherwise coagulation may take place. On the other hand, the co-solvents possibly used with the water-soluble resin must be compatible with the primary dispersion (no coagulation).

Nearly all these combinations require the addition of antifoaming additives.

Hybrid systems are used for fast-drying paints for corrosion protection, paints for general industrial use (primer, primer surfacers and topcoats), for wood and house paints.

Typical formulation for a hybrid system: water-borne, reddish-brown primer for general industrial paints

This example [12] is of a combination of an oxidative-cure water-borne alkyd resin and a styrene-butadiene dispersion. The pigments are selected for corrosion protection and comprise red iron oxide, talcum, calcite, and zinc phosphate. The mill base consists of the pigments and extenders, the greater portion of the alkyd resin, neutralized with ammonia, along with co-solvent, dispersing agent and water. In this example, the siccatives, consisting of a mixture of cobalt and manganese salts, are added to the mill base. Dispersing is carried out on a pearl mill to the required level of fineness. Then the residual amount of alkyd resin, again neutralized with ammonia, and further amounts of co-solvent are added. After addition of an antifoaming agent, the batch is finished with the primary dispersion and more deionized water. Homogenization takes place in a dissolver. Details of the formulation are presented in Table III-3.2.

The ratio of water-soluble alkyd resin to primary dispersion is about 1 : 1.

P/B = 1 : 1

$$\mathrm{PVC} = \frac{3.80/2.8 + 7.70/2.7 + 7.40/3.5 + 6.70/3.9}{3.80/2.8 + 7.70/2.7 + 7.40/3.5 + 6.70/3.9 + 12.53/1.2 + 12.70/1.2} \cdot 100\%$$

PVC = 28%

Table III-3.2: Water-borne reddish brown primer

pos.	raw material	solids [wt.%]	density [g/cm³]	formulation [wt.%]
pigment dispersion				
01	water thinnable alkyd resin (30% special fatty acids AN: 35-45, 75% in co-solvent)	9.00	1.20	12.00
02	ammonia (25% in water)			0.80
03	deionized water			21.00
04	butoxy propanol			1.20
05	talc	3.80	2.80	3.80
06	extender calcite	7.70	2.70	7.70
07	zinc phosphate	7.40	3.50	7.40
08	red iron oxide	6.70	3.90	6.70
09	cobalt siccative, 8% Co			0.25
10	manganese siccative, 9% Mn			0.20
11	wetting agent			0.50
completion				
12	butyl glycol			1.70
13	water thinnable alkyd resin (30% special fatty acids AN: 35-45, 75% in co-solvent)	3.53	1.20	4.70
14	ammonia (25% in water)			0.20
15	antifoam additive			0.25
16	styrene butadiene dispersion 50% in deionized water	12.70	1.20	25.40
17	deionized water			6.20
sum		50.83		100.00

pos. 01, 13: Worléesol 61 A, 75% in butyl glycol / sec. butanol (Worlée)
pos. 04: Dowanol PnB (Dow)
pos. 05: Talkum ST micro (Naintsch)
pos. 06: Millicarb (Omya)
pos. 07: Zinkphophat PZ 20 (SNCZ)
pos. 08: Servosyn WEB Co 8% (Servo)
pos. 09: Servosyn WEB Mn 9% (Servo)
Pos. 11: Hydropalat 535 (BASF-Cognis)
pos. 15: Surfinol 104 E (Air Products)
Pos. 16: Lipaton SB 5521 (Polymer Latex, Evonik Degussa)

The pH value of the primer is 7.2 to 8.0. The solids content is 50.8 wt.%. Co-solvents amount to just 5.9 wt.%. The viscosity is about 140s (DIN 53211 flow cup 4/20 °C). A 100 µm wet film is dust-dry in 20 minutes and tack-free in 45 minutes.

3.2 Two-component, water-borne systems

3.2.1 Two-component, water-borne polyurethane paints

Reaction of polyisocyanates in aqueous systems

As already mentioned in Chapter II-1.3.1, polyisocyanates can react with water. Initially, an unstable intermediate compound, a substituted carbaminic acid, is formed. This immediately decomposes into carbon dioxide and a primary amine. This amine reacts spontaneously with other isocyanate groups to form urea linkages. These reactions are presented in Figure III-3.1.

This reaction proceeds more slowly for the relatively hydrophobic polyisocyanate adducts than for hydroxyl groups or amine groups of partner resins. This statement applies especially to aliphatic and cycloaliphatic polyisocyanate adducts and more particularly for sterically hindered isocyanate groups. All this opens up the possibility of performing isocyanate crosslinking reactions in water-borne systems as well. The reaction takes place preferably at the hydroxyl groups or amine groups of resins. Analytical studies show that hardly any reaction occurs with the carboxylic groups of water-thinnable resins. The most important condition for the reaction is that the two components be mixed efficiently. When polyisocyanate hardeners are added to water-borne systems, they form relatively coarse emulsions. Diffusion processes then lead to smaller particles which will cause the components to be mixed. This affords an opportunity for an effective crosslinking reaction between the resins and the polyisocyanates.

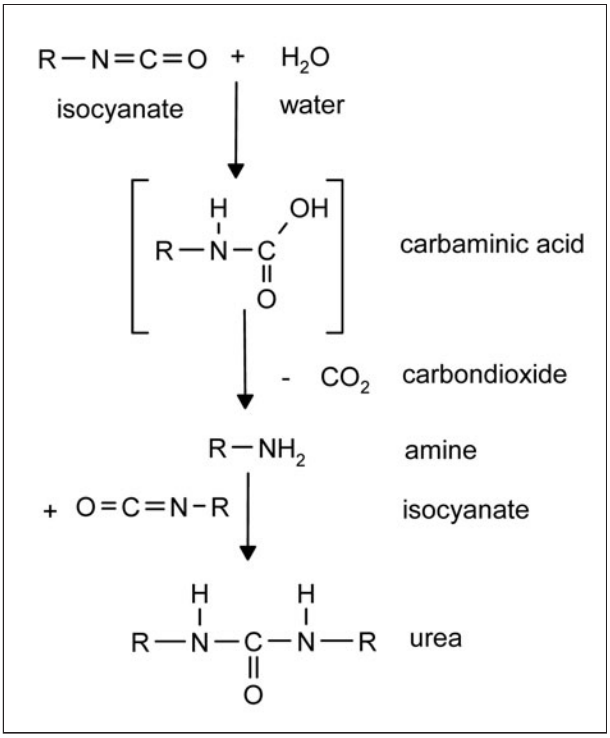


Figure III-3.1: Reaction of isocyanates with water

This can be boosted in two ways. First, the polyisocyanates can be rendered more hydrophilic. Usually, this modification takes the form of a reaction between some of the isocyanate groups and monofunctional polyethylene glycol ether. Of course, some of the isocyanate groups are no longer available for the crosslinking reaction. Admixing polyisocyanates modified in this manner leads immediately to the formation of small particles, which have a greater probability of combining with the colloidal particles of hydroxyl resins. This is the preferred method for producing crosslinked films that feature optimum levelling and gloss.

The second way is to use hydrophobic polyisocyanates, but to accelerate the diffusion rate. This will happen if the viscosity of the polyisocyanates is very low [14]. Polyisocyanate adducts with a narrow molar mass distribution have a low viscosity. Furthermore, allophanate adducts are much less viscous than the other adducts. It is also possible and sense to choose those polyisocyanate adducts which are suitable for solvent-borne systems and to dissolve the products in relatively polar solvents. These solutions can serve as hardeners for two-component, water-borne systems. Of course, the solvents may not bear free hydroxyl groups, as these would be able to react with the isocyanates. Recommended solvents are esters (e.g. butyl acetate), diethers and ether esters of propylene glycol (e.g. methoxy propyl acetate) and ether acetates of ethylene glycol (containing higher alcohols, e.g. butyl glycol acetate). These solvents are only sparingly water-soluble, but the goal is to lower the viscosity of the hardener solution to accelerate the diffusion rate of hardener and resin in aqueous phase. After the diffusion process, the anionically stabilized particles can carry not only the hydrophobic hardener but also the sparingly water-soluble solvents. Of course, after that the solvents have to evaporate.

Additionally, it is possible to add emulsifiers to the polyisocyanate adducts. But although these emulsifiers may support the dispersion process in water, they must not hinder the diffusion process of hardener and resin particles in the aqueous phase.

Reaction partners for polyisocyanates in water-borne paints

The type of hydroxyl resin also greatly influences the mixing efficiency of the polyisocyanate adduct in aqueous phase. Resins with low molar masses that form colloidal solutions are easy to mix. Resins with high molar masses that are more likely to form dispersed particles in aqueous phase have to be mixed more intensively. Water-soluble polyester resins are easier to mix than water-borne acrylic resins. And, of course, secondary dispersions are easier to mix with polyisocyanates in aqueous phase than primary dispersions.

As already mentioned above, for two-component polyurethane systems, the delivery form of hydroxyl resins must not contain solvents with hydroxyl groups. Tertiary amines (e.g. triethyl amine) are preferred that do not contain other functional groups, e.g. hydroxyl groups or NH groups, for neutralization.

Although the choice of resins and hardeners is aimed at improving efficient homogenization, reactions between isocyanate and water must be taken into account. Polyisocyanates that are nonpolar, have a low viscosity and less reactive will react only to a slight extent with water. Polyisocyanate adducts which have been rendered hydrophilic are easier to bring into the aqueous phase, but will react in significant amounts with water.

But with solvent-borne systems, too, there are reactions between isocyanate groups and atmospheric moisture (see Chapter II-1.3.1.1 and [12]). In all cases, the formation of urea linkages does not influence the film properties as negatively as might be expected at first. If it is expected that higher amounts of isocyanates will react with water, or if this has been established by analytical methods, it make sense to choose an excess of hardener. Then the ratio of isocyanate to hydroxyl groups can be 1.2 to 1.5 : 1.0 (for calculation method, see Chapter II-1.3.1.5).

Application of two-component, water-borne polyurethane paints

Like solvent-borne systems, ready mixed water-borne polyurethane paints have a limited pot-life. Unlike the case for solvent-borne systems, the viscosity does not increase simply with elapsed time. Sometimes, the viscosity is observed to drop initially. The reason for this is the formation of denser particles in the aqueous phase during reaction. If problems arise with levelling problems and loss of appearance during application, the pot-life is limited.

Thus, suppliers of two-component, water-borne polyurethane systems should define the pot-life very precisely and provide this information to customers. It should not be forgotten, of course, that the temperature has a significant influence on the pot-life.

It is also possible to catalyse the isocyanate reaction in water-borne systems. Special metal complex compounds are commercially available. Adding catalysts will shorten the pot-life. Tertiary amines can serve as catalysts, but they must evaporate during curing.

Film properties of two-component, water-borne polyurethanes are nearly on a par with those of two-component, solvent-borne polyurethanes. They are notable for excellent chemical resistance and weather resistance if aliphatic or cycloaliphatic polyisocyanate adducts are chosen. Emissions of organic compounds (VOC) are significantly lower than in the case of solvent-borne products. Thus, application fields are those requiring high-performance coatings and low emissions.

But, as already mentioned, the main problem is the procedure for mixing the base component and the hardener in the aqueous phase. If the batch approach is used for preparing two-component, water-borne paints, a mechanical stirrer for ensuring homogeneous mixtures must be employed. Provided that the pot-life of the mixture is also taken into consideration, there are no further problems. This is why two-component, water-borne paints have found widespread acceptance in general industrial coatings technology.

The problems remain, though, in the case of continuous application with central paint storage, e.g. automotive OEM coatings application. Static mixing equipment is not adequate for effective mixing of such systems. Special mixing equipment needs to be installed, e.g. a jet stream dispersing machine [15]. The use of such equipment will require retrofits to available equipment and appropriate capital investment. Additional problems can be caused by cycle times and film forming conditions. Automotive OEM paints have restricted flash-off times and, of course, the film formation takes place in a stoving process. Under these conditions and due to the special properties of water (see Chapter III-1.1), the water-borne paints may cause problems in the form of blisters or other film defects. In such cases, it is necessary to employ relatively high amounts of co-solvents and to use specific additives to eliminate the defects.

There are also problems with the use of two-component, water-borne paints for automotive repair coatings. In Europe, most repair shops use two-component, solvent-borne paints. The expense of mixing such paints is relatively low. However, the application of two-component, water-borne paints incurs much more expense. This is why two-component, water-borne paints are still not widespread in repair shops there.

Formulation example: Two-component, water-borne polyurethane primer

The following example of a two-component, water-borne polyurethane primer is suitable for general industrial coatings. The formulation is described in Table III-3.3.

The chosen resin [16] for the base component is a water-borne acrylic resin dispersion (45 wt.% solids) with a hydroxyl content of 3.2% (calculated on solids), which is a suitable binder for the mill base. The hardener is a solution of a low-viscosity HDI trimer (NCO-content 23.0%, calculated on solids). The pigments for the mill base are titanium dioxide and yellow iron oxide and the extenders are barium sulphate and talcum. The functional pigments are mica (for passive corrosion protection) and zinc phosphate (for active corrosion protection). Additionally, the mill base contains the following: antifoam agent, dispersing additive and corrosion protection additive. The remaining quantity of the acrylic resin dispersion is used for letting down. Additives for completing the batch are a wetting agent for the surface (in the case of metals) and a thickener.

The stoichiometric ratio for crosslinking is to be NCO : OH = 1.5 : 1.

Table III-3.3: Water-borne two-component polyurethane primer for general industry coatings

pos.	raw material	solids [wt.%]	density [g/cm³]	formulation [wt.%]
pigment dispersion				
01	acrylic dispersion (45% in deionized water) OH-content 3.2% on solids	9.8	1.2	21.8
02	deionized water			7.8
03	antifoam additive			0.6
04	dispersing agent			0.5
05	titanium dioxide	9.9	4.1	9.9
06	talc	2.3	2.7	2.3
07	barium sulphate	10.4	4.3	10.4
08	mica	6.9	2.7	6.9
09	zinc phosphate	11.6	3.5	11.6
10	yellow iron oxide	3.8	3.9	3.8
11	anti corrosive agent	0.4		0.4
completion				
12	acrylic dispersion (45% in deionized water) OH-content 3.2% on solids	10.0		22.3
13	wetting agent			0.4
14	thickener (10% in deionized water)	0.1		1.3
sum		65.2		100.0
hardener				
15	low viscous HDI-trimer 100%, NCO 23.0%	59.0	1.2	59.0
16	butyl acetate			31.1
17	butyl glykol acetate			10.0
sum		59.0		100.0

mixing ratio 100 : 17,3 or 85,3 : 14,7
pos. 01, 12: Setalux 6520 AQ-45 (Nuplex)
pos. 03: Foammaster (BASF Cognis)
pos. 04: Disperse Aid W 22 (Daniel Products)
pos. 05: Kronos 2059 (Kronos Int.)
pos. 06: Talkum AT extra (Norwegian Talc S/A)
pos. 07: Blanc fixe micro (Sachtleben)
pos. 08: Plastorit Naintsch micro (Naintsch)
pos. 09: Delaphos 2 (ISC Alloys)
pos. 10: Bayferrox 3910 (Bayer)
pos. 11: Forbest 600 (Lucas Meyer)
pos. 13: Byk 348 (Altana Byk)
pos. 14: Viscalex HV 30 (BASF Swiss, Ciba Specialties)
pos. 15: Desmodur N 3600 (Bayer)

The following equations show how the isocyanate base value is calculated for the combination of acrylic resin (OH content 3.2%) and polyisocyanate (NCO content 23.0%).

$$\text{NCO base value} = \frac{\text{OH-\%} \cdot M_{\text{NCO}} \cdot 100}{\text{NCO-\%} \cdot M_{\text{KOH}}} = \frac{3.2 \cdot 42 \cdot 100}{23 \cdot 17} = 34.4\ \text{g}/100\ \text{g acrylic resin}$$

$$m_{\text{hardener}} = \frac{\text{NCO-base value} \cdot m_{\text{acrylic resin}} \cdot \text{crosslinking ratio}}{\text{solids}_{\text{hardener}}} = 17.3\ \text{parts by weight}$$

The base component of the primer consists of 19.8 wt.% (solids) acrylic resin. Due to the specified crosslinking ratio, 10.2 parts (solids) polyisocyanate is required. Since the hardener consists of 59% polyisocyanate, the resultant quantity of hardener is 17.3 parts hardener per 100 parts base component.

After mixing of the two components, the solids content of the mixture is 64 wt.%. For application, the mixture is thinned with deionized water to a viscosity of 50 s (DIN 53211 flow cup 4/23 °C). The solids content for application is then 56 wt.%.

The ratio of pigment to binder in the film, and the PVC are calculated with the aid of the following equations:

$$P/B = 1.6 : 1$$

$$\mathrm{PVC} = \frac{9.9/4.1 + 2.3/2.7 + 10.4/4.3 + 6.9/2.7 + 11.6/3.5 + 3.8/3.9}{9.9/4.1 + 2.3/2.7 + 10.4/4.3 + 6.9/2.7 + 11.6/3.5 + 3.8/3.9 + 19.8/1.2 + 10.2/1.2} \cdot 100\%$$

$$\mathrm{PVC} = 33\%$$

After application, the primer cures at room temperature.

3.2.2 Water-borne two-components epoxy paints

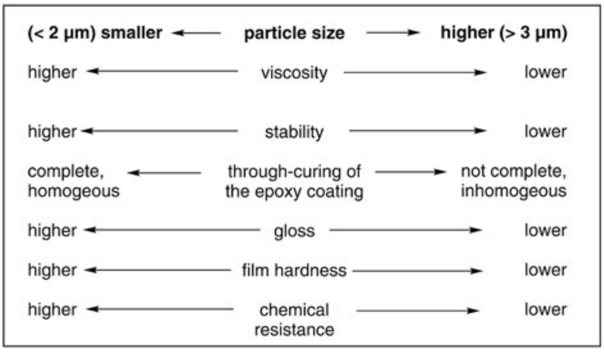
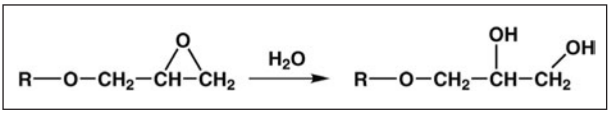


Figure III-3.2: Influence of the particle size on the properties of epoxy emulsions and coatings



$$R{-}O{-}CH_2{-}\overset{O}{CH{-}CH_2} \xrightarrow{H_2O} R{-}O{-}CH_2{-}\overset{OH}{CH}{-}CH_2{-}OH$$

Figure III-3.3: Hydrolysis of epoxy resins

In water-borne two-components epoxy paints, the base component (epoxy resin) as well as the hardener (polyamines) can be pigmented and diluted with water. As with all other water-borne paint systems, the pigments and fillers should have the lowest-possible content of soluble salts (electrolytes).

For the most part, liquid, emulsifiable epoxy resins are used, although solid epoxy resins can also be dispersed in water. The emulsifiability of an epoxy resin is controlled by its viscosity; high-viscosity resins are difficult to emulsify [17]. Furthermore, the stability of an epoxy resin emulsion depends on the viscosity; medium viscosities confer maximum stability on epoxy resin emulsions. The particle (droplet) size of an emulsion greatly determines the properties of the epoxy resin emulsion and epoxy coating. Also important are the type and concentration of the emulsifier; e.g. high concentrations of very hydrophilic emulsifiers lead to emulsions of small particle size. Fine epoxy emulsions have a better range of properties than coarse emulsions [17] (Figure III-3.2).

The storage stability of epoxy emulsions is limited because slow hydrolysis to glycols may occur [18] (Figure III-3.3).

Emulsification of epoxy resins is carried out by phase inversion (Figure III-3.4). First, water is emulsified in epoxy resin (w/o emulsion); with increasing addition of water, phase inversion occurs to produce the desired emulsion of epoxy resin in water (o/w emulsion).

At the phase inversion point, the viscosity is a maximum (Figure III-3.5). At this point, the particle size of aqueous epoxy emulsions (o/w emulsions) can be influenced by varying the shear force and shearing time.

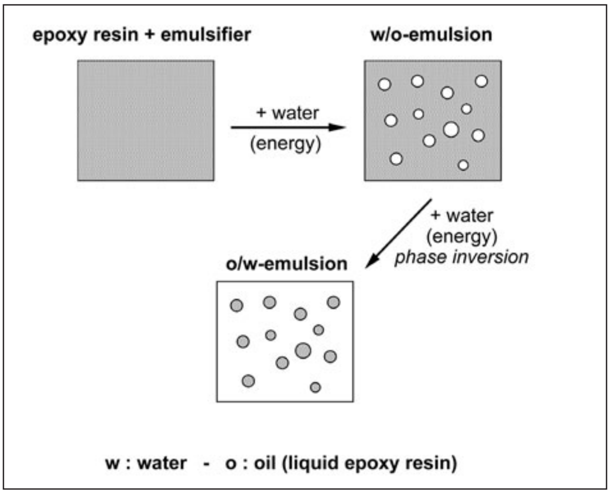


Figure III-3.4: Emulsification of liquid epoxy resins by phase inversion

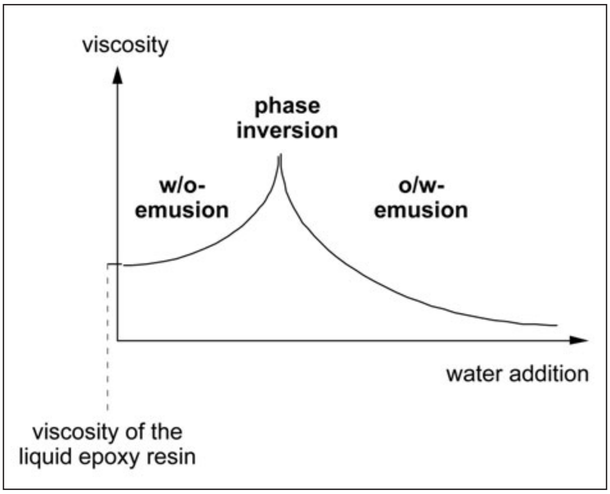


Figure III-3.5: Simplified diagram of the change in viscosity during emulsification of liquid epoxy resins by phase inversion

Emulsification of liquid epoxy resins is explained below [19]. The starting point is a liquid epoxy resin that contains emulsifier (100% solids), has an epoxy value of 0.53 and has an average epoxy equivalent mass of 189; see also the formulation in Table III-3.4 below. This epoxy resin is mixed with water in the ratio 6 : 1 and stirred for 10 to 15 min with the aid of a dissolver at about 6m/s peripheral speed to produce a pasty substance. This w/o emulsion (85 wt.%) can be diluted during stirring by adding portions of water. The outcome is a stable o/w emulsion with an average particle size of 1.2 µm (Figure III-3.6 curve 0).

If a hardener is added to this epoxy resin emulsion, the particle size decreases slightly (average particle size about 0.7 µm; Figure III-3.6, curve 1). The hardener is an amine (50% in water) with an NH-equivalent mass of about 335 (calculated on the solution) [19]. After standing for 6 hours, the emulsion's average particle size has increased to 5 µm because of the crosslinking reaction (Figure III-3.6, curve 2); the viscosity has not changed significantly.

With solvent-borne two-components epoxy systems, however, addition of the hardener causes the viscosity to increase steadily as far as gelation because of the crosslinking reaction. The end of the pot-life is therefore detected easily. In water-borne two-components epoxy systems, the crosslinking reaction takes place inside the emulsion droplets (microgel formation) and so the viscosity does not rise; this means that the viscosity cannot be used to detect the end of the pot-life.

During the crosslinking reaction in the epoxy emulsion droplets, the minimum film forming temperature MFFT (or Tg) of the epoxy resin increases and the emulsion is converted into a dispersion. If the MFFT of the epoxy dispersion particles rises above the application temperature, film formation is insufficient and the gloss decreases (Figure III-3.7). In water-borne two-components epoxy systems, the pot-life is determined indirectly by

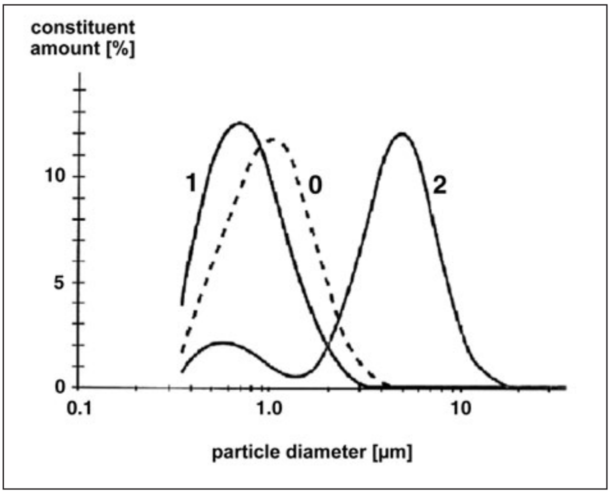


Figure III-3.6: Particle size distributions of an epoxy resin emulsion
0: Epoxy resin emulsion
1: Epoxy resin emulsion and hardener directly after addition of the hardener
2: Epoxy resin emulsion and hardener after 6 hours

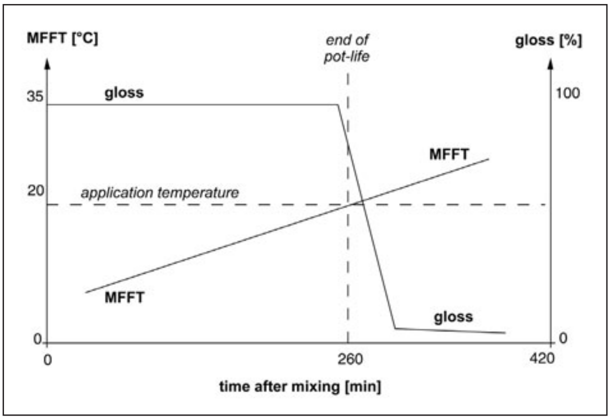


Figure III-3.7: Simplified diagram of the dependence of the MFFT and gloss on the time elapsed after addition of hardener to a water-borne epoxy resin

measuring the gloss of the coatings; if too much crosslinking occurs, the gloss decreases [4]. A 10% drop in gloss indicates the end of the pot-life (Figure III-3.7).

Figure III-3.8 is an example from the lab showing gloss versus time after mixing of three water-borne, two-components epoxy topcoats (one base component mixed with three different hardeners). The influence of the various hardeners on pot-life is obvious (Figure III-3.8). In practice, determining the pot-life via the decrease of gloss can sometimes be difficult because primers exhibit very low gloss due to the high level of pigmentation; so, a significant drop in gloss cannot be observed. For this reason, topcoats are shown in Figure III-3.8 (high initial gloss due to low pigmentation).

It should be noted that certain combinations of water-borne epoxy resins and hardeners may also lead to gelation (just as in the case of solvent-borne systems).

Epoxy resin emulsions or dispersions and amine hardeners do not crosslink homogeneously. After both components have been mixed, the hardener diffuses into the epoxy resin emulsion droplets and crosslinking starts at the droplet surface (Figure III-3.9). The more extensively the particle surface is crosslinked, the more slowly the hardener diffuses into the particles. As a consequence, only about 80% of the functional groups react with each other [20]. In contrast to epoxy groups, unreacted amino groups are hydrophilic and lower the water resistance of coatings. Therefore, it is often the case that less than the stoichiometric quantity of hardener is added to water-borne two-components epoxy paints (see formulation in Table III-3.5 below).

Generally, water accelerates the reaction between epoxy resins and amines because it is a protic and highly polar solvent. This is why the pot-life of water-borne systems is shorter than that of solvent-borne two-components epoxy paints [18]. Another consequence is that crosslinking in a dry film is slower than in aqueous medium [20].

Epoxy-reactive surfactants

Because of their interface, the small epoxy emulsion droplets need plenty of emulsifier. Generally, polar emulsifiers lower the water resistance of coatings. To this end, epoxy-reactive surfactants (ERS) are used. ERS react during curing with amine hardeners to become part of the crosslinked network. As a result, they lose their emulsifying and hydrophilic properties. The synthesis of epoxy-reactive surfactants starts with polyoxyalkylene monoamines "Jeffamines", Figure III-3.10) [21].

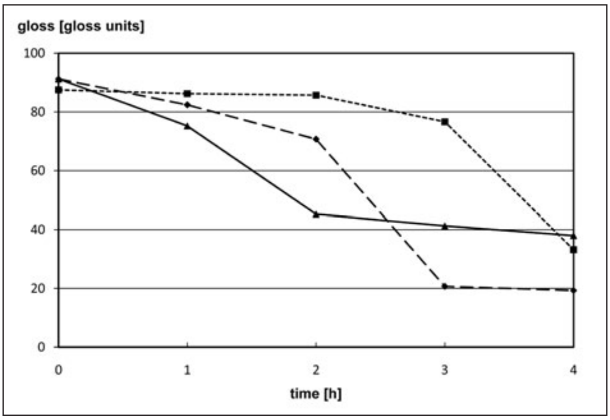


Figure III-3.8: Gloss (60°) versus time after mixing of three water-borne, two-components epoxy topcoats (one base component mixed with three different hardeners)

These polyoxyalkylene monoamines are made to react with an excess of a liquid bisphenol A-epoxy resin (epoxy equivalent mass 188, epoxy value 0.53) [21]. It may be concluded from the data for the epoxy resin that it consists predominantly of bisphenol A-diglycidyl ether (epoxy equi-valent mass 170, epoxy value 0.59, Figure III-3.11).

Put simply, this reaction may described as the reaction between 2 moles bisphenol A-diglycidyl ether and 1 mole (mono)amine-terminated polyether to yield an amphiphilic molecule, the epoxy-reactive surfactant (Figure III-3.12). This is a nonionic emulsifier and its two epoxy groups can react with amine hardeners.

These epoxy-reactive surfactants are synthesized in situ, i.e., in a large excess of epoxy resin. The reaction between 100 parts by weight of liquid epoxy resin (epoxy equivalent mass 188) and 10 parts by weight Jeffamine M-1000 or M-2070 (Figure III-3.12) at 125 °C (under nitrogen) leads after one hour to a conversion rate of more than 95% for the primary to the tertiary amine (Figure III-3.12). Thus, self-emulsifying epoxy resins with good film forming properties are obtained [21].

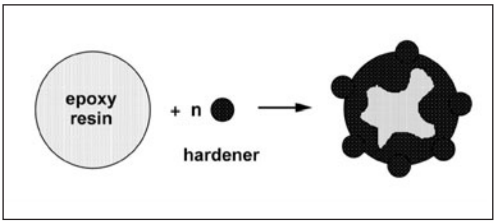
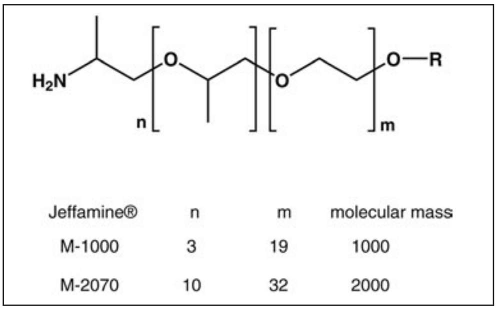


Figure III-3.9: Simplified diagram of the reaction between a single epoxy resin emulsion droplet and amine hardeners

Formulations

Generally, disperse resin systems, such as epoxy emulsions and epoxy dispersions, exhibit worse pigment wetting than dis-



Jeffamine®	n	m	molecular mass
M-1000	3	19	1000
M-2070	10	32	2000

Figure III-3.10: Polyoxyalkylene monoamines

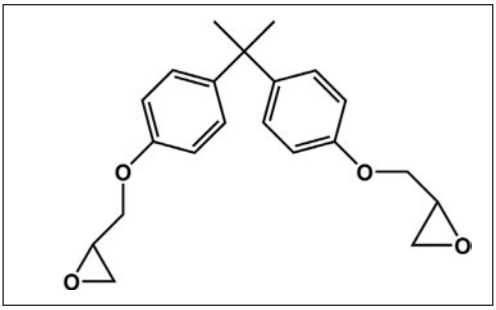


Figure III-3.11: Bisphenol A - diglycidyl ether

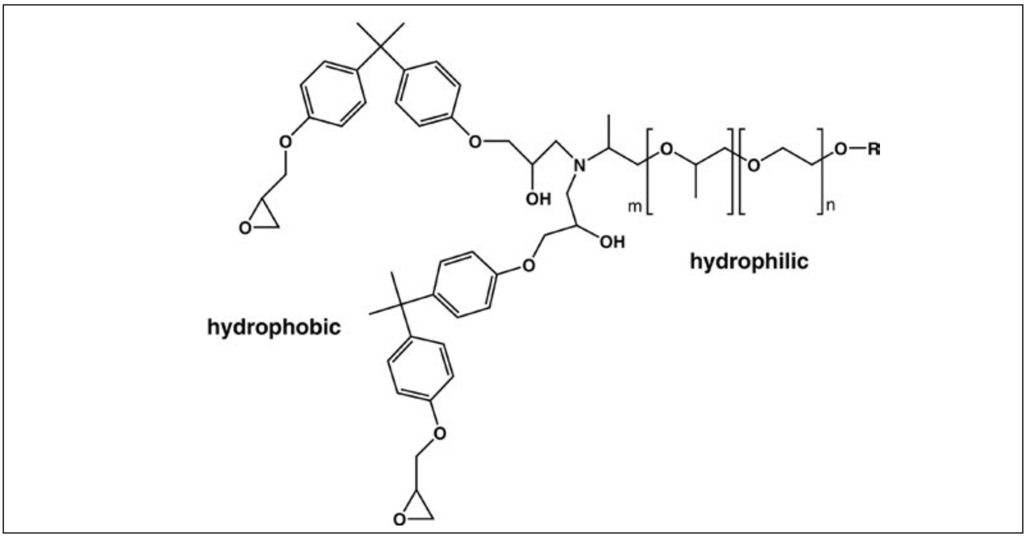


Figure III-3.12: Simplified diagram of epoxy-reactive surfactants

solved resins, such as amine hardeners. Thus, pigments can also be ground in amine hardeners. Table III-3.4 shows such a formulation based on an epoxy emulsion in which the pigments are ground in the hardener.

The characteristic values of the formulation (Table III-3.4) are calculated as follows.

P/B = (17.7 +17.8) : (19 + 10.5) = 35.5 : 29.5 = 1.2 : 1

Table III-3.4: Formulation of a water-borne two-components paint based on an epoxy resin emulsion

pos.	**raw material**	**parts by weight**	**solids**	**density [g/cm³]**
A-component				
01	polyaminoamide adduct	21.0	10.5	1.2*
02	red iron oxide	17.7	17.7	5.0
03	barium sulphate	17.8	17.8	4.1
04	butyl glycol	2.0		
05	rheology modifier	0.5		
06	defoamer	0.2		
07	water	12.4		
B-component				
08	epoxy resin emulsion	28.4	19.0	1.2*
sum		100.0	65.0	

** crosslinked*

pos. 01: hardener, 50% in water, NH-equivalentmass 210 (solution), e.g. Merginamid A155/2 (Hobum Oleochemicals)

pos. 02: red pigment, e.g. Bayferrox 140

pos. 03: filler, e.g. Blanc fixe N

pos. 05: HEUR-additive, e.g. Borchigel L 75N

pos. 06: for example Byk 020

pos. 08: liquid epoxy resin (+emulsifier), 67% emulsified in water, epoxy equivalent mass 189 (solids), epoxy value 0.53 (solids), e.g. Araldite PZ 756/67 (Huntsman)

$$\text{PVC} = \frac{17.7\,/\,5 + 17.8\,/\,4.1}{17.7\,/\,5 + 17.8\,/\,4.1 + 29.5\,/\,1.2} \cdot 100\% = 24\%$$

Ratio hardener/epoxy resin:

g hardener (solution)/100g epoxy resin (solid) =
NH-equivalent mass · epoxy value = 210 · 0.53 = 111.3

In other words, 21.1 g hardener/19 g solid epoxy resin; therefore the reaction is approximately stoichiometric.

Not only epoxy resin emulsions, but also appropriate epoxy resin dispersions can be used. (Table III-3.5) [22].

The characteristic values of the formulation (Table III-3.5) are calculated as follows.

P/B = (5 +5.8 +8.5 +9.2) : (28 + 5.7) = 28.5 : 33.7= 0.85 : 1

$$\text{PVC} = \frac{5\,/\,2.7 + 5.8\,/\,5 + 8.5\,/\,4.3 + 9.2\,/\,3}{5\,/\,2.7 + 5.8\,/\,5 + 8.5\,/\,4.3 + 9.2\,/\,3 + 33.7\,/\,1.2} \cdot 100\% = 21.5\%$$

Hardener addition (solution)/100 g epoxy resin (solid) = 225 · 0.18 = 40.5

Hardener addition (solution)/28 g epoxy resin (solid) = 40.5 · 0.28 = 11.3; i.e., 16% less hardener than the stoichiometric amount is added in the formulation (Table III-3.5).

As pointed out above, often only 80 to 90% of the stoichiometric hardener amount is added to water-borne two-components epoxy paints to improve the water resistance and the corrosion protection of these coatings [20].

Table III-3.5: Starting formulation for a water-borne primer based on an epoxy resin dispersion

pos.	raw material	parts by weight	solids	density [g/cm³]
base component (A-component)				
01	epoxy resin dispersion (56 wt.%)	50.0	28.0	1.2
02	red iron oxide	5.8	5.8	5.0
03	talc	5.0	5.0	2.7
04	baryte	8.5	8.5	4.3
05	zinc phosphate	9.2	9.2	3.0
06	anticorrosion additive	0.9		
07	defoamer	0.6		
08	water	20.0		
sum		100.0	56.5	
hardener (B-component)				
09	amine adduct	9.5	5.7	1.2

pos. 01: 56% in water + 7% ethoxy propanol, epoxy equivalent mass 540 to 560 (solids), average epoxy value 0.18 (solids), e.g. Waterpoxy 1455 (Cognis)
pos. 02: red pigment
pos. 03 und 04: fillers
pos. 05: active anticorrosion pigment
pos. 06: zinc salt of an organic nitrogen compound, active substance content 46 to 48%, e.g. Alcophor 827
pos. 07: e.g. Foamaster TCX
pos. 09: 60% in water, NH-equivalent mass 225 (solution), e.g. Waterpoxy 751

A comparison of the epoxy equivalent mass of the liquid epoxy resin (Table III-3.4) with the epoxy equivalent mass of the epoxy resin dispersion (Table III-3.5) shows that the epoxy equivalent mass of the dispersion is three times as high. This means that the epoxy resin dispersion contains only one third of the epoxy groups of the liquid resin. The crosslink density of coatings made with the dispersion is therefore much lower. Because of the higher epoxy equivalent mass, the epoxy resin dispersion has a higher molar mass and is able to dry physically. Consequently, coatings made with the epoxy dispersion become tack-free in a shorter time [20]. The crosslinking reaction of epoxy resin dispersions is slower because the (larger) molecules are less mobile than epoxy emulsions.

Typical applications for water-borne two-components epoxy paints are coatings on mineral substrates (e.g. concrete, brickwork); even wet mineral substrates can be coated. A further application is that of anticorrosion primers for steel.

3.3 References

[1] H. Kittel, K. D. Ledwoch (editor), Lehrbuch der Lacke und Beschichtungen, Vol. 3, Bindemittel für wasserverdünnbare Systeme, Chapter 3.1.3.1.1; S. Hirzel Stuttgart Leipzig 2001

[2] E. T. Turpin: Hydrolysis of Water-Dispersible Resins, J. Paint Techn. 602, 40 (1975)

[3] R. Wayne: Studies on the Esterification of Trimellitic Anhydride, J. Coat. Techn. 55 Nb. 702, 57 (1983)

[4] T. Kou, W. W. Blount, K. M. Moody: Water dispersible Polyester Resins for Surface Coatings, Polym. Sc. and Eng., Vol. 66, Proceedings 1992, p. 168

[5] H. Kittel, K. D. Ledwoch (editor), Lehrbuch der Lacke und Beschichtungen, Vol. 3, Bindemittel für wasserverdünnbare Systeme, Chapter 3.1.3.1.2; S. Hirzel Stuttgart Leipzig 2001

[6] Commercial products, in O. Lückert: Karsten – Lackrohstofftabellen, 10th Edition, Chapter 2.2.6, Publisher Vincentz Network, Hannover, 2000

[7] Int. Min. & Chem. Corp. (Publication): A Complete Guide to DMPA Brand of Dimethylolpropionic Acid (1986)

[8] Patent DE 3 219 413 of Cytec Surface Specialties Vianova

[9] H. Wagner, H. F. Sarx: Lackkunstharze, S 193; Carl Hanser, München, 1971

[10] Commercial products, in O. Lückert: Karsten – Lackrohstofftabellen, 10th Edition, Chapter 36, Publisher Vincentz Network, Hannover, 2000

[11] Formulation guideline Nb. 177/1, Worlée

[12] Formulation guideline Nb. 468/1, Worlée

[13] L. Kahl, M. Bock, E. Jürgens, H. J. Laas: Wässrige 2K-PUR-Klarlacke für die Automobilerstlackierung, Farbe & Lack 102, 3 (1996), p. 88

[14] W. Kubitza: Wässrige Zweikomponenten-Polyurethan-Reaktivsysteme, Farbe & Lack, 97, 4 (1991), p. 201

[15] Patent DE 3 829 5897 of Bayer AG (1990)

[16] Nuplex, Resin Specialties, Formulation guideline REC 99020

[17] A. Wegmann, Phänomen Farbe, Nr. 11 (1996) p. 22-25, “Struktur/Eigenschaftsbeziehungen in wasserbasierenden Epoxidharz-Emulsionen”

[18] A. Wegmann, Phänomen Farbe, Nr. 5 (1998) p. 34-40, “Wasserbasierte 2K-Epoxidharz/Amin-Beschichtungssysteme”

[19] Publication of Vantico Company (today Huntsman): “Wasser – die alternative Lösung”, 1996

[20] C. Godau, “Wasserverdünnbare Epoxidharze und Spezialhärter für den Korrosionsschutz” in “Korrosionsschutz mit wässrigen Lacksystemen” (Editor J.-P. Schik), Expert-Publisher, Renningen-Malmsheim 1997

[21] Publication of Huntsman Company: “The Jeffamine Polyoxyalkyleneamines” and “Water-Reducible Epoxy Coatings via Epoxy Resin Modification with Jeffamine MATP‘s – In situ Epoxy Reactive Surfactant”

[22] V. Foglianisi et al., Welt der Farben, Nr. 11 (1999) S. 10-13, “Wässrige Epoxidharzsysteme”

4 Water-borne stoving enamels

4.1 Guidelines for water-borne stoving enamels

The industrial use of water-borne stoving enamels started in the early 1950s [1]. In the 1960s, the most important water-borne stoving paints were anionic electrodeposition primers (EDPs) [2]. At the end of the 1970s, cationic electrodeposition primers replaced the anionic EDPs [3] (and see Chapter III-4.4).

Water-borne primer surfacers and topcoats were surprisingly late newcomers in the coatings industry. The reason was mainly the problem of effective evaporation of water in the first part of the stoving process. Due to the special physical behaviour of water used as dispersing agent (see Chapter III-1.1), there is the risk of blistering (popping) and other film defects. Although the problem still exists, it can be compensated with special additives, or co-solvents, which influence the evaporation process, and by varying the evaporation conditions, e.g. introducing temperature steps during flash-off and final stoving. Nevertheless, since the principal goal is to eliminate emissions of volatile organic compounds, the use, and more particular, the quantity of co-solvents are restricted. Thus, the issue of emissions reduction has created competition between water-borne paints and so-called high-solids, which also contain reduced amounts of solvent. Moreover, the requisite evaporation and stoving conditions for water-borne paint must fit in with the processing steps of industrial production-line application.

The resins selected for water-borne stoving enamels belong to the same classes as used in solvent-borne paints. Resins containing hydroxyl groups for water-borne stoving enamels are mainly alkyd resins, saturated polyesters, acrylic resins and further polyurethanes, epoxy esters, butadiene oils modified with maleic anhydride and polyols, and maleinised oils. Crosslinkers for these resins are amino resins, phenolic resins, and blocked polyisocyanates. Most of these systems contain anionic stabilization for water compatibility. Neutralization agents are ammonia and amines. There are only a few products that are water-soluble without the need for neutralization. On the other hand, there are products which are stabilized with cations in aqueous phase, such as modified epoxy resins and special acrylic resins. These resin types require volatile organic acids for neutralization. Due to the content of acids, the cationically stabilized systems require higher temperatures for film forming than their anionically stabilized counterparts. Therefore, they are suitable for paint formulations that allow relatively high stoving temperatures, e.g. cationic electrodeposition primers for automotive OEM (original equipment manufacturing).

Since, like solvent-borne systems, nearly all water-borne stoving enamels consist of two-component (e.g. hydroxyl resin and crosslinker), it is important that the two components be mixed efficiently. As water-borne systems, unlike organic solutions, are more likely to be colloidal, the components have to be mixed by diffusion processes. The optimum situation here is if the components come together as the paint is being mixed. However, it is still necessary to ensure that the storage stability is still guaranteed. Chemical reactions may occur between the components, leading to an increase in molar masses. The possibility of this is greater than in solvent-borne systems if the local concentration of functional groups is higher in the colloidal particles of water-borne systems. Such pre-reactions may cause problems during film forming, e.g. restricted levelling or loss of gloss.

The aforementioned diffusion processes are helpful for combining ionically stabilized resins with other components that are not water-soluble or dilutable. If such components are incorporated into the colloidal particles of ionically stabilized resins, the ionic part of the stabilization may be able to effectively carry the non-water-compatible parts.

4.2 Water-borne stoving enamels based on amino resins

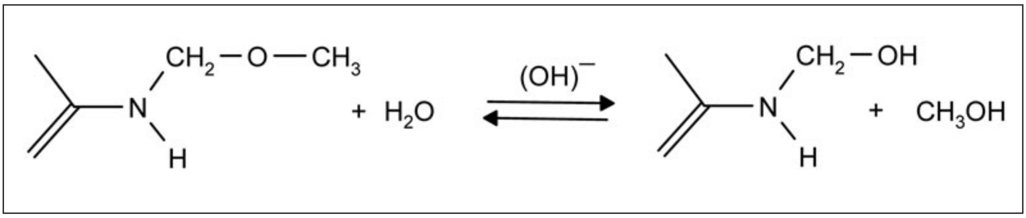


Figure III-4.1: Hydrolysis of amino resins

Selecting amino resins

As already mentioned in Chapter 2.2.1, Part II, amino resins that are either not etherified or etherified with methanol are water-soluble as such, or at least water-dilutable. Since the non-etherified resins have no adequate storage stability and are not compatible with many other resins, the methanol-etherified types are preferred for water-borne paints. The most important types of amino resins belong to the group of melamine resins [4 to 7]. The highly etherified types, which consist of residue imino groups, are more water-soluble than the highly methylolated, fully etherified types (HMMM resins). However, the latter are easily brought into aqueous phase with co-solvents or with anionically stabilized resins.

Melamine resins can hydrolyse in aqueous phase. The hydrolysis of imino grades takes place under basic and acidic conditions as well. The reaction mechanism is presented in Figure III-4.1 [9].

The free methylol groups generated by hydrolysis of imino grades are more reactive than the etherified methylol groups. Pre-reactions are possible and storage stability is limited. Combinations of anionically stabilized resins containing hydroxyl groups and HMMM resins are much more stable under basic conditions. As the melamine resins for water-borne paints mainly have low molar masses, they mix easily with hydroxyl resins and diffuse into the colloidal particles very well. Due to the unusual pseudoplastic behaviour of the viscosity of the systems, more intensive mixing is required .

Examples of commercial products of HMMM resins are: Luwipal 066 (BASF), Cymel 303 (Cytec), Maprenal MF 900 (Ineos).

Examples of methanol etherified imino grades are: Luwipal 072 (BASF), Cymel 327 (Cytec), Maprenal MF 927 (Ineos).

Combination resins for water-borne stoving enamels

The most important partners for melamine crosslinkers in water-borne paints are alkyd resins, saturated polyester resins, and acrylic resins. These all contain hydroxyl and carboxyl groups. The carboxyl groups are neutralized by amines to become water-soluble or water-thinnable. The resins have relatively low molar masses, so there is the possibility of effective mixing with crosslinkers by diffusion in the aqueous phase, yielding optimum crosslinking reactions.

As already mentioned in Chapter 3.2, alkyd resins and saturated polyester resins have to be modified such that they are optimally resistant to saponification. This property is achieved by selecting molecular structural elements that form esters which are relatively resistant to saponification. Other important parameters for stability are molar masses and the type and content of functional groups (acid number, hydroxyl number). Additionally, the choice of neutralization agent and the type and quantity of co-solvent can assist in protecting the ester groups against saponification. All these influences can thus be exploited to enable all the positive properties of alkyd resins and polyesters in water-borne stoving enamels to be used.

Alkyd resins in water-borne paints therefore confer optimum wetting of pigments and substrate surfaces, their films are highly glossy and have an excellent appearance. The resins are used in water-borne topcoats, one-coat paints, and primers.

In water-borne paints, saturated polyesters confer optimum balance of hardness and flexibility. They are therefore preferred for primer surfacers and basecoats.

Acrylic resins are notable for having greater saponification stability than alkyd and polyester resins. Due to their large, linear but coiled molecules, acrylic resins have relatively dense colloidal particles. The colloidal particles of acrylic resins in aqueous phase have more the appearance of dispersions than of solutions, especially if the molar masses of the acrylics are high. In such cases, the efficiency of mixing with crosslinkers is limited, and that leads to lower crosslinking efficiency. Water-borne acrylic resins are used in topcoats, clear coats, and basecoats.

Hybrid systems

Combinations of water-thinnable resins with primary dispersions that form films only by physical drying are suitable for special applications. Such resin combinations are called hybrid systems, and are distinguished by rapid film formation. They are therefore used for paints that have to achieve rapid physical drying, e.g. water-borne basecoats for the two-coat process, where the clear coat is applied over the basecoat without separate stoving in between.

Neutralization agents

The carboxyl groups of resins for water-borne paints have to be neutralized by amines. The most common product for stoving enamels is N,N-dimethylethanolamine (DMEA). Other suitable products are 2-amino-2-methylpropanol (AMP) [9] (see Chapter 1.4.2) and di-isoproanolamine (DIPA). Since triethylamine (TEA) is classified in the German TA-Luft regulation as a class 1 air pollutant, the use of the amine is restricted. Amines containing hydroxyl groups (alkanolamines) have the advantage not only of acting as neutralization agents, but also of having the properties of co-solvents. Suitable pH values after neutralization are between 7.5 and 8.5. In this regard, the degree of neutralization is 0.75 to 1.00 moles of amine per carboxyl group. Although hydrolysis may take place at this low concentration of protons, there is the advantage that reactions of functional groups on melamine resins (start of co-crosslinking or self-crosslinking) are widely restricted. Amines as neutralization agents have to evaporate effectively during stoving. Their evaporation rate is influenced not only by the vapour pressure at the given temperature, but also by the basic strength of the amine and its interaction with the anion. Sometimes lower vapour pressures bring about advantages as regards application behaviour and film forming.

Co-solvents for water-borne stoving enamels

Suitable co-solvents for water-borne stoving enamels are alcohols, glycol ethers, and glycol ether esters (see Chapter 1.4.3). It must be remembered that the ester groups of co-solvents may saponify at the given pH values. The hitherto commonly used N-methylpyrrolidone is now classified as harmful and should no longer be considered. In addition, the methyl and ethyl ethers of ethylene glycol and their acetates are classified as teratogenic and are no longer considered. Butyl glycol (monobutyl ether of ethylene glycol) is the most important co-solvent for this group of water-borne paints. Due to the molecular structure of butyl glycol (polar and nonpolar part of the molecule, see comments in Chapter 1.4.3), the co-solvent supports the stability of colloidal solutions. Additionally, use of butyl glycol enhances gloss and levelling during film formation. In water-borne solutions of resins, the butyl glycol is distributed more in the colloidal particles and less in the mobile phase. This leads to lower amounts of water in the colloidal particles, which decreases the saponification reaction. At the end of the evaporation process, the colloidal particles with butyl glycol are in the state of an organic solution. This avoids blistering and confers optimum gloss and levelling. The monoethers of propylene glycol are classified as toxicologically harmless, but lag behind butyl glycol when it comes to application. Solvents that are more hydrophilic than butyl glycol are distributed mainly in the mobile phase (aqueous phase). They only support the film forming properties if their evaporation rate is relatively high. But non-water-soluble solvents, e.g. higher alcohols, esters and aromatic hydrocarbons, can also be added in small amounts to water-borne systems. These solvents are thought to diffuse almost completely into the colloidal phase where they are then borne by the ionically stabilized resins. They can benefit diffusion processes, help to avoid foam and blistering and support levelling. Figure III-4.2 shows the distribution of different co-solvents between colloidal particles and the aqueous phase.

Mixing ratios and crosslinking

The same rules apply to the mixing ratios of the resins containing hydroxyl and carboxyl groups and amino resins (particularly melamine resins) used in water-borne systems as

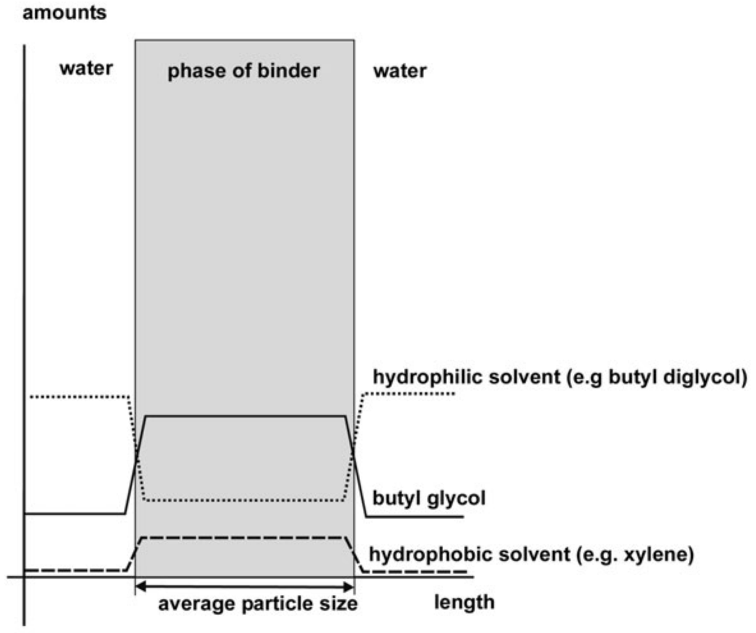


Figure III-4.2: Distribution of co-solvents in water-borne resin solutions apply to solvent-borne systems. The ratios can vary from 65 : 35 to 85 : 15. Since mainly the HMMM resins, which have relatively low molar masses and a high content of functional groups, are preferred for water-borne paints, the preferred ratios are lower amounts of melamine resin, e.g. 75 : 27 to 85 : 15 (resin containing hydroxyl groups versus HMMM resin). If the stoving temperatures are below 160 °C, only the hydroxyl groups will react with functional groups of melamine resins. However, self-crosslinking of melamine resin will also take place. The carboxyl groups will remain in the film and, as they are less hydrophilic than carboxylic anions, they do not significantly influence sensitivity to humidity. However, the crosslinking has to be perfect. Carboxyl groups act as catalysts for the reactions of functional groups of melamine resins. As the content of carboxyl groups in resins for water-borne paints is significantly higher than in resins for solvent-borne systems, the reactions are accelerated to a greater extent. Therefore, HMMM resins crosslink effectively in water-borne systems at much lower temperatures than in solvent-borne systems. In other cases, storage stability has to be monitored carefully.

Acid catalysts

In most cases, there is no need to use catalysts for crosslinking melamine resins as the usually high content of carboxyl groups is adequate for effective crosslinking. However, if the stoving temperature is low, it is possible to accelerate the reaction rate with catalysts. For this, it makes sense to use the water-soluble amine salts of compounds containing sulphonic, phosphoric or carboxylic groups. The products are mainly commercially available in alcohol solution [10]. The suppliers of such acid catalysts offer products that contain, in addition to strong acid groups, hydrophobic molecule parts, which confer excellent compatibility with resin molecules. Besides p-toluene sulphonic acid, dodecyl benzene sulphonic acid, naphthalene sulphonic acid and naphthalene disulphonic acid [11] are preferred. Neutralization agents for the acids are DMEA, TEA, AMP, morpholine and substituted oxazolidines. However, solutions of the free acids are also suitable; with these, it is necessary to add more neutralization agents to the whole paint formulation. As the pH values are sufficiently high, there is no restriction on storage stability. Figure III-4.3 shows examples of amine salts of sulphonic acids.

Film properties

As already mentioned, amino resins in water-borne paints react by self-crosslinking in addition to co-crosslinking. Depending on the type of melamine resin, the mass ratios of hydroxyl resin and the stoving conditions, the amount of self-crosslinking can be higher than in solvent-borne paints. The resultant film properties reflect this. The same trends

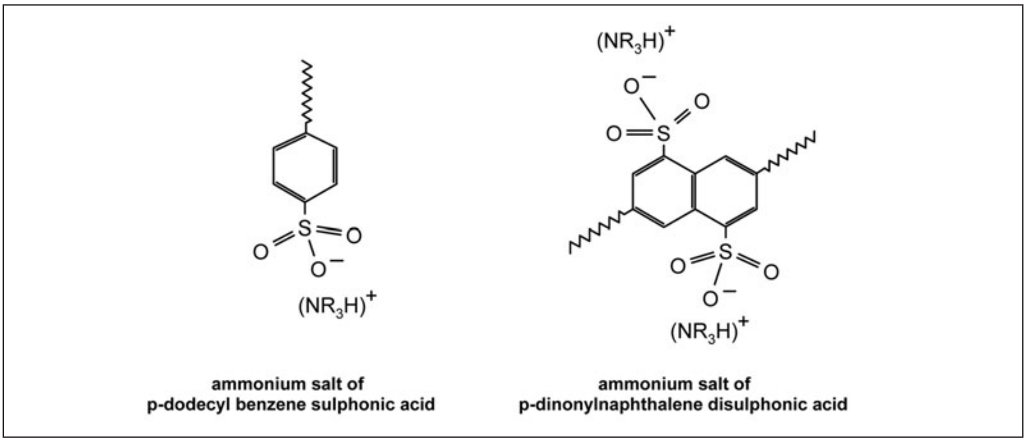


Figure III-4.3: Amine salts of acid catalysts described for solvent-borne systems (see Chapter II-2.2) apply. Self-crosslinking promotes hardness and solvent resistance, while co-crosslinking promotes flexibility, chemical resistance and weather resistance.

Additives

Many of the additives used in solvent-borne paints are also suitable for water-borne systems. However, the suppliers of additives offer products that are developed and produced specifically for water-borne paints [12]. Due to their surfactant-like structures, anionically stabilized resins have excellent inherent wetting properties for pigments and substrates. Nevertheless, special wetting agents for water-borne paints are available. Water-borne systems need additives, such as antifoam agents and corrosion inhibitors, which are not necessary for solvent-borne paints.

Formulation examples: Water-borne stoving primer for general industrial use

Resins chosen for a water-borne stoving primer for general industrial use are [13] a water-thinnable, short oil alkyd containing 29 wt.% unsaturated, vegetable fatty acid and a reactive melamine resin, partly etherified with iso-butanol. The pigment colorants are titanium dioxide and yellow iron oxide and black iron oxide. The functional pigments are two types of talcum of different particle size and a corrosion protection pigment. The neutralization agent is DMEA. The co-solvent is butyl glycol. Additionally, the formulation consists of an antifoam agent and an anti-skinning additive. Details of the formulation are presented in Table III-4.1.

Table III-4.1: Grey water-borne stoving primer for general industry application

pos.	raw material	solids [wt.%]	density [g/cm³]	formulation [wt.%]
pigment dispersion				
01	short-oil alkyd (70% in methoxy propanol)	20.86	1.2	29.80
02	dimethyl ethanolamine			1.80
03	titanium dioxide	4.80	4.1	4.80
04	talc (6.7 µm)	6.50	2.7	6.50
05	talc (0.85 µm)	6.50	2.7	6.50
06	aluminium triphosphate	3.10	3.5	3.10
07	yellow iron oxide	1.50	4.0	1.50
08	black iron oxide	0.20	4.7	0.20
09	antifoam agent			0.05
10	anti-skinning agent			0.05
11	butylglycol			2.60
12	deionized water			6.50
completion				
13	melamine resin (70% in iso-butanol)	5.25	1.5	7.50
14	deionized water			29.10
sum				100.00

pos. 01: Setal 146 SS-70 (70% in methoxy propanol, Nuplex)
pos. 03: Ti-Pure 900 (DuPont)
pos. 04: Microfill HC 3 (IMI)
pos. 05: Micro-Talc AT extra (Norwegian Talc)
pos. 06: K-White 84 (Bromhead & Denison)
pos. 07: Eisenoxidgelb 930 (Bayer)
pos. 08: Eisenoxidschwarz 318 M (Bayer)
pos. 09: Agitan 218 (Münzing Chemie)
pos. 10: Exskin 2 (Condea Servo BV)
pos. 13: Setamin MS-15 IB-70 (70% in iso-butanol, Nuplex)

The mill base for the water-borne primer consists of the organic alkyd resin solution, neutralization agent, pigments and extenders, co-solvent and a portion of deionized water. The dispersion process is started in a dissolver, followed by a stirrer mill, and continued to a fineness of 15 µm (Hegmann measurement). The melamine resin and the remaining larger portion of deionized water are added. The finished primer has a 48.8 wt.% solids content and is delivered with a viscosity of 140 s (DIN 53211 flow cup 4/20 °C). If necessary, the pH value has to be adjusted to 8.5 by adding extra DMEA.

P/B = 0,88 : 1

$$\text{PVC} = \frac{4.8 / 4.1 + 6.5 / 2.7 + 6.5 / 2.7 + 3.1 / 3.5 + 1.5 / 4.7 + 0.2 / 4.7}{4.8/4.1 + 6.5/2.6 + 6.5/2.7 + 3.1/3.5 + 1.5/4.7 + 0.2/4.7 + 20.9/1.2 + 5.3/1.3} \cdot 100\%$$

PVC = 25.4%

For spray application, the primer is thinned with deionized water until the viscosity is 30 s (DIN 53211 flow cup 4/23 °C). Steel panels, pre-treated with zinc phosphate, are the substrate for application. Flash-off is performed after spraying. The stoving conditions are 30 min at 130 °C. Target film thickness is 30 µm dry film.

Water-borne metallic basecoat for automotive OEM

The choice of resins for the water-borne basecoat[14] produces a combination of two saturated polyesters with melamine resin and a thermoplastic acrylic polymer dispersion. One of the polyesters is needed for the preparation of aluminium paste. The acrylic dispersion confers pseudoplastic viscosity on the basecoat. The aluminium pigment is pre-treated for use in

Table III-4.2: Water-borne metallic basecoat for automotive OEM

pos.	raw material	solids [wt.%]	density [g/cm³]	formulation [wt.%]
A. resin combination				
01	acrylic dispersion (24% in deionized water)	11.52	1.20	48.00
02	melamine resin (80% in deionized water)	3.76	1.50	4.70
03	butyl glycol			4.10
04	deionized water			25.50
05	DMEA (10% in deionized water)			1.00
B. aluminium slurry				
06	aluminium pigment (pre-treated, 65%)	2.44	2.70	3.75
07	butyl glycol			3.30
08	saturated polyester (60% in butyl glycol)	1.89	1.20	3.15
09	DMEA (100%)			0.10
completion				
10	saturated polyester (26% in deionized water/BG)	1.66	1.20	6.40
sum		21.27		100.00

pos. 01: Setalux 6802 AQ-24 (24% in deionized water, Nuplex)
pos. 02: Setamine MS 155 AQ-80 (80% in deionized water, Nuplex)
pos. 06: Hydrolac WHH 8154 (65%, Altana Eckardt)
pos. 08: Setal 6306 SS-60 (60% in butyl glycol, Nuplex)
pos. 10: Setal 6407 SQ 26 (26% in deionized water/butyl glycol, Nuplex)

water-borne systems. The neutralization agent is DMEA and the co-solvent is butyl glycol. Details of the formulation are presented in Table III-4.2.

The first step in preparing the basecoat is to take the acrylic dispersion and gradually and carefully add melamine resin, butyl glycol, deionized water and a portion of the neutralization agent, with intensive stirring. The particles of the acrylic dispersion will swell, and so confer the rheological behaviour on the basecoat. The aluminium slurry is produced separately by mixing the aluminium paste with the special polyester solution and the other portion of DMEA. The aluminium slurry is admixed to the first resin combination. Finally, the basecoat is completed by adding the second already water-borne polyester solution. The pH value is adjusted to 7.8 with DMEA and needs to be checked after 16h and adjusted, if necessary.

The basecoat has a solids content of 21.3 wt.%, 10.5 wt.% co-solvent, 0.2 wt.% DMEA and 68.0 wt.% water.

Ratio of polyester/melamine resin = 48 : 52

P/B = 0.13 : 1

For application, the basecoat is thinned with deionized water until the viscosity is 28 s (DIN 53211 flow cup 4/23 °C). The basecoat is applied by spraying on a panel coated with primer surfacer. The flash-off conditions are 2 minutes at room temperature, followed by 8 minutes at 80 °C. The film thickness is 14 μm (dry film). After cooling, the basecoat is convered by spraying of a two-component, solvent-borne clear coat. Flash-off of the clear coat takes 2 minutes at room temperature, ahead of stoving for 20 minutes at 140 °C.

Development of formulations for two water-borne stoving topcoats

Two water-borne topcoats are based on a water-borne alkyd resin and a reactive melamine resin. The ratio of the two resins is to be 100 : 25 first and then 100 : 40. The pigmentation consists of titanium dioxide and phthalocyanine blue in the ratio 9 : 1. The pigment to binder ratio is to be 0.6 : 1. The solids content is to be 60 wt.%. Both topcoats are to be produced from the same mill base.

The resin is a short oil alkyd with unsaturated fatty acids (delivery form: 75% in butyl glycol and sec.-butanol). The acid number is 40 mg KOH/g (on solids).

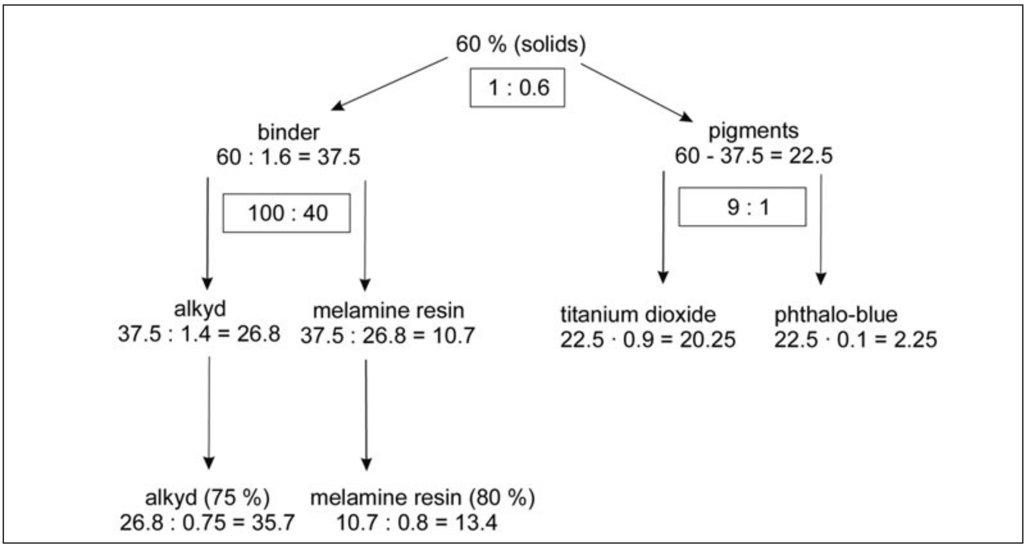


Figure III-4.4: Development of a formulation for a topcoat (resin ratio 100 : 40)

Table III-4.3: Formulation for a water-borne stoving topcoat (alkyd : melamine resin = 100 : 40)

pos.	**raw material**	**solids [wt.%]**	**density [g/cm³]**	**formulation [wt.%]**
01	water soluble alkyd resin (75% in butyl glycol/iso-butanol)	26.80	1.20	35.70
02	melamine resin (80% in iso-butanol)	10.70	1.50	13.40
03	titanium dioxide, rutile	20.25	4.10	20.25
04	phthalocyanine blue	2.25	1.60	2.25
05	DMEA			1.70
06	additives			2.00
07	deionized water			24.70
sum				100.00

pos. 01: Worléesol 07A (75% in butyl glycol/iso-butanol 1 : 1, Worlée) pos. 02: Cymel 327 (80% in iso-butanol, Cytec)

Table III-4.4: Formulation for a water-borne stoving topcoat (alkyd/melamine resin = 100 : 25)

pos.	**raw material**	**solids [wt.%]**	**density [g/cm³]**	**formulation [wt.%]**
01	water soluble alkyd resin (75% in butyl glycol/iso-butanol)	**30.00**	1.20	**40.00**
02	melamine resin (80% in iso-butanol)	**7.50**	1.50	**9.40**
03	titanium dioxide, rutile	20.25	4.10	20.25
04	phthalocyanine blue	2.25	1.60	2.25
05	DMEA			**1.90**
06	additives			2.00
07	deionized water			**24.20**
sum				100.00

pos. 01: Worléesol 07A (75% in butyl glycol/iso-butanol 1 : 1, Worlée) pos. 02: Cymel 327 (80% in iso-butanol, Cytec)

The crosslinker is a melamine resin partly etherified with methanol (delivery form: 80% in iso-butanol).

Development of the formulation starts with the topcoat in the ratio 100 : 40 (alkyd resin to melamine resin) as this contains a minor amount of alkyd resin (see Figure III-4.4). Then, the second topcoat with the resin ratio of 100 : 25 can be prepared from the same mill base by adding more alkyd resin.

Development of the formulation with resin ratio 100 : 40 is presented in Figure III-4.4.

The resultant formulation is presented in Table III-4.3. As the alkyd resin has to be neutralized for transfer to the aqueous phase, the amount of DMEA for neutralization has to be calculated. The calculation for 100% neutralization is given by the following equation.

$$m_{DMEA} = \frac{M_{DMEA} \cdot AV_{alkyd} \cdot m_{alkyd}}{56110} = \frac{89 \cdot 40 \cdot 26.8}{56110} = 1.7 \text{ parts by weight}$$

The additives which are listed in Table III-4.3 and which are necessary are wetting agents, dispersing agents, antifoam agents, and rheological additives. The choice of additives depends on the application conditions.

The PVC is calculated as follows:

$$\text{PVC} = \frac{20.25 / 4.1 + 2.25 / 1.6}{20.25 / 4.1 + 2.25 / 1.6 + 26.80 / 1.2 + 10.7 / 1.5} = 17.7\ \%$$

The calculation recipe for the topcoat, which consists of alkyd resin and melamine resin in the ratio 100 : 25, is formulated in the same way as presented in Figure III-4.4. The formulation for that is presented in Table III-4.4. Numerical values which differ from those in the formulation in Table III-4.3 are emboldened.

The differences in amounts that result from the differences in the ratio of alkyd to melamine resin are: 4.3 wt.% more alkyd resin and 4.0 wt.% less melamine resin. Of course, the amount of neutralization agent has to be adjusted for the higher amount of alkyd resin.

A check of the P/B value and the PVC produces the following figures:

P/B = 22.5 : 37.5 = 0.6 : 1

$$\text{PVC} = \frac{20.25 / 4.1 + 2.25 / 1.6}{20.25 / 4.1 + 2.25 / 1.6 + 30.00 / 1.2 + 7.50 / 1.5} \cdot 100\ \% = 17.5\%$$

The small deviation in PVC results from the difference in dry film densities of alkyd resin and melamine resin.

The mill base consists of the smaller portion of alkyd, neutralization agent, deionized water, additives, and pigments. The formulation is presented in Table III-4.5. The type of additive determines whether it has to be added to the mill base or at the end.

It is essential to measure the pH value before and after grinding. The target is a pH value of 8. If necessary, it must be adjusted with more DMEA.

Table III-4.5: Mill base for both topcoats

pos.	raw material	solids [wt.%]	density [g/cm³]	formulation [wt.%]
01	water soluble alkyd resin (75% in butyl glycol/iso-butanol)	40.95	1.2	54.60
02	DMEA			2.60
03	deionized water			6.10
04	wetting and dispersing agents			1.50
05	titanium dioxide rutile	31.00	4.1	31.00
06	phthalocyanine blue	3.40	1.6	3.40
07	antifoam agent			0.80
sum		75.35		100.00

Table III-4.6: Completion of topcoat (alkyd/melamine resin = 100 : 40)

pos.	raw material	solids [wt.%]	density [g/cm³]	formulation [wt.%]
01	mill base (see Table III-4.5)	62.50		83.00
02	melamine resin (80% in iso-butanol)	13.60	1.5	17.00
sum		76.10		100.00

Adjusting the required viscosity by adding deionized water.

Table III-4.7: Completion of topcoat (alkyd/melamine resin = 100 : 25)

pos.	raw material	solids [wt.%]	density [g/cm³]	formulation [wt.%]
01	mill base (see Table III-4.5)	62.08		82.45
02	DMEA			0.25
03	water soluble alkyd resin (75% in butyl glycol/iso-butanol)	4.07	1.2	5.43
04	melamine resin (80% in iso-butanol)	9.49	1.5	11.86
sum		75.64		100.00

Adjusting the required viscosity by adding deionized water.

The well-dispersed mill base is suitable for both topcoats. The formulation for completing the topcoats is presented in Tables III-4.6 and III-4.7.

Adjustment of the viscosity with deionized water has to be carried out carefully step by step to avoid over-thinning, and, importantly, the pH value has to be checked, and adjusted as necessary.

4.3 Water-borne stoving enamels based on thermosetting phenolic resins (resols)

Resols in the form of mononuclear or binuclear phenol alcohols (molar mass up to 300) are water-soluble, but they cannot be used as binders for water-borne paints because they do not form adequate films, are not stable in storage and exhibit little compatibility. Their dilutability with water can be improved by incorporating carboxylic groups, such as so-called resol carboxylic acids. These can be obtained by making ”diphenolic acid” (Figure III-4.5) react with formaldehyde [15].

As the para-position in “diphenolic acid” is occupied, methylol groups can only be introduced in the ortho-position to the aromatic hydroxyl group.

Like solvent-borne paints based on thermosetting phenolic resins (Chapter II-3.2), water-borne resols yield brittle coatings when they are the sole binder. As a rule, resols are combined with other binders or modified (plasticized).

For example, there are water-borne phenol-epoxy resin precondensates which are synthesized from polyalkylidene phenols (novolak resins) having molar masses of 300 to 600 [16] (Figure III-4.6).

The polyalkylidene phenol reacts with bisphenol A-epoxy resins (type 7 or 4) at about 130 °C in the melt (Figure III-4.7).

The polymer melt is then diluted with suitable organic solvents (e.g. acetone or 1-butanol) and water. In the second step, the epoxy adduct reacts to form carboxylic and methylol groups (Figure III-4.8).

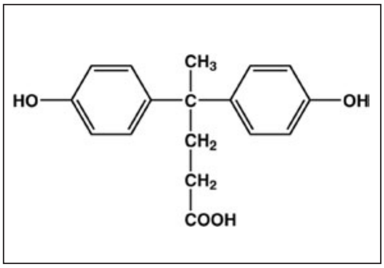


Figure III-4.5: 4,4-Bis(4-hydroxyphenyl)pentanoic acid (“diphenolic acid”) catalysts

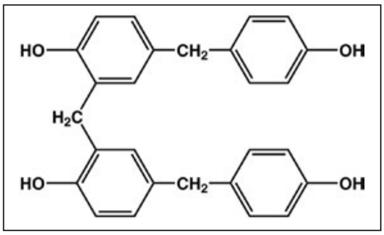


Figure III-4.6: Simplified diagram of a polyalkylidene phenol (molar mass 412)

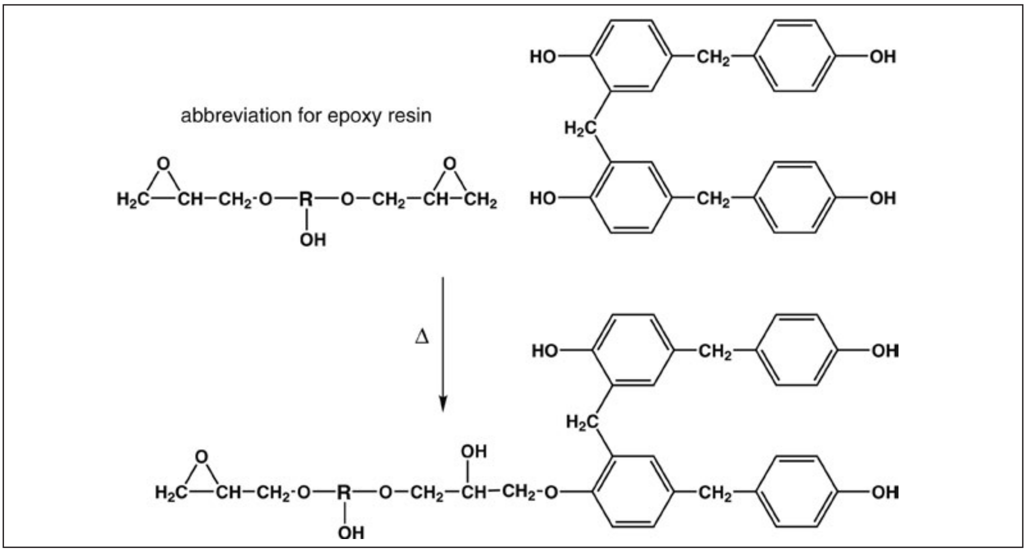


Figure III-4.7: Addition of an epoxy resin to a polyalkylidene phenol

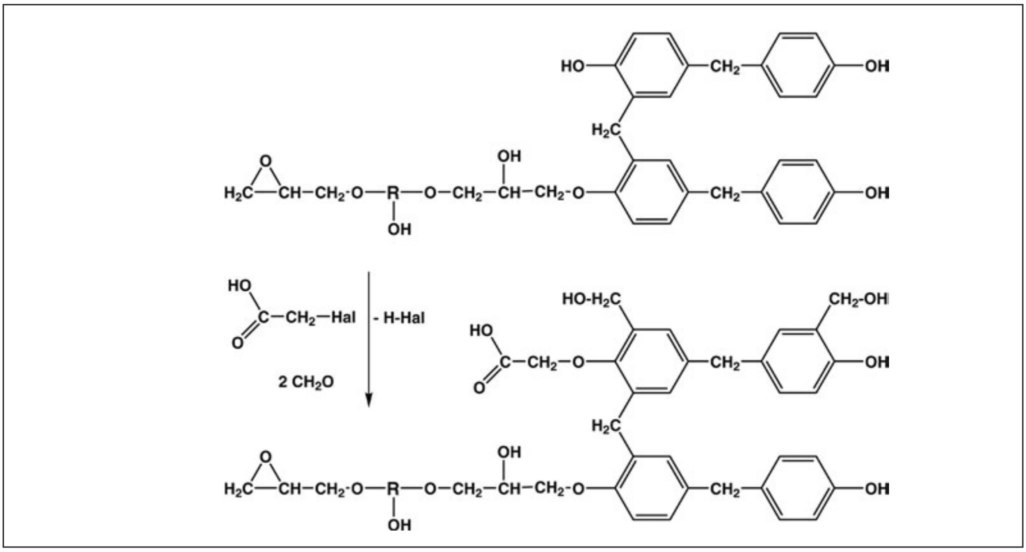


Figure III-4.8: Reaction of the epoxy adduct to form carboxylic and methylol groups (Hal = halogen, e.g. chlorine)

Byproducts (e.g. H-Hal) are then removed, an appropriate amine is added for neutralization and the organic solvent is stripped off. The result is a thermosetting, self-crosslinking (methylol, hydroxylic, carboxylic and epoxy groups) resol-epoxy system with a molar mass of about 10,000 [16]. This is probably a secondary dispersion (particle size 60 to 100 nm) that dries to a dense, pore-free, glossy film.

As the glass temperature of non-crosslinked resol-epoxy resins is somewhat higher than room temperature, coalescing agents must be added (e.g. hexyl or butyl glycol). Sometimes small amounts of HMMM resins are also added, and act as levelling agents.

The inherent colour of phenolic resins prevents them from being used for decorative coatings. However, they are used for functional coatings because of their excellent adhesion on metal substrates and because of their good chemical resistance.

Table III-4.8: Interior coating for drums

pos.	raw material	parts by weight	solids	density [g/cm^3]
01	phenol-epoxy resin	50.00	27.5	1.2
02	butyl glycol	10.00		
03	iron oxide red	9.85	9.85	5.0
04	deionized water	10.00		
dispersing pigment				
05	phenol-epoxy resin	18.15	10.0	1.2
06	HMMM resin	2.00	2.0	1.5
sum		100.00	about 49	

pos. 01 and 05: 55% in water (2% 1-butanol), e.g. Phenodur VPW 1942 (see Figure III-4.8)
pos. 03: synthetic iron oxide red pigment, e.g. Bayferrox 130 M
pos. 06: about 100% solids, e.g. Maprenal MF 904
adjustment of pH value with DMEA
stoving: 15 min 230 °C

Formulations

The first formulation [17] is an interior coating for drums (Table III-4.8).

The characteristic values of the formulation (Table III-4.8) are calculated as follows.

$$P/B = 9.85 : (27.5 + 10 + 2) = 9.85 : 39.5 = 0.25 : 1$$

$$PVC = \frac{9.85/5}{9.85/5 + 37.5/1.2 + 2/1.5} \cdot 100\% = 5.7\%$$

The pigment/binder ratio and the PVC are fairly low and the content of organic cosolvents (11 wt.%) is relatively high. This formulation works also with a reduced quantity of cosolvent.

The second formulation is a "gold varnish" – a clear coat for can interiors (Table III-4.9) [17]. The golden colour results from the metallic substrate and the inherent colour of the binder.

The content of organic cosolvents in this formulation (Table III-4.9) is about 5.5 wt.% and so lower than in Table III-4.8.

The relatively high curing temperatures are typical of water-borne coatings based on resols (Tables III-4.8 and III-4.9).

Table III-4.9: Sterilization-resistant coating for can interiors ("gold" coloured)

raw material	parts by weight
phenol-epoxy resin (55%)	80.0
hexyl glycol	5.0
desalinated water	15.0
sum	100.0

phenol-epoxy resin see Table III-4.8, adjusting of pH value to about 7
stoving: 12 min 200 °C

4.4 Electrodeposition paints

4.4.1 Electrodeposition processes

Historical development

Objects of complex surface geometry and, more particularly, those with hollow spaces cannot be spray-coated effectively. For such objects, dipping paints were developed. Even in the past, the application of automotive OEM primers was the most important field for dipping paints. Unfortunately, as the dipping primers were solvent-borne and relatively large objects such as automotive bodies had to be painted, the dipping tanks were a source of vast solvent emissions. At first, these emissions were seen as a problem of explosion protection. However, of course, emissions are also health hazards, even though the process was automated.

In the early 1950s, H. Hönel [1] developed and prepared the first water-borne thermosetting paint systems. By the end of that decade, the auto makers were using water-borne dip primers. In the 1960s, to optimize the deposition of paint material, electrophoretic deposition was introduced for automotive OEM primer systems. The mechanism of electrophoresis had been known for a long time (Reuß, 1809). The first patents for electrophoretic deposition of paints were filed in the 1930s. The first available were anionic electrodeposition primers in which the object is connected as an anode in a DC circuit. The dip primers for these consist of anionically stabilized resins. Mainly with a view to improving corrosion protection, cationic electrodeposition primers were introduced into the paint industry in the late 1970s. They have widely replaced the anionic systems for automotive primers.

Principles behind the process

Electrophoresis is the transport of electrically charged particles between two DC electrodes. The medium – in this case, water – has to have a high dielectric constant. The particles move in the electrical field to the partner electrode. Even particles of very different sizes can be transported. The particles may also consist of uncharged parts that are carried by the charged parts. Finally, the particles may contain pigments which are wetted by ionically stabilized resin parts of the paint. All the particles are deposited on the partner electrode and must form a smooth film. Anionically stabilized systems are deposited at the anode to form acid media with oxidation potential. Cationically stabilized systems are deposited at the cathode and form basic film media with reduction potential. The deposition takes place by discharge and coagulation. The film formed in this way acts as a dielectric membrane. Nevertheless, migration and osmosis may take place. Electric osmosis is the reason that the water, together with soluble ingredients in the film matrix, is driven out. The film thickness is limited. The limitation is influenced by type of resin, degree of neutralization, solids content of the dipping material, temperature, electrical power, dipping time and rotation of material in the dipping tank. Rotation of material is important for long-term stability. If all the parameters are checked and controlled very closely, the results are homogeneous and highly reproducible films and film properties. A high level of automation is possible.

The material deposited on the objects during dipping needs to be replenished, of course, and this is done by adding “compensation material”, time by time or more or less continuously. There are different methods for adding compensation materials. If the addition material is non-aqueous and not neutralized, this concentrate needs to be pre-mixed with a portion of the tank material to be partly neutralized and then transferred to the aqueous phase. Such concentrates often contain small amounts of co-solvents. The second method is the use of aqueous concentrates which have already been partly neutralized. Addition in this case is much simpler. However, it must be borne in mind that the amount of neutralization agent in the tank will increase over time, and the excess will have to be removed. Replenishment of neutralization agent is much more important if fully neutralized concentrate is added to the tank. The concentrates for cationically stabilized primers are mostly fully neutralized and delivered without co-solvents. Therefore, the neutralization acid has to be removed carefully and continuously. To this end, the electrodes (here, the anode) are wrapped in a semi-permeable membrane (anode boxes), where the neutralization agent accumulates and is removed by pumping into the anodic material loop. The lost material is replaced with deionized water. Furthermore, the material from the anode boxes is separated in an ion exchanger, regenerated and returned to the system. A special method is currently used for cationic primer components. The main dispersion is unsuitable for preparing pigment dispersions. Accordingly, the fully neutralized dispersion and the pigment paste, which is based on special grinding resins, are added separately but at the same time (in parallel) for compensation purposes.

The objects (car bodies) for coating with electrodeposition primer (EDP) are transported on a conveyor belt into the tank. The dipping process is automated. The electrical voltage is switched on only when the object (car body) is dipped. The deposited primer film is relatively stable and the film surface is cleaned by spraying with regenerated or deionized water. To avoid generation of too much waste water, all processes are set up for recycling. For example, the rinsing water is fed into the dipping tank. To maintain the same level within the dipping tank, tank material is also circulated and treated by ultrafiltration. Additionally, the material in this circuit is cooled in a heat exchanger to compensate for the increase in temperature (energy charging) arising from the deposition process and the rotation of tank material by pumps. The residue from the ultrafiltration is recycled into the dipping tank; the liquid phase is collected in a storage tank and used for the first rinsing steps. However, deionized water is used for the last rinsing step in order that clean surfaces for the following coating process (primer surfacer) may be assured. The overall process is illustrated in Figure III-4.9 [19].

Advantages of electrodeposition

The main advantage of electrodeposition is the possibility of generating homogeneous primer layers all over complex object surfaces (e.g. car bodies). Additionally, cavities are covered with primer. The efficiency with which cavities are covered is called throwing power. Only when the outer surface has been covered with primer material, which forms an electrically resistant film, does the electric field reach the surfaces of cavities to effect deposition on those parts. Since the electric field has the highest density on edges and burrs, this ensures that those parts are covered efficiently, a fact which is important for corrosion protection.

The whole process is easy to control since there are well-defined physical parameters. The parameters are available continuously during the process and therefore form the basis for effective control. The transfer efficiency of material is up to 95 wt.%. Although the equipment is expensive, the process itself incurs low costs. Contributory factors are that the process is

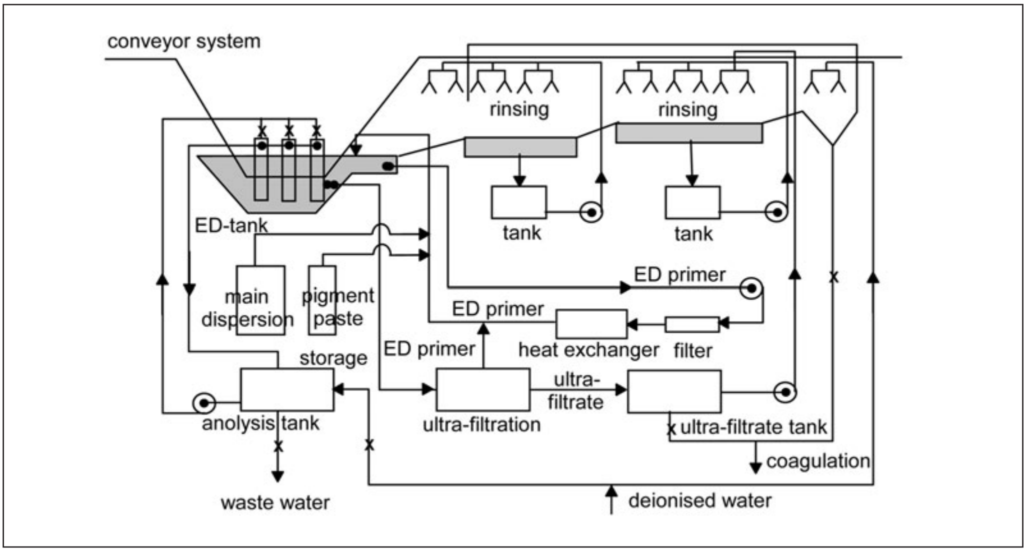


Figure III-4.9: General outline of the cationic deposition equipment and process one of continuous application, it is automated, it has a high transfer efficiency of material, it is suitable for large series of objects, the application time is short and which is followed by short cycle sequences. There is no environmental contamination and no fire hazard and so insurance costs are lower than for the corresponding solvent-borne installations.

4.4.2 Anionic deposition paints

Reactions at electrodes

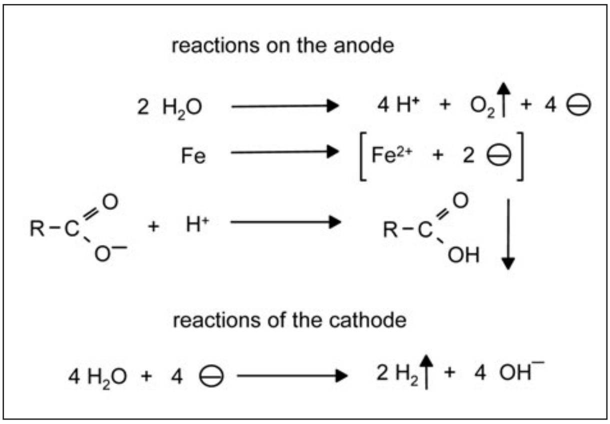


Figure III-4.10: Reactions at electrodes during anionic deposition

Anionic electrodeposition utilises anionically stabilized resin systems (e.g. those stabilized with carboxylic anions) and amines as neutralization agents. In an applied electrical field, the colloidal particles of the paint system move onto the object that constitutes the anode in the DC circuit.

The anions of the resin are discharged and – since they no longer have adequate water solubility – the resins coagulate to form a film. However, the water at the anode also forms protons and molecular oxygen, which escapes into the air. Additionally, since iron is contained in the anode, it may form iron-II-ions. The iron-II-ions can support the coagulation of resins, but may also trigger corrosion processes (if they may form local cells together with the uncharged iron).

The amines, acting as neutralizing agents, move to the cathode and are initially discharged. But, also at the cathode, water is decomposed into hydrogen and hydroxyl ions (it is electrolysed). The hydroxyl ions become partners for the amines. Without any compensation, the pH value of the dipping tank would increase continuously.

The equations for the reactions at the electrodes are presented in Figure III-4.10.

Selection of resins

Principally, all resins that have been anionically stabilized are suitable for electrodeposition. However, there is a special constraint on selection. Since dipping tanks operate with continuous replenishment, the resin systems employed have to be adequately stable, especially as regards saponification. Preferred resins for anionic electrodeposition are:

- Maleinised oils (adduct of maleic anhydride and linseed oil or stand oil)
- Maleinised polybutadienes
- Maleinised epoxy esters
- Acrylic resins with free carboxyl groups

Since maleinised products contain C-C bonds formed by the addition of maleic anhydride across double bonds, they are resistant to saponification. These anhydride adducts are opened by adding polyols. Thus, the resins contain carboxyl groups as well as hydroxyl groups for the crosslinking reaction. As the carboxyl groups were neutralized by amines the resins become water-soluble. However, the ester groups of the maleinised oils and epoxy esters can still be saponified.

Naturally, the polymer chains of the acrylic resins are totally stable in basic media.

Crosslinkers for all the aforementioned resins are:

- Phenolic resins
- Amino resins (melamine or benzoguanamine resins)

For stability reasons, the phenolic resins employed are resols, which are not water-soluble. These have to be mixed with the main resins in organic phase, or – preferably – mixed and pre-condensed.

Amino resins used in electrodeposition paints can contain ethers of hydroxycarboxylic acids. The free carboxylic groups can be neutralized to yield water-soluble anions. But HMMM resins are also water-soluble and adequately stable under the basic conditions of anionic electrodeposition paints.

Properties and application areas

The first commercial resins for automotive electrodeposition primers contained maleinised linseed oil. They later contained maleinised polybutadienes, which bear hydroxyl groups for crosslinking by addition of polyols to open the anhydride ring structure. Suitable crosslinkers were phenolic resins. These systems are distinguished by adequate stability, excellent wetting of substrates and pigments, and produce flexible and chemically resistant films. The stoving temperatures are 160 to 180 °C. The films are not weatherable and will turn yellow on exposure to light and heat. Although the level of corrosion protection afforded is acceptable, iron ions in the film pose a risk (see reaction at electrodes). Therefore, for automotive electrodeposition primers, these systems were replaced by primers containing cationically stabilized resins which afford excellent corrosion protection (see Chapter III-4.4.3). Nonetheless, anionic electrodeposition paints are still suitable for many other general industrial applications.

Combinations of maleinised epoxy esters and melamine resins are used not only for primers but also for one-coat electrodeposition paints. These are distinguished by excellent adhesion (on substrates and intercoats), adequate corrosion protection, hardness, and chemical resistance. They are not resistant to yellowing.

As electrodeposition paints have to offer resistance to yellowing and weathering, it is necessary to choose a combination of acrylic secondary dispersions and water-soluble melamine resins. Such combinations additionally offer hardness and chemical resistance. These products are preferred for one-coat paints (also white) for general industrial applications.

Example:
White, one-coat, anionic-electrodeposition paint for general industrial use

For a white, one-coat, anionic-electrodeposition paint for general industrial use [20], a combination of an acrylic resin containing carboxyl and hydroxyl groups (delivery form is an organic solution) with an HMMM resin is chosen. The mill base is prepared in organic solution and contains acrylic resin solution, melamine resin, co-solvent, and titanium dioxide. The concentrate for addition to the dipping tank is prepared by adding DMEA to neutralize this paste. For application in the dipping tank, water is added until the total solids content is 12 wt.%. Details of the formulation are presented in Table III-4.10.

The mill base is produced in a dissolver. It is then ground on a pearl mill for 30 minutes. The degree of neutralization is 60%. The paste containing the neutralization agent is mixed in a dissolver. The contents of the tank consist of 60 wt.% of deionized water and 16 wt.% of the concentrate (neutralized paste).

Table III-4.10: White, one-coat, anionic-electrodeposition paint for general industrial use

pos.	raw material	solids [wt.%]	density [g/cm³]	formulation [wt.%]
pigment dispersion				
01	acrylic resin (70% in butyl glycol/butanol 1 : 1)	60.00	1.2	85.70
02	HMMM-resin (90% in butyl glycol)	20.00	1.5	22.20
03	Texanol			4.00
04	titanium dioxide	40.00	4.1	40.00
	millbase (solids79 %)			151.90
compensation material				
05	DMEA			4.00
	pigment paste (solids 77%)			155.90
content of electrodeposition tank				
06	deionized water			844.10
sum				1000.00

pos. 01: Viacryl SC 323w (70% in butyl glycol/butanol 1 : 1; AN: 70 - 85 mgKOH/g; Cytec, Surface Specialties, Vianova
pos. 02: Maprenal MF 910 (90% in butyl glycol; INEOS)
pos. 03: 2.2.4-trimethyl-1,3-pentandiol-1-isobutyrate (Eastman)
pos. 04: Titandioxid 2059 (Kronos)

Acrylic resin / melamine resin (solids) = 75 : 25

The ratio of pigment to resin and the PVC are calculated as follows:

P/B = 0.5 : 1

$$\text{PVC} = \frac{40.0 / 4.1}{40.0 / 4.1 + 60.0 / 1.2 + 20.0 / 1.5} \cdot 100\,\% = 13\,\%$$

The pH value of the dipping paint is adjusted to 8.3 ± 0.3. The temperature in the tank has to be 23 to 30 °C, and the specific conductivity is 900 ± 100 μS/cm. The deposition process takes 60 to 120 s and a voltage of 100 to 200 V. After dipping and rinsing, the paint is stoved for 30 minutes at 160 °C.

4.4.3 Cationic electrodeposition paints

Development of cationic electrodeposition primers

Currently, cationic electrodeposition paints are mostly used for automotive OEM primers, but they are also suitable for other application areas. These systems have widely replaced anionic electrodeposition primers for OEM. The main reason is the superior corrosion protection afforded by cationic systems compared to that of their anionic counterparts. Although the structural elements of the cationic electrodeposition primers were well known, it was important to select the various parts and to put together a system that conferred many of the required properties[3]. Today, the same basic composition is used around the world, although many variants and improvements have been created.

Composition of cationic electrodeposition primers

The main component of the cationic electrodeposition primers is aromatic epoxy resins. These offer excellent adhesion and corrosion protection. Due to their relatively high glass-transition temperatures, they form more or less brittle films; they therefore have to be plasticized. Modifications for plastification contain polyethers, polyesters, and alkyl phenols. The epoxy group lends itself very readily to reactions with hydrogen atoms of primary and secondary amines. On one hand, the addition forms amine-modified epoxy resins, which offer the possibility of neutralization with acids. On the other, further functional groups for crosslinking reactions can be introduced. The amines for addition across epoxy groups are therefore amino alcohols, e.g. N-methyl ethanolamine, diethanolamine, which introduce hydroxyl groups; or polyamines, e.g. dipropylene triamine. For the addition reaction, the primary amine groups of the dipropylene triamine are blocked by reaction with ketones (e.g. methyl isobutyl ketone, MIBK) to form ketimines. Thus, only the secondary amine group can add on epoxy groups. Later, when the resin is transferred into the aqueous phase, the ketimines will hydrolyse and re-form primary amine groups, which are reactive groups for crosslinking.

Neutralization agents for the amine-modified epoxy resins are volatile organic acids: acetic acid, lactic acid, and formic acid.

A model of such a neutralized, modified epoxy resin is presented in Figure III-4.11.

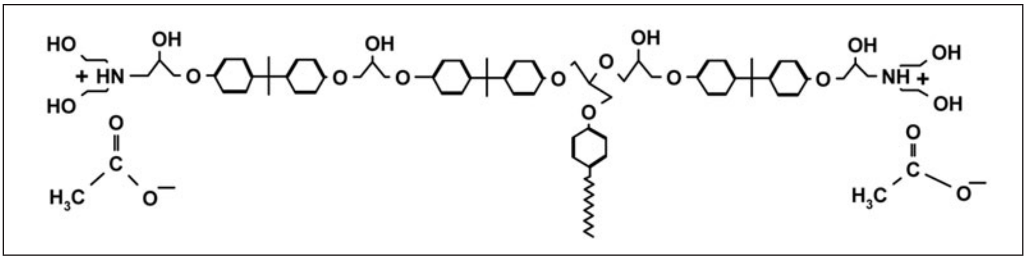


Figure III-4.11: Model of a neutralized modified epoxy resin for cationic ED coats

The modified epoxy resins contain different functional groups: primary hydroxyl groups of adducts of amino alcohols, secondary hydroxyl groups on the chain of the epoxy resin, and – optionally – primary amine groups as reaction products of the addition of ketimines that are hydrolysed in aqueous phase. Suitable partners for crosslinking are blocked polyisocyanates. In contrast to crosslinking with amino resins, the reaction of blocked polyisocyanates is catalysed (accelerated) by basic components. This dovetails excellently with the basic reaction of the amine-modified epoxy resin. The blocked polyisocyanates are not water-soluble themselves. However, when they are mixed with the amine-modified epoxy resin in organic phase (organic solution or in melt), they are transferred along with it into the aqueous phase. The cationically stabilized epoxy resin forms a carrier for the non-hydrophilic crosslinker. The crosslinker consists of toluene diisocyanate adducts or adducts of MDI (methylene di-phenylisocyanate, 4,4'-diisocyanato diphenyl methane) and its homologues. The preferred blocking agents for the crosslinker in ED primers are alcohols (e.g. 2-ethylhexanol) or monoethers of ethylene glycol (e.g. propyl glycol). Since the reactivity of aromatic blocked isocyanates is high and especially in combination with primary amine groups despite the unusual blocking agents, the effective reaction temperatures are between 160 and 185 °C. Nevertheless, it is necessary to add relatively high amounts of catalysts. Until now, the most important catalyst was dibutyl tin oxide (DBTO). But, as mentioned above (see Chapter III-1.3.1), alkyl tin compounds are classified as hazardous and harmful to the environment and so have to be replaced. Currently, bismuth or vanadium compounds are particularly recommended as the crosslinking catalysts for ED coatings.

A combination of modified epoxy resin and blocked polyisocyanate crosslinker, neutralized and in aqueous phase, serves as the dispersion concentrate (compensation material) that is added to the dipping tanks for electrodeposition. This dispersion is unsuitable for grinding pigments. A special resin exists for the preparation of mill bases for ED primers. This binder is also based on epoxy resin and contains quaternary ammonium salts. It is relatively low-molecular and forms solutions rather than dispersions in aqueous phase. This special resin can wet pigments efficiently. The mill bases consist of coloured pigments (e.g. titanium dioxide and carbon black), extenders (e.g. clays) and a functional pigment (e.g. for corrosion protection). The mill base is the second compensation material added to the dipping tank, and is added in parallel to the so-called main dispersion. The details of the process are presented in Figure III-4.9.

Reactions at electrodes

In the electric field of dipping tanks for cationic electrodeposition systems, of course, the cationically stabilized resins move to the cathode, where they are discharged and form films by coagulation. Additionally, at the cathode, the electrolysis of water forms molecular hydrogen which escapes, and hydroxyl ions. The hydroxyl ions support the discharge of the ammonium salts to form amines and water. Additionally, metal cations may be discharged.

At the anode of the DC circuit, water forms molecular oxygen, which escapes, and protons by electrolysis. The protons are partners for the acid anions to form acids. Without any replenishment of these acids, the pH value of the material in the dipping tank would drop steadily. But the aforementioned anode boxes remove the excess acid and send it through an ion exchanger. Additionally, metals may be oxidised to metal cations at the anode and move to the cathode, where they are reduced back to metals.

The equations for the electrode reactions are presented in Figure III-4.12.

Other cationic electrodeposition paints

Phenols can react with formaldehyde and amines or alkanol amines to form so-called Mannich bases. Again, this reaction takes place on bisphenol moities of aromatic epoxy resins. The products form cations by neutralization. Suitable crosslinkers are phenolic resins or blocked polyisocyanates.

Furthermore, acrylic resins are suitable for preparation of cationically stabilized binders.

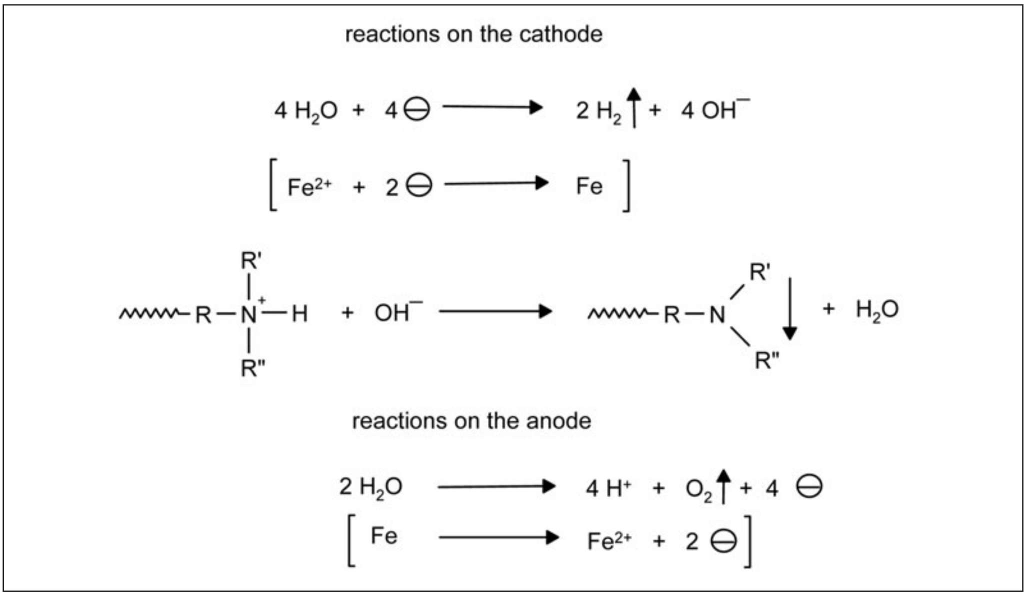


Figure III-4.12: Electrode reactions of cationic electrodeposition paints

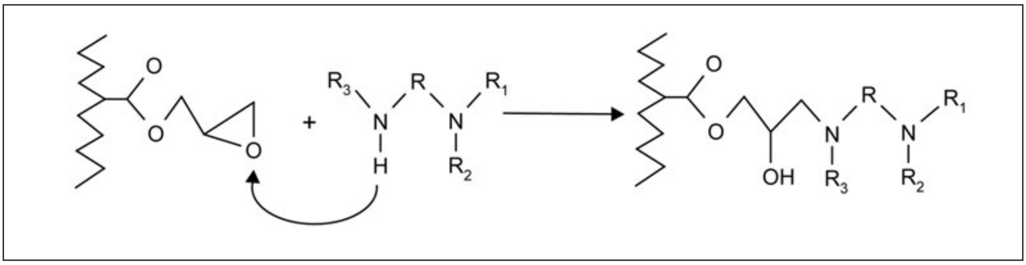


Figure III-4.13: Reaction for the modification of epoxy acrylics by adding secondary amines

First, it is possible to produce acrylic resins which contain aminoalkyl esters of acrylic acid (e.g. N,N-dimethyl aminoethyl methacrylate) as comonomers.

The second way of forming cationically stabilized binders is the addition of secondary diamines to epoxy acrylates. The equation for this reaction is presented in Figure III-4.13.

Both resin groups are water-soluble or water-thinnable after neutralization with acids. Crosslinkers for these resins are melamine resins. Unlike the cationic binders based on epoxy resins or phenols, combinations of acrylic and melamine resins do not yellow and are weatherable. Thus, the systems are highly suitable for one-coat paints.

Finally, maleic anhydride adducts on polymers may be particularly modified by adding primary-tertiary diamines to form imide rings. The remaining tertiary amine groups may be neutralized with acids to form cationically stabilized water-borne binders.

Table III-4.11: Main resin for ED-primer

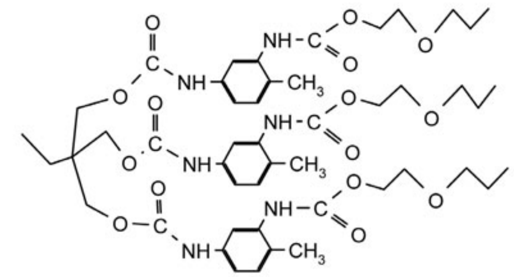
pos.	**raw material**	**solids [wt.%]**	**formulation [wt.%]**
Patent US 5,936,013; example 2.3, main resin 3			
01	epoxy resin [EP-EW 190 g/mol]	17.81	17.81
02	methoxy propanol		9.90
03	ethylhexyl amine	3.62	3.62
charge, add, stir, heat on 60 °C, hold			
03	polyamine adduct [NH-EW 870 g/mol] (80 wt.% in methoxy propanol)	4.07	5.09
add, hold for 2 h on 60 °C			
04	epoxy resin [EP-EW 190 g/mol] (75 wt.% in methoxy propanol)	31.16	41.55
05	diethanol amine	5.90	5.90
06	in methoxy propanol		5.50
07	N,N-dimethylamino propyl amine	2.44	2.44
08	in methoxy propanol		1.69
add, heat over 2 h on 120 °C, hold until final constants are achieved			
09	methoxy propanol		6.50
thin at solids		65.00	100.00
characteristics: amine number: 117 mg KOH/g OH-value: 323 mg KOH/g			

Formulation example

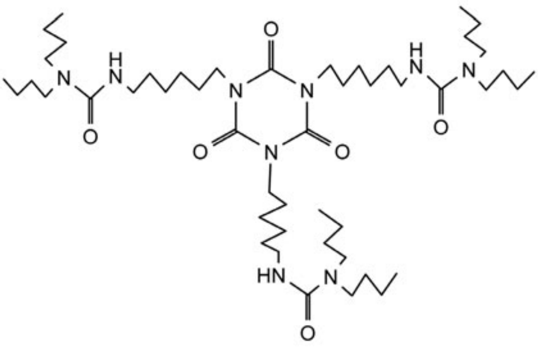
As already mentioned, cationically doped epoxy resins are the preferred main resins for automotive electrodeposition primers (ED primers). No other application field is as extensively covered by patent applications as that of electrodeposition coatings. The following examples from a patent [21 to 26] describe such an ED primer, which consists of the main resin, a crosslinker, the pigment paste including special dispersing resin, and a catalyst solution. The system complies with current legislation and is free of lead and tin.

The main dispersion [21] consists of two different aromatic epoxy resins (one with EP-EW 190 g/mol, 3 equivalents, the second with EP-EW of 475 g/mol; 2.1 equivalents) and a mixture of amines: 2-ethylhexylamine (0.9 moles), diethanolamine (1.8 moles), N,N-diethylaminopropylamine (0.6 moles), and an adduct of epoxy resin and 2-ethylhexyl glycidyl ether and diethylene triamine [NH-equivalent weight of adduct is 870, 0.15 equivalents). The process solvent is methoxy propanol. The composition and production of the main resin for ED primer are presented in Table III-4.11.

The crosslinker [22] consists of one mole of diethyl malonate which is made to react with one mole of trimethylolpropane by transesterification, with cleavage of one mole of ethanol. The resulting compound is made to react with one mole of toluene diisocyanate, which is partly blocked with one mole of ethylene glycol monoethyl ether. The crosslinking takes place by trans-urethanisation of blocked isocyanate groups, and – in addition – by some transesterification of malonate ester. The end product is diluted in diethylene glycol dimethyl ether (DGDME), and has a solid contents of 80 wt.%. The model formula is shown in Figure III-4.14.



adduct of TDI and TMP, blocked with propyl glycol



HDI isocyanurate trimer, blocked with dibutyl amine

Figure III-4.14: Model formula of crosslinker for cationic ED primer

The pigment paste [23] consists of a dispersing binder [24] and pigments. Like the main resin, the dispersing binder contains adducts of 2-ethylhexylamine (2.0 moles) and N,N-diethylaminopropylamine (2.0 moles) with the two different aromatic epoxy resins (one with EP-EW 190 g/mol (1 mole), the second with EP-EW of 475 g/mol (3 moles). The process solvent is butyl glycol. In addition, a reaction occurs with para-formaldehyde (potentially 2.2 moles CH_2O), yielding Mannich bases by cleavage of water (2 moles). The binder resin is neutralized with acetic acid (30 wt.% in water) and thinned with deionized water to 40 wt.% solids.

The pigments are titanium dioxide and carbon black. Additional neutralization is done by adding a small quantity of formic acid. The catalyst solution is added to the pigment paste.

The catalyst [25] is the reaction product of bismuth III oxide

(1 mole Bi_2O_3) with lactic acid (3 moles) in aqueous solution. The resulting bismuth lactate solution in water is combined with a portion of the main resin [21]. The bismuth content of the catalyst solution is 32.7 wt.%.

The ingredients of the pigment paste are mixed, pre-dispersed in a high-speed stirrer and then ground on a bead mill to the required particle size. The composition of the pigment paste is presented in Table III-4.12.

Table III-4.12: Pigment paste for ED-primer

pos.	raw material	solids [wt.%]	formulation [wt.%]
Patent US 5,936,013; example 3.1, pigment paste 3			
01	dispersing resin, patent US 5,936,013 example 2.4, resin 4 (40.5 solids)	10.00	25.00
02	carbon black	0.40	0.40
03	titanium dioxide, rutile	49.60	49.60
04	formic acid		0.92
05	water, deionized		24.08
sum		60.00	100.00

The main resin, crosslinker and pigment paste are combined to yield the entire ED primer. First, the organic main resin solution [21], the crosslinker solution [22], and the pigment paste are mixed intensively. The mixture is neutralized and deionized water is added until the solids content is 18 wt.%. The content of the ED primer is presented in Table III-4.13.

The aforementioned mixture of main resin solution, crosslinker and pigment paste is also the compensation material for the ED tank, which is in continuous use.

The pigment binder ratio and the PVC of the primer film result from the calculation of the composition of the entire bath material, which is given in Table III-4.13. The results are presented in the following equations.

$$P/B = \frac{5.17}{15.05 + 1.43} = 0.31 : 1.0$$

Table III-4.13: Content of finished ED-primer

pos.	raw material	solids [wt.%]	density [g/cm³]	formulation [wt.%]
Patent US 5,936,013; example 3.2, ED-primer				
01	example 2.3, main resin 3 (65% solids)	7.560	1.30	11.63
02	example 2.7, crosslinker 3 (80% solids)	3.240	1.30	4.05
03	example 3.1, pigment paste (60% solids)	7.200		12.00
	resin 4	1.200	1.30	
	titanium dioxide	5.952	4.10	
	carbon black	0.048	1.70	
04	example 3, KAT 3, catalyst preparation	0.300		0.91
05	acetic acid (30% in water)			3.15
06	water, deionized			68.26
sum		18.300		100.00

$$\text{PVC} = \frac{0.058/2.1 + 0.557/6.4 + 0.748/2.6 + 3.771/4.1}{0.058/2.1 + 0.557/6.4 + 0.748/2.6 + 3.771/4.1 + 15.05/1.26 + 1.43/1.3} \cdot 100\%$$

PVC = 9 %

Figure III-4.15: Start of the dipping process of a car body (source: BASF Coatings)

The patent mentioned that the application of ED-primer takes place regarding the common application conditions. Those are for example: dipping tank consists of ED-primer where pH-value is adjusted on 6.0 ± 0.3, and the solid content on 18 wt.%. The bath temperature has to be 27 °C. For laboratory tests panels are used, which are pre-treated with zinc phosphate. The deposition time is two minutes at a voltage of about 300 V. The panels are rinsed carefully with deionized water, and then – following now the patent advises – baked for 20 minutes at 170 °C. The film thickness after stoving is 22 ± 2 µm.

The film properties are indicated with: impact test [ASTM-D-2794-90] ≥ 80 i. p.; mandrel bend test [ASTM-D-522-88]: O.K.; salt spray test [ASTM-B-117-90] after 360 hours: ≤ 2 mm.

The bath storage stability after four weeks under continuous stirring is O.K., there are no sediments, and the sieve analysis shows less than 20 mg/l (Perlon sieve, 28 µm meshes). Test panels prepared after storage show the same properties than for fresh bath material. Figure III-4.15 shows the start of the dipping process of a car body in a here described electrodeposition tank.

4.5 References

[1] Hönel: Neue Wege in der Anstrichtechnik, Farbe & Lack 59, 174 (1953), Vincentz Network (Hannover)

[2] Cooperation of Glidden (Cleveland, Ohio, USA) and Ford Motor Corp. (Detroit, Michigan, USA), A. Gilchrist: Electrodeposition, Metal Prod. Magazine 1964 (February)

[3] USP 37 99 854 Method of Electrodepositing Cationic Comitems. PPG Ind. Inc. (1974), USP 39 22 353 Self Crosslinking Cationic Electrodepositable Comitems. PPG Ind. Inc. (1975)

[4] H. Wagner, H. F. Sarx: Lackkunstharze, Chapter II-3.1, C. Hanser München 1971

[5] H. van Dijk: The Chemistry and Application of Amino Crosslinking Agents or Aminoplasts, Publisher J. Wiley and Sons, London etc. 1998

[6] D. Stoye, W. Freitag (Editor): Lackharze, Chapter 6.2.3, C. Hanser, Munich Vienna 1996

[7] H. van Dijk: The Chemistry and Application of Amino Crosslinking Agents or Aminoplasts, Kapitel II-7, Publisher J. Wiley and Sons, London etc. 1998

[8] H. Kittel, Lehrbuch der Lacke und Beschichtungen, Volume 2, Chapter 3.1.5.3, Wasserverdünnbare Aminoharze, 2nd Edition, Publisher S. Hirzel 1998

[9] H. Kittel, Lehrbuch der Lacke und Beschichtungen, Volume 2, Chapter 3.1.2.3, Neutralizationsmittel, 2nd Edition Publisher S. Hirzel, 1998

[10] O. Lückert: Karsten – Lackrohstofftabellen, Chapter 38.16, Catalysts, 10th Edition, Vincentz Network, Hannover, 1996

[11] Publications of King Industries

[12] O. Lückert: Karsten – Lackrohstofftabellen, 10th Edition, Chapter 38.5, Entschäumer und Entlüfter, Vincentz Network, Hannover, 1996
[13] Nuplex, Specialty Resins, (2001), REC 97014
[14] Nuplex, Specialty Resins, (2001), REC 99004
[15] H. Kittel (editor K.-D. Ledwoch): Lehrbuch der Lacke und Beschichtungen, Volume 3, 2nd Edition, p. 49 – 51, Bindemittel für wasserverdünnbare Systeme, S. Hirzel (2001)
[16] P. Oberessel, T. Burkhardt, P. Oldring: The Chemistry and Application of Phenolic Resins or Phenoplasts, Wiley/Sita Series in Surface Coatings Technology, Volume 5, Chapter 1 (1998) p. 52-56
[17] Starting formulation of Cytec Surface Specialties, former Vianova
[18] BP 496 945 of Crosse & Blackwell Ltd. for cans
[19] F. Loop: Verfahren der kathodischen Elektrotauchlackierung; Industrie-Lackierbetrieb 47 (1979) 253
[20] Formulation recommendation of Cytec Surface Specialties (Vianova): White anodic electrodeposition paint for general industry applications
[21] Patent US 5,936,013, Vianova, example 2.3, main resin 3
[22] Patent US 5,936,013, Vianova, example 2.6, crosslinker VK 3
[23] Patent US 5,936,013, Vianova, example 3.1, pigment paste 3
[24] Patent US 5,936,013, Vianova, example 2.4, dispersion binder, resin 4
[25] Patent US 5,936,013, Vianova, catalyst, KAT 2
[26] Patent US 5,936,013, Vianova, example 3.2, ED-primer

Part IV Solvent-free coatings

Part IV Solvent-free coatings

1 Two-components systems

1.1 Two-components polyurethane coatings

Solvent-free ambient temperature curing coatings based on two-components polyurethanes can be formulated in different ways, e.g. by:

- Reaction between a liquid polyol (component A) and a liquid, usually aromatic polyisocyanate (component B, hardener).
- Reaction between a liquid prepolymer terminated with blocked isocyanate groups (component A) and a liquid polyamine (component B, hardener).

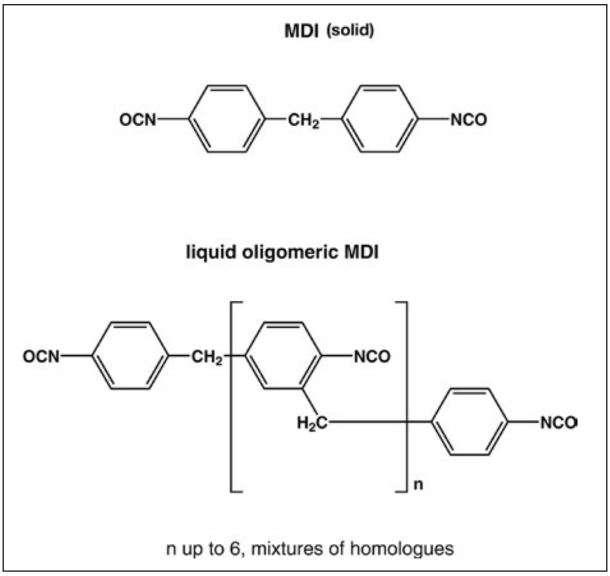


Figure IV-1.1: Monomeric and oligomeric diphenylmethane-4,4'-diisocyanate (MDI)

Polyol and aromatic polyisocyanate

The polyols used are mostly polyetherpolyols, polyesterpolyols, polyether/polyesterpolyols or castor oil. As a rule, oligomeric MDI serves as the polyisocyanate hardener (Figure IV-1.1).

When calculating the characteristic values of the formulation in Table IV-1.1, we have to add the castor oil (desiccant paste) to the binder (isocyanate base value - see Chapter II-1.3.1).

$P/B = (32.4 + 4.9) : (37.3 + 3.7 + 18) \approx 0.6 : 1$

$$\text{Isocyanate base value} = \frac{42 \cdot 100 \cdot \%\,\text{OH}}{17 \cdot \%\,\text{NCO}}$$

Table IV-1.1: Self-levelling coating composition for concrete floors (indoors) [1]

pos.	raw material	parts by weight
A-component		
01	polyol	37.3
02	desiccant	7.4
03	baryte (filler)	32.4
04	pigment mixture	4.9
B-component (hardener)		
06	aromatic polyisocyanate	18.0
sum		100.0

pos. 01: branched polyether/polyester, 5% OH, OH-equivalent mass 340, e.g. Desmophen 1150. The low OH- equivalent mass (respectively the high content of OH) leads to a high crosslink density and a high hardness.
pos. 02: molecular sieve (pore size 2 bis 3 Å), 50 wt% in castor oil, e.g. Baylith L-Paste
pos. 06: aromatic polyisocyanate (oligomeric MDI), 31.5% NCO, e.g. Desmodur VL. For monomeric MDI 33.6% NCO are calculated

$$\text{Hardener addition (calculated on Desmophen 1150)} = \frac{42 \cdot 37.3 \cdot 5}{17 \cdot 31} = 14.9$$

Moreover, 3.7 parts by weight castor oil (desiccant-paste) have to be considered. The average hydroxy number of castor oil is 162 mg KOH/g.

$$\%\text{OH} = \text{hydroxy number} \cdot 0.0303 = 162 \cdot 0.0303 = 4.9$$

$$\text{Hardener addition (calculated on castor oil)} = \frac{42 \cdot 3.7 \cdot 4.9}{17 \cdot 31} = 1.4$$

Hardener addition (total) 14.9 + 1.4 = 16.3

So, the above formulation (Table IV-1.1) uses an excess of 10% polyisocyanate, probably for increasing the hardness of the floor-coating by reaction between the excess isocyanate groups and atmospheric moisture.

Alternatively, the NCO/OH ratio of a fixed formulation may be calculated as follows:

$$\text{NCO/OH ratio} = \frac{\text{parts by weight polyisocyanate} \cdot 17 \cdot \%\text{NCO}}{\text{parts by weight polyol} \cdot 42 \cdot \%\text{OH}} =$$

$$= \frac{18 \cdot 17 \cdot 31}{(37.3 \cdot 42 \cdot 5) + (3.7 \cdot 42 \cdot 4.9)} = 1.1$$

Blocked polyisocyanates and polyamines

Blocked polyisocyanates can react at ambient temperature with polyamines to form urea linkages; the precise mechanism has not yet been elucidated. Figure IV-1.2 shows this reaction in simplified form.

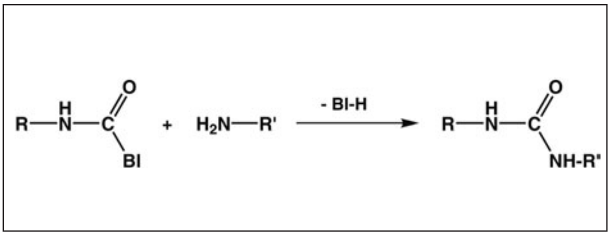


Figure IV-1.2: Reaction between blocked polyisocyanates and polyamines (Bl = blocking agent)

Applications of solvent-free two-components polyurethane coatings

- Buildings, structures:
  - Coatings for floors and roofs (film thickness up to 2 mm)
  - Planar seals (e.g. foundations)
  - Resin-based mortars
- Thick-film anti-corrosion coatings (steel constructions)

1.2 Two-components epoxy coatings

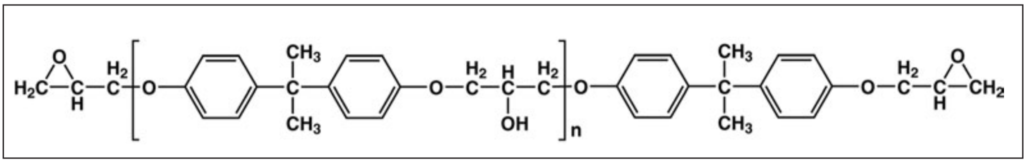


Figure IV-1.3: Bisphenol A-epoxy resins

Solvent-free, room temperature curing coatings based on epoxy resins crosslink in the same way as the respective solvent-borne systems (see Chapter II-1.3.2). There are two main differences regarding formulation:

- Only low-molecular liquid epoxy resins are used.
- The viscosity of the coating composition may be reduced by adding reactive diluents.

Liquid epoxy resins

The liquid epoxy resins used here (Figure IV-1.3) have a value for n of about 0.15 (epoxy equivalent mass about 190); i.e., the main constituent of these resins is bisphenol A-diglycidyl ether (epoxy equivalent mass 170). In aqueous epoxy emulsions (Chapter III-3.2.2), similar epoxy resins are used. For comparison, solid epoxy resins of type 1 in solvent-borne paints have values for n of 2 to 2.5 (Chapter II-1.3.2).

The use of low-molecular liquid epoxy resins retards the drying time (Figure IV-1.4) and shortens the pot-life [2]. Solid epoxy resins for solvent-borne paints are dry to the touch in a shorter time because they are additionally able to dry physically (Figure IV-1.4).

Reactive diluents

Generally, reactive diluents are low-viscosity compounds which are able to dilute the coating composition and they remain in film by chemically reacting with the binder. Reactive diluents differ from plasticizers, which remain in the film only because of their low volatility. In solvent-free two-components epoxy coatings, low-viscosity glycidyl ethers of short-chain aliphatic alcohols or alkyl phenols serve as reactive diluents (Figure IV-1.5).

The addition level of reactive diluents is limited because the monofunctional reactive diluents, especially, reduce the crosslinking density (similar to chain termination). As a rule, 10 to 15 wt.% of reactive diluent is added, but sometimes this figure may be as much as 20 wt.%. For example, 10 wt.% 2-ethylhexyl glycidyl ether lowers the viscosity of a liquid epoxy resin (epoxy equivalent mass 187) from an initial 12,000 mPa s to about 2,000 mPa s [3].

The aforementioned reactive diluents are used in solvent-free coatings, epoxy adhesives, resins for lamination, fibre-reinforced composites and casting resins for electronic devices.

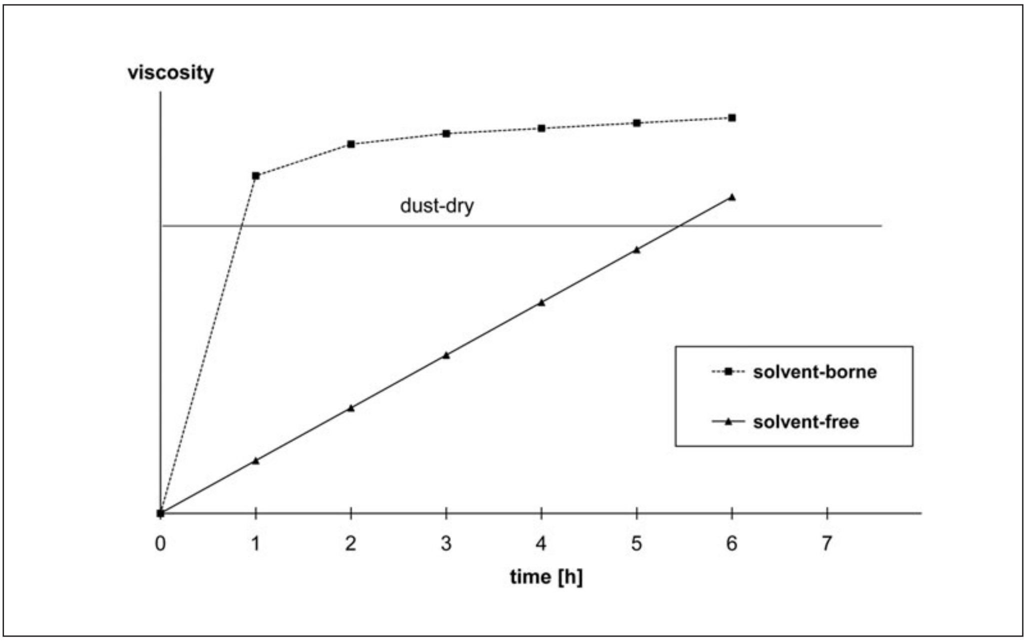


Figure IV-1.4: Simplified diagram of the relationship between viscosity and time with reference to curing of different two-components epoxy coatings[2].
Solvent-borne : solvent-borne two-components epoxy paints based on <u>*solid*</u> *epoxy resins*
Solvent-free : solvent-free two-components epoxy coatings based on <u>*liquid*</u> *epoxy resins*

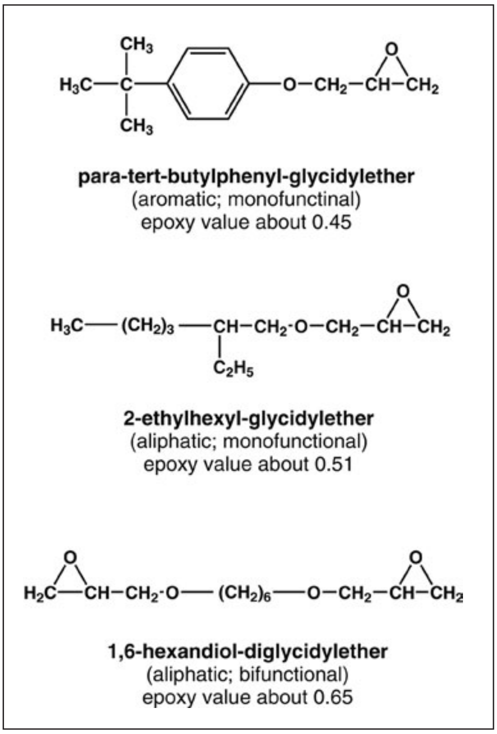


Figure IV-1.5: Examples of reactive diluents in solvent-free two-components epoxy coatings

Table IV-1.2: Self-levelling, solvent-free, two-components epoxy coating composition, e.g. for floors[6]

pos.	raw material	parts by weight
A-component		
01	epoxy resin	42.0
02	pigment	5.0
03	quartz powder (filler)	49.0
04	defoamer	2.0
05	benzyl alcohol	2.0
sum A		100.0
B-component (hardener)		
06	polyamine	20.0

pos. 01: low-viscous, liquid epoxy resin based on bisphenol A and F (+ monofunctional reactive diluent), epoxy value 0.52, epoxy equivalent mass 193, e.g. Polypox E 403 (UPPC).
pos. 03: silica flour, average particle size d_{50} *10 µm, density 2.65* g/cm^3*, e.g. Sikron SF 300 (Quarzwerke)*
pos. 04: e.g. mixture of two defoamers: Byk A 530 and Efka 2020
pos. 05: levelling agent
pos. 06: modified cycloaliphatic polyamine (solvent-free), NH-equivalent mass about 93, e.g. Polypox H 354 L (UPPC)

Formulation

Characteristic values of the formulation (Table IV-1.2):

P/B = (5 + 49) : (42 + 20) = 0.87 : 1

Mostly, solvent-free coatings contain lower amounts of pigments and fillers than solvent-borne paints.

Hardener addition/100 g epoxy resin = epoxy value · NH-equivalent mass = 0.52 · 93 = 48.4. For 42 g epoxy resin, 20.3 g hardener is needed; the reaction is virtually stoichiometric.

Applications of solvent-free two-components epoxy coatings

- Buildings, structures:
  - Coatings for mineral substrates
  - Resin-based mortars and concrete
  - Resins for injection
- Thick-film anticorrosion coatings (e.g. interior coatings for containers)

1.3 Coatings based on unsaturated polyester resins

Two-components systems based on unsaturated polyester resins differ from two-components polyurethane and two-components epoxy coatings in that the hardener is not a reactive binder component but rather an initiator (peroxide) which triggers the crosslinking reaction (radical polymerization) of the unsaturated polyesters. Thus, the addition level of the hardener in two-components systems based on unsaturated polyester resins is much lower than for two-components polyurethane and epoxy coatings.

Unsaturated polyester resins are mostly linear, soluble polycondensates of unsaturated (in some cases saturated) difunctional carboxylic acids and multifunctional alcohols. Unsaturated dicarboxylic acids are mostly maleic anhydride (MAA) or fumaric acid. The usual multifunctional alcohols are ethylene glycol, 1,3-propanediol, diethylene glycol, 2,2-dimethyl-1,3-propanediol (neopentyl glycol) and others.

Reactive diluents

As a rule, unsaturated polyester resins or coating compositions thereof contain one copolymerizable monomer by way of reactive diluent, mostly styrene. In spite of its negative physiological effects, styrene is still the most common reactive diluent because of its cost, hardness, gloss and reactivity. New developments are aimed at styrene-free and monomer-free systems.

Peroxide hardeners

Coating compositions based on unsaturated polyesters react after addition of a peroxide hardener by free-radical (co-)polymerization. Since a unsaturated polyester resin has more than one double bond per molecule, crosslinking occurs during copolymerization with styrene. Moreover, unsaturated polyester resins, as one-component systems, may be cured by radiation (see Chapter IV-2).

Suitable peroxides (Figure IV-1.6) are mostly made in a paste in an inert liquid (e.g. plasticizer) and are added at about 2 wt.% (calculated on unsaturated polyester + styrene) shortly before application.

Hydroperoxides are cleaved by cobalt soaps to yield free-radicals (compare dryers, Chapter II-1.2.3); addition to unsaturated polyester: 0.02 to 0.05 wt.% cobalt metal. Possible health risks of cobalt compounds shoud be borne in mind.

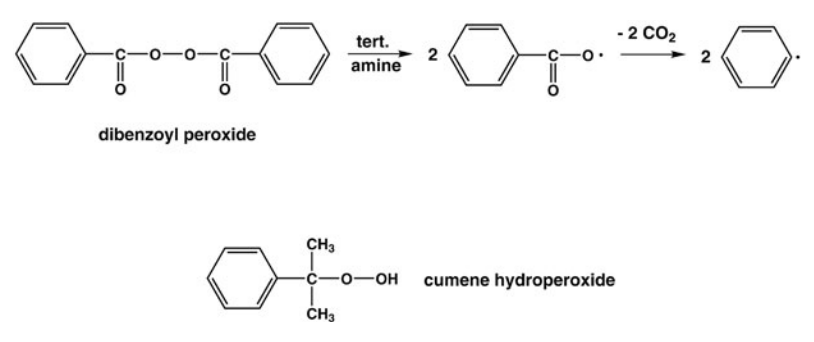


Figure IV-1.6: Two examples of peroxide hardeners, illustrated by the decomposition reaction of dibenzoyl peroxide

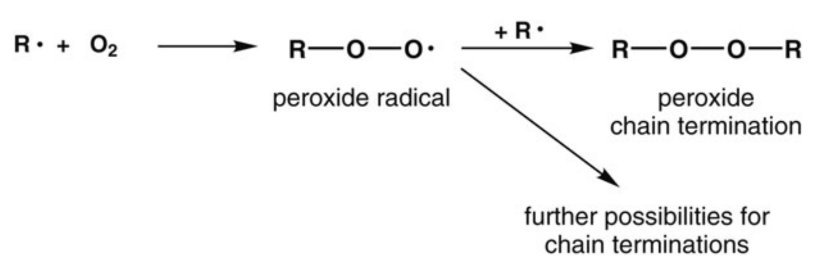


Figure IV-1.7: Inhibition by oxygen; diradical oxygen O_2 : "• O-O •"

Acyl peroxides (e.g. dibenzoyl peroxide) are decomposed quickly by tertiary amines (Figure IV-1.6) and are used in knifing fillers for automotive repair. Often, the amines are already added by the resin manufacturer to unsaturated polyester resins for knifing fillers (see formulation in Table IV-1.3). Moreover, additives such as promoters (e.g. acetyl acetone) and stabilizers (e.g. hydroquinone) may be used.

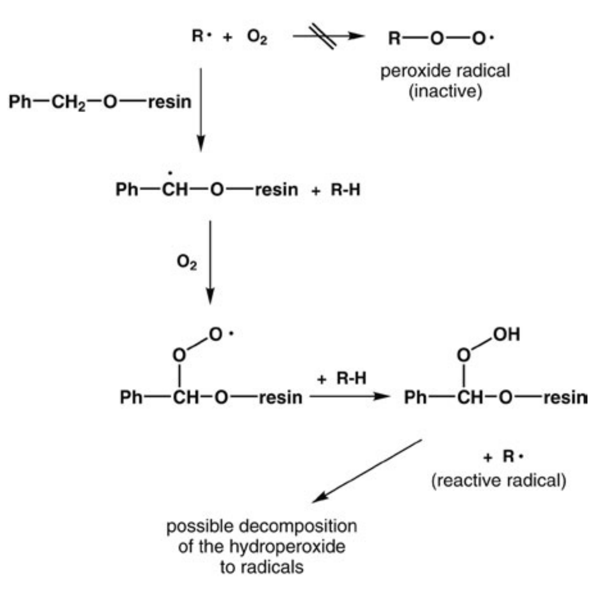


Figure IV-1.8: Possible explanation of the action of benzyl ethers (Ph = phenyl)

Inhibition by oxygen

Because of its diradical properties, atmospheric oxygen inhibits the free-radical copolymerization of the common unsaturated polyester resins (MAA, phthalic acid and glycols) with styrene. Thus, in thin layers, they yield only soft films; thicker layers remain tacky on the surface. The reason for this inhibition by oxygen is the formation of relatively stable peroxide radicals, which may cause premature chain termination (Figure IV-1.7) [4, 5].

Thus, small portions of masking materials (e.g. hard paraffins, waxes) are added to coating compositions based on unsaturated polyester resins. During copolymerization (increase in molar mass), the paraffin loses its solubility and separates on the film surface to form a protective (and flat) layer.

The second way to obtain hard films is to incorporate autoxidisable functional groups (e.g. allyl or benzyl ethers, Figure IV-1.8) into the unsaturated polyester resin (air-drying or gloss polyesters). Certain amines may act similarly.

Furthermore, several methods now exist for obtaining fully cured, hard coatings based on unsaturated polyester resins [4].

Formulation

It is important in knifing fillers that the filler particles (extenders) do not cause too much sanding resistance. For this reason, plenty of talc is often used because it is the softest filler (extender) and has a Mohs' hardness of 1.

Table IV-1.3: Knifing filler for automotive repair based on unsaturated polyester [7]

pos.	raw material	parts by weight
A-component		
01	unsaturated polyester resin (65 wt.% in styrene)	30.0
02	additive (wetting)	0.5
03	additive (rheology)	1.0
04	pigment (inorganic)	2.5
05	talc	44.0
06	other fillers (extenders)	20.0
07	styrene	2.0
sum A		100.0
B-component (hardener)		
08	dibenzoyl peroxide paste (50 wt.% in plasticizer)	1.5 - 3.0

pos. 01: high reactive, amine accelerated unsaturated polyester resin, 65 wt.% in styrene, acid number max. 15 mg KOH/g, e.g. Roskydal K 40 T (Bayer)
pos. 05: talc, max. particle size < 50 µm
pos. 06: dolomite, carbonate or baryte
pos. 07: styrene for adjusting viscosity
sroduced with a dissolver
potlife (20 °C) 6 to 4 min; sanding is possible after 20 to 10 min (depending on hardener addition level)

The pigment/binder ratio of the knifing filler is calculated as follows.

P/B = (2.5 + 44 + 20) : (30 + 2 + 1.1*) = 66.5 : 33.1 = 2 : 1

* Plasticizer from the benzoyl peroxide paste (average value)

The reactive diluent styrene remains in the film and has to be calculated as binder.

For example, coatings based on unsaturated polyester resins are used in closed-cell coatings for wooden furniture (knifing fillers, primers, primer surfacers, topcoats) and automotive coatings (knifing fillers).

1.4 References

[1] Starting formulation of Bayer AG
[2] M. I. Cook, D. A. Dubowik, F. H. Walker, Farbe & Lack 106, No. 4 (2000) p. 28-43
[3] Brochure of Witco (now Huntsman) "Oberflächenschutz II"
[4] D. Stoye, W. Freitag, Lackharze, Hanser-Verlag 1996, p. 85-89
[5] B. Vollmert, Makromolekulare Chemie, Vol. 1, Vollmert-Verlag 1982, p. 76
[6] Starting formulation of UPPC AG
[7] Starting formulation of Bayer AG (RR 4480)

2 Radiation curing

2.1 Definitions

When specific compounds, mainly those containing double bonds, are exposed to high-energy electromagnetic waves, the results are crosslinked polymers. The reaction is very effective. It is possible to start with really low-molecular compounds and to effectively crosslink them into higher molecular structures. The low-molecular starting compounds may be liquids of relatively low viscosity, i.e. they can serve as the basis of solvent-free formulations.

There are two types of radiation curing, crosslinking by ultraviolet light (UV) and by electron beam (EBC).

UV curing occurs when films of paint containing unsaturated compounds are treated with ultraviolet light emitted by special UV radiators. The UV light reacts with UV initiators (photoinitiators) to generate free-radicals. The free-radicals trigger polymerization of the unsaturated compounds. Sometimes it is necessary to combine the UV initiators with UV sensitisers. If the unsaturated compounds of the paint coat contain enough double bonds, the process yields coatings of high crosslinking density.

Other compounds (e.g. epoxy resins) can be crosslinked by UV light with the aid of catalysts that generate cations. This process is rarely used for coatings.

High-voltage electron beams can generate free-radicals in unsaturated compounds directly. Again, a free-radical polymerization process yields a crosslinked molecular network. There is no need to use initiators.

2.2 UV curing

2.2.1 Principles of UV curing

UV light consists of electromagnetic waves with wavelengths ranging from 100 to 400 nm. Since this wavelength range is shorter than the violet light visible to the human eye, such radiation is called ultraviolet light. The photons in this chapter of the electromagnetic spectrum have energies ranging from 300 to 760 kJ/mol. As the energies of chemical bonds are of the same order of magnitude, UV light can activate the bonds for reactions[1].

However, the very highly energetic light of short electromagnetic radiation (wavelengths of 100 to 280 nm) is absorbed by the upper layers of a film, and that leads to incomplete curing of the lower layers. Consequently, for the entire film to be cured effectively, UV light of longer wavelength is preferred (315 to 380 nm).

To start the reaction, it is necessary to use UV initiators, sometimes in combination with UV sensitisers. The UV initiators form free-radicals. As is the case for other free-radical polymerization reactions, atmospheric oxygen inhibits polymerization, primarily on the upper film layers. In practice, curing is effected by a compromise of mainly UV light of longer wavelengths (315 to 380 nm), complemented with additional, smaller amounts of UV light of wavelengths below 315 nm. This smaller portion guarantees that the surface of the film will be cured efficiently and decreases the inhibitory effect of oxygen.

As the energy density of UV light is inadequate for the polymerization reaction, photo-initiators and sometimes photo-sensitisers have to be used. The UV light transforms the reactive group of an UV absorber or a UV sensitiser into an excited state. The excited molecules form free-radicals by cleavage of bonds or by adding hydrogen atoms. The processes are described in detail in the literature [1, 2].

The free-radicals trigger free-radical polymerization at the double bonds of the ingredients of the UV system. The reactions are the same as those which take place when peroxy initiators are used, e.g. in the curing of unsaturated polyester resins (see Chapter IV-1.3). Here, too, the sequence is initiation, chain propagation, chain termination by re-combination, free-radical transfer or disproportionation. However, in the case of UV curing, there is a possibility of side-reactions by deactivation of initiator molecules and emission of light (fluorescence or phosphorescence) or by reaction with free-radical scavengers. Direct recombination of initiator free-radicals may also take place and the aforementioned inhibition by oxygen of air.

2.2.2 UV coating process

After application, UV systems are cured in very short times by irradiation with UV light from various UV emitters.

Protective measures

UV curing paints are so-called 100% systems and, as such, play an important role in environmental protection because there is nearly no emission of volatile organic compounds. Nevertheless, precautions are needed when UV systems are handled and used. Some of the ingredients of UV paints are a health hazard. Contact with skin has to be avoided. Although UV systems crosslink at ambient temperatures, heat is evolved and may cause some amount of the UV coating can evaporate. For this reason, extraction and cooling of the waste air are required.

Further, human skin and especially the eyes have to be protected against UV light because it is harmful (causes burns, cancer). Finally, UV light leads to the production of ozone (the extent of that depends on the type and intensity of emitter), which also has to be exhausted carefully.

UV coating equipment

The viscosity of solvent-free UV paints earmarks the systems primarily for roller coating or curtain coating. There are only a few instances of spray application.

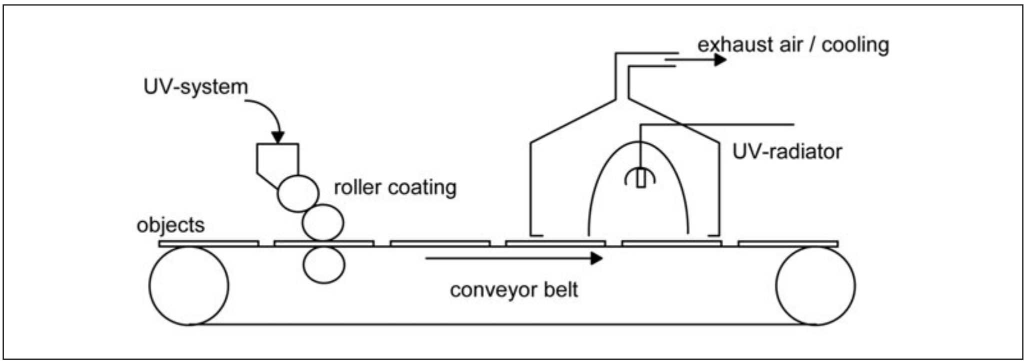


Figure IV-2.1: Schematic diagram of UV coating equipment

UV curing is particularly suitable for coating of planar objects (wood plates, laminate sheets and foils). It can be applied continuously and in automated systems, a fact which perfectly meets the aforementioned protection requirements (masking of the coating line, exhausting). Special measures are needed for coating more complex geometrical surfaces. A schematic diagram of typical equipment is presented in Figure IV-2.1. It consists of a conveyor belt for the objects (e.g. wooden slabs), paint feed and application rollers, UV emitter and exhausting box. The emitter is installed inside the box. Sometimes, the emitter or objects have to be cooled.

UV emitter

Of course, the most important part of the equipment is the UV emitter. There are different types. The most common are high-pressure mercury vapour lamps. Such lamps emit light in the range from 50 to 2000 mm in length. They deliver between 80 and 120 W/cm. The radiation yield is 25% over the full UV range and about 60% over the infrared range. A large amount of heat is therefore generated. The working temperature of the lamp is about 600 °C. Cooling ensures that the surface of the lamp is a maximum temperature of 400 °C. There are two reasons for cooling. First, it increases the service life to at least 2,000 hours. Second, the crosslinking reaction is much more reproducible. There are various forms of cooling equipment: air only, water only, or a combination of both. Air-cooling requires volumes of 30 to 50 m^3/h for each kW of energy emanating from the emitter. High-pressure mercury vapour lamps have emission maxima at wavelengths of 254; 302; 313; 366; 405 and 436nm. The spectrum of radiation energy emitted by a typical high-pressure mercury vapour lamp is presented in Figure IV-2.2 [3].

High-pressure mercury vapour lamps can be modified by doping them with iron or gallium compounds. This extends their energy ranges.

There are also UV radiators whose light is excited by microwaves. In this case, the high-energy microwaves produce a plasma in light tubes containing a readily ionisable gas (e.g. mercury vapour). The plasma induces UV light. The type of vapour employed determines the spectrum of light generated.

Low-pressure mercury vapour lamps have also been in use for a long time. They are comparable to the familiar fluorescent tubes, but contain a vapour that emits UV light. The radiation

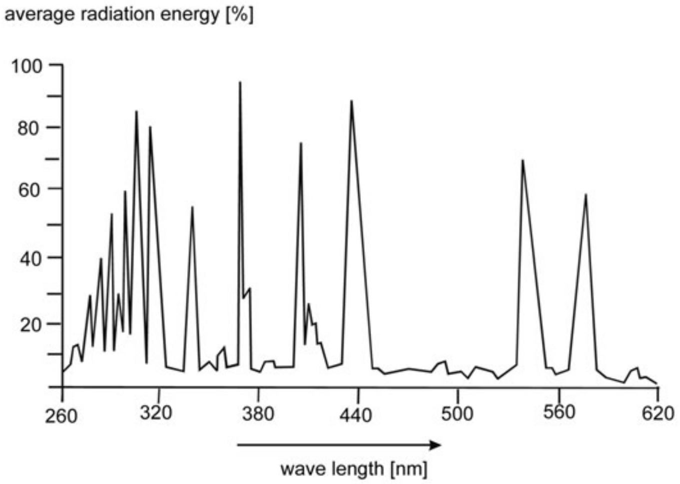


Figure IV-2.2: Radiation energy emitted by a typical high-pressure mercury vapour lamp energy of these lamps is relatively low, with the maximum emission occurring at 355 and 405 nm. UV light of such wavelengths can penetrate deeply into coatings. This type of lamp is therefore preferred for curing pigmented systems, which, however, must contain specific UV initiators. The advantage of such lamps is that they do not need any cooling.

The choice of UV lamp employed depends on the application, i.e. the type of UV paint and substrate. UV curing is, of course, influenced by the radiation energy, light spectrum and exposure time. These should be matched to the type of UV paint and the UV initiator which it contains.

Besides the lamp, the UV emitter consists of an elliptical or parabolic reflector that serves to direct the UV beams onto the substrate efficiently. The reflectors are cooled either by air or by water.

2.2.3 UV initiators and sensitizers

As mentioned above, UV initiators are compounds that absorb UV light to form excited bond states, followed by cleavage into free-radicals. However, UV sensitisers are compounds which also absorb UV light, but which transfer the absorbed energy to other molecules, which can cleave into free-radicals (intermolecular reaction). There are different classes of UV initiators, all developed for different application fields. Most of them contain a benzoyl moiety in the molecule. The other molecular groups and substituents define the wavelengths of the absorption maxima, the reactivity, and the yield of free-radicals. All these properties determine the optimum field of application for the initiator.

Besides reactivity, the choice of UV initiator depends on storage stability (in the dark, of course), solubility, compatibility, and yellowing resistance. The initiator should readily miscible with the UV systems, and so liquid products are preferred. The products have to be harmless and not have a strong odour. Last but not least, costs must be considered [2].

The simplest UV initiator is **benzophenone**. Benzophenone and its alkyl derivatives can form free-radicals together with hydrogen donors (see Figure IV-2.3). The free-radicals

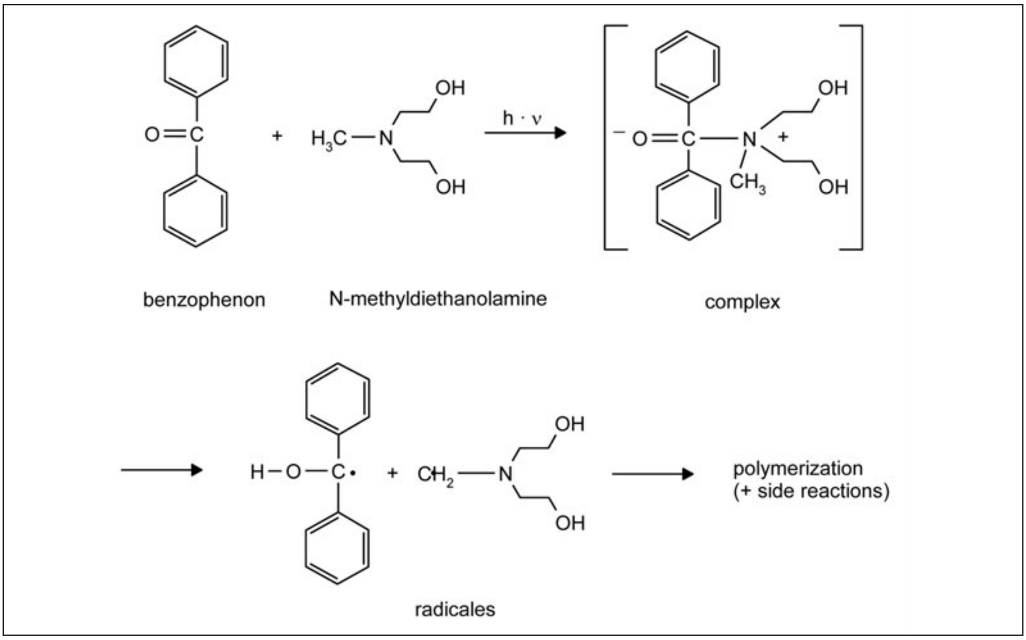


Figure IV-2.3: Free-radical formation of benzophenone and N-methyl diethanolamine

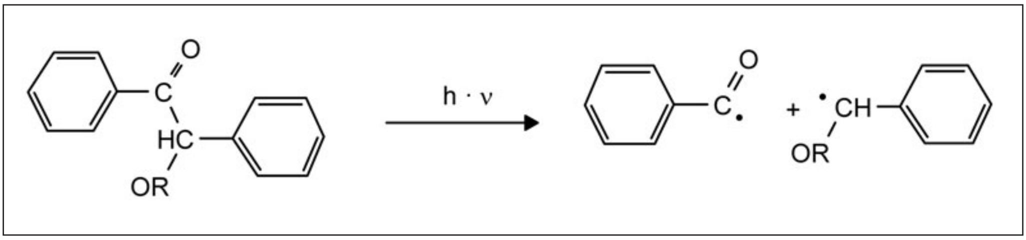


Figure IV-2.4: Free-radical formation of benzoin ethers

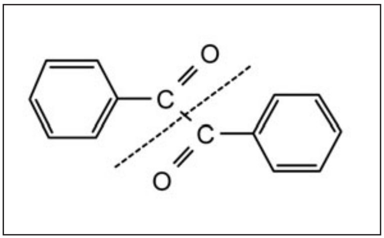


Figure IV-2.5: Benzil

(diphenyl hydroxy methyl radical) can initiate the polymerization process, but can also form dimers (benzo pinacol). Hydrogen donors are mainly tertiary amines (e.g. N-methyl diethanolamine amine, triethanolamine). Also suitable are polymers and oligomers that contain tertiary amine groups. Combinations of benzophenone and tertiary amines are inexpensive. They suffer from a tendency to yellow. Because the amine counteracts inhibition by oxygen, surfaces cure well. But thick layers do not cure fully.

Also long established are the **benzoin ethers** (see Figure IV-2.4). These form free-radicals directly (so called α-cleavage), which are highly reactive. However, systems containing benzoin ethers have poor storage stability. Like benzophenone combinations, they also exhibit yellowing, especially when the coatings are exposed to sunlight. Benzoin ethers are suitable for UV coatings on wood that contain unsaturated polyesters as the main resin component.

Benzil [2] and its alkyl derivatives (see Figure IV-2.5) are UV initiators which, like benzophenone, need hydrogen donors. On one hand, benzil combinations have the advantage of absorbing UV light up to wavelengths of 450 nm, and so they are highly suitable for pigmented UV paints. On the other hand, their use is restricted because the initiator systems generate much yellowing.

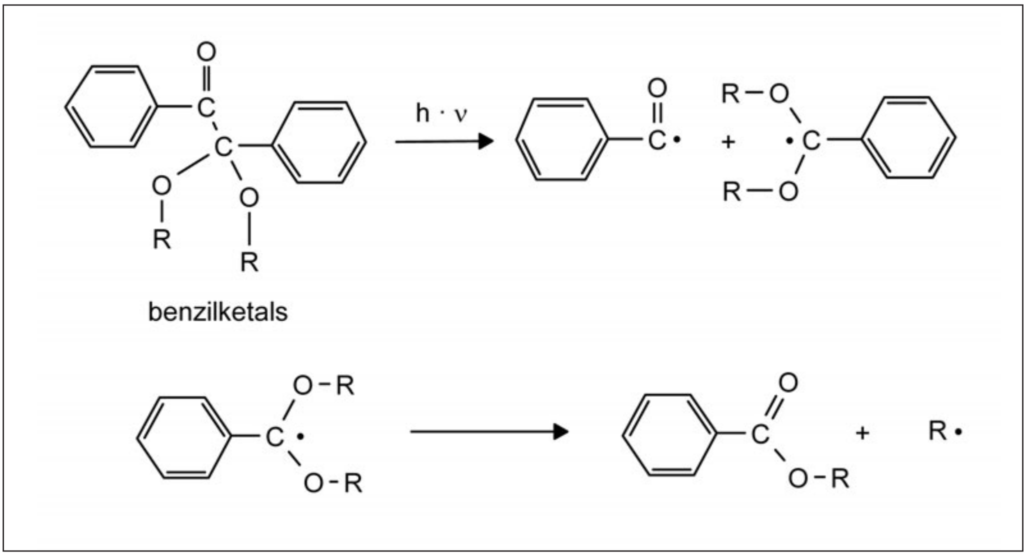


Figure IV-2.6: Free-radical formation of benzil ketals

Much less yellowing is exhibited by **benzil ketals**, which are very reactive. These form free-radicals directly (α-cleavage). Their reactivity stems from the higher yield of free-radicals since one molecule of benzil ketal can form four free-radicals (see Figure IV-2.6). This means it is possible to lower the amount of initiator added. Benzil ketals are used for clear coats and wood paints. They also cure effectively in thick layers. Due to their wide absorption spectrum, the initiators are suitable for pigmented UV systems. Their use offers optimum cost-effectiveness.

Due to the directing effect of their hydroxyl group, **α-hydroxy alkyl phenones** have high reactivity. Furthermore, these initiators are heat resistant [2]. Derivatives that contain aliphatic side chains are liquids, and are more suitable for solvent-free paints. But 1-hydroxy cyclohexyl phenyl ketone (see Figure IV-2.7) is a solid notable for its excellent storage stability. Additionally, it is virtually odourless.

The **α-amino alkyl phenones** (an example is shown in Figure IV-2.8) have structures comparable to those of α-hydroxy alkyl phenols. In contrast to the hydroxyl group in the α-position, it is the amino group which shifts the absorption maxima to higher

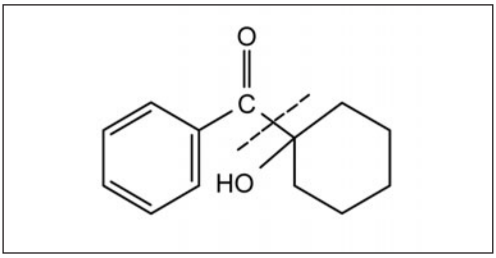


Figure IV-2.7: 1-Hydroxy cyclohexyl phenyl ketone

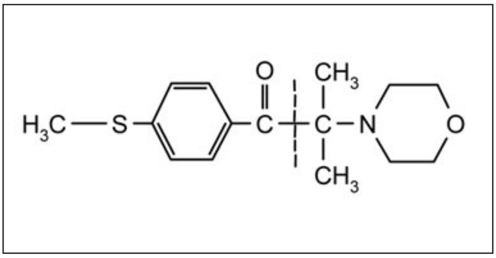


Figure IV-2.8: α-Amino alkyl phenone

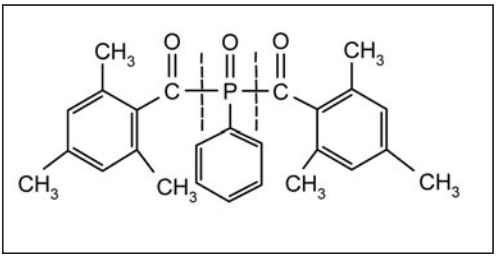


Figure IV-2.9: Dibenzoyl phosphine oxide

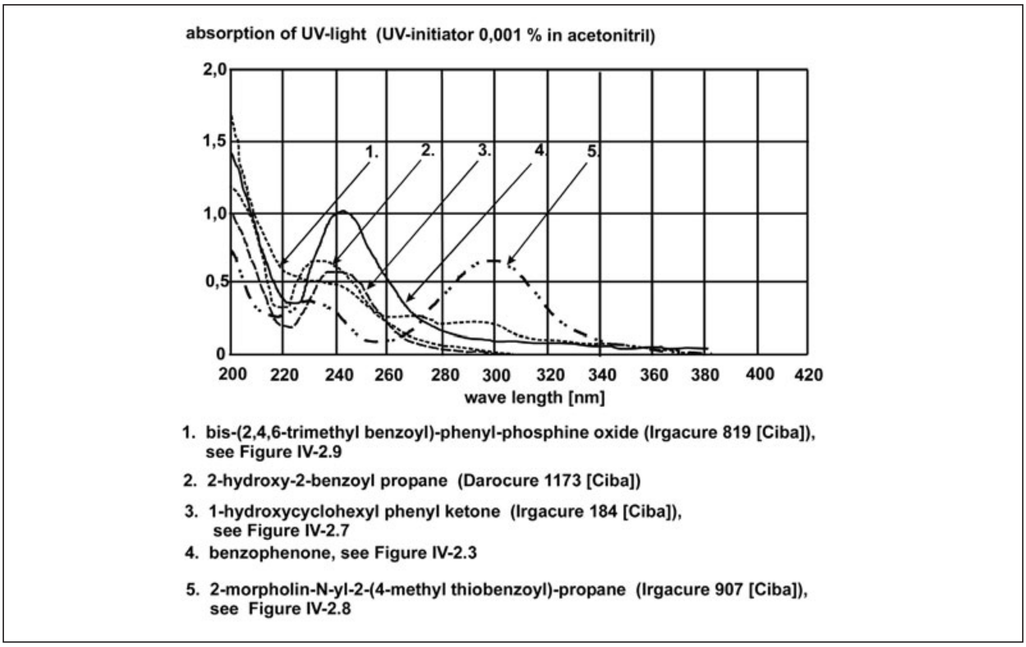


Figure IV-2.10: Absorption curves for various UV initiators wavelengths. Initiators from this group are therefore suitable for pigmented UV systems. However, this fact is also the reason for an enlarged yellowing tendency.

The latest group of UV initiators is that of **benzoyl phosphine oxides** (mono- and dibenzoyl phosphine oxides). The commercial products are characterized by high reactivity combined with excellent stability. The dibenzoyl phosphine oxides have high free-radical yields because two types of cleavage are possible. Benzoyl phosphine oxides absorb UV light of higher wavelengths. An example is presented in Figure IV-2.9. Although they show initial yellowing, this discolouration disappears after a time, when all initiator molecules have decomposed. The products are also recommended as initiators for pigmented UV systems.

The free-radical yield and the range of wavelengths for absorption determine the choice and type and amount of UV initiators to use. Figure IV-2.10 shows the absorption curves for some typical UV initiators [4]. The amount of initiator addition varies with the type of UV paint, but can be as much as 3 wt.%. Some suppliers recommend mixtures of initiators that are claimed to confer optimum reactivity and full cure.

2.2.4 Resins for UV coatings

Unsaturated polyesters

Unsaturated polyesters, which are described in Chapter IV-1.3, are a group of resins also suitable for UV curing [1, 2]. Constituents of unsaturated polyester are maleic anhydride and other dicarboxylic acids and diols. The most commonly used reactive diluent is styrene. Those resins which are chosen for UV curing are modified with compounds that avoid the inhibitory effect of oxygen on the curing process (e.g. tetrahydrophthalic anhydride, allyl ethers of polyols).

Besides the aforementioned method of using initiators (peroxides) or accelerators (cobalt salts, amines) to effect crosslinking of unsaturated polyesters at ambient temperatures by means of polymerization, a combination of unsaturated polyesters and styrene is also cured by UV light and the effect of UV initiators. The resultant films are hard, glossy and chemically resistance, but not weather resistance. The systems are mainly used for wood finishing.

Resins with acrylic groups

The second, more important group of resins for UV coatings are polymers or oligomers that contain unsaturated acrylic groups. Acrylic acid or its esters are preferred over methacrylic acid or esters, since acrylic acid incorporated into resin molecules is much more reactive in UV curing. There are different ways of incorporating acrylic acid or its derivatives into resin molecules. The following resin sub-groups exist: epoxy acrylates, polyester acrylates, polyether acrylates, polyurethane acrylates, unsaturated acrylic resins, and silicone acrylates.

Epoxy acrylates

Epoxy acrylates are produced by the reaction of epoxy resins (aromatic types containing bisphenol A) with free acrylic acid. In the reaction, the acrylic acid adds to the epoxy group to form β-hydroxy esters (see Figure IV-2.11). The products of the reactions are dissolved in reactive diluents (see Chapter IV-2.2.5). UV paints containing epoxy acrylates are distinguished by high reactivity, hardness, and excellent chemical resistance. However, they are not weather resistance and exhibit yellowing.

Polyester acrylates

Polyester acrylates are the products of the condensation reaction between mostly linear polyesters bearing terminal hydroxyl groups and acrylic acid. The esterification has to be

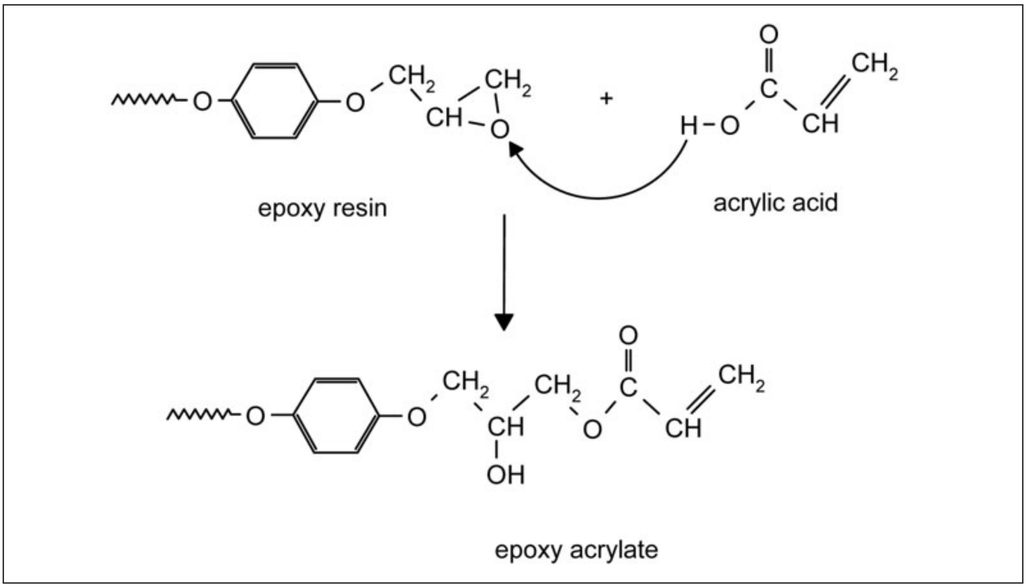


Figure IV-2.11: Preparation of epoxy acrylates

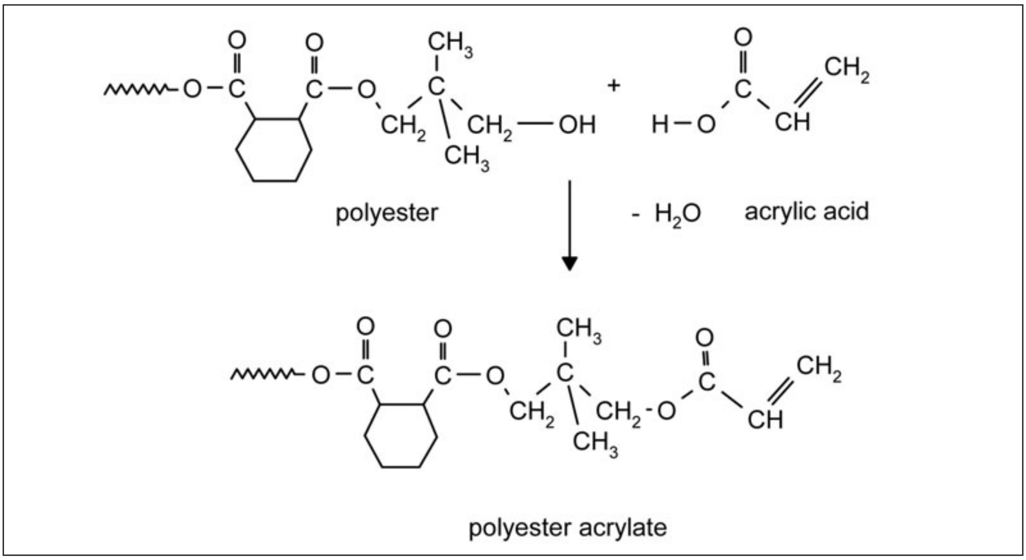


Figure IV-2.12: Preparation of polyester acrylates

carried out at low temperatures, and that requires the use of catalysts. Additionally, polymerization inhibitors have to be added to protect the double bonds of the acrylic acid.

The choice of polyester molecule can be used to determine whether the resins yield flexible or hard films after curing. Judicious choice of polyester building blocks will ensure the cured films are weather resistance and free from yellowing. The products are highly suitable for pigmented UV paints. While polyester acrylates may have lower chemical resistance than epoxy acrylates, it is much better than that of many other types of chemically cured paint systems.

Polyether acrylates

Like polyester acrylates, polyether acrylates are products of linear polyethers containing terminal hydroxyl groups (polyethylene glycols, polypropylene glycols, and copolymers

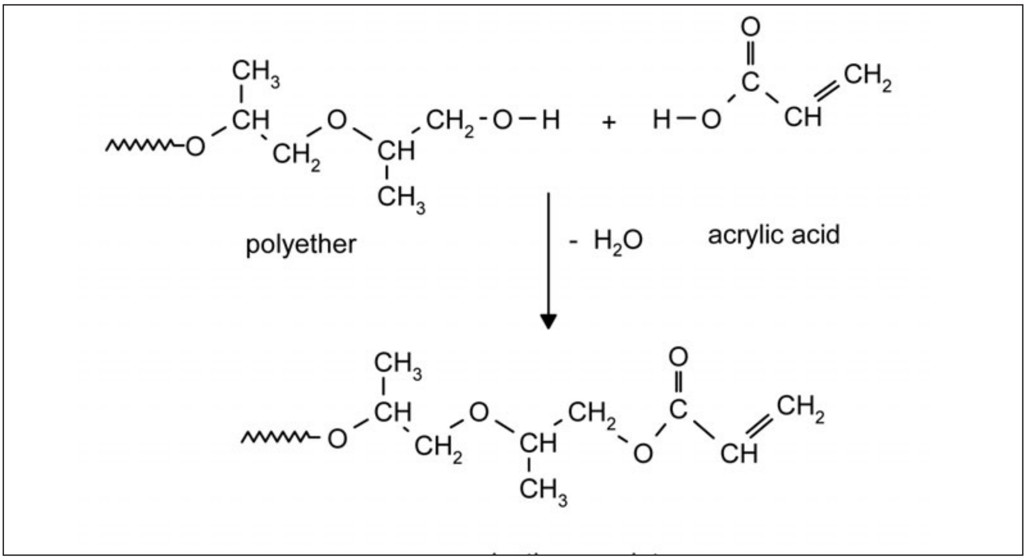


Figure IV-2.13: Preparation of polyether acrylates

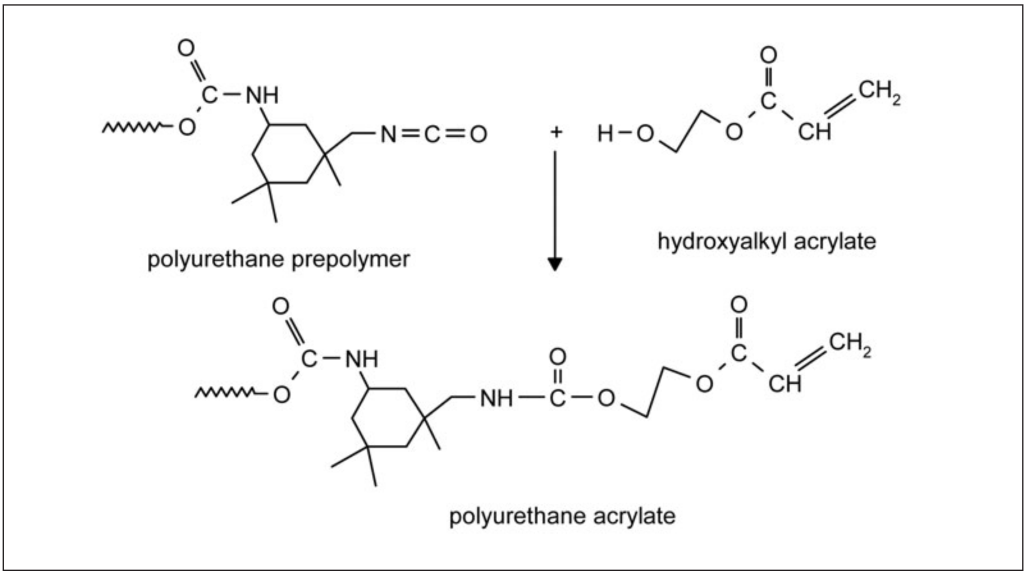


Figure IV-2.14: Preparation of polyurethane acrylates

of both) and acrylic acid. The polyethers are prepared by adding definite amounts of ethylene oxide or propylene oxide on diols. But there are also branched products, where the polyethers are formed by reaction of polyols (triols and tetraols) with ethylene or propylene oxide. The films formed by UV curing are distinguished by particular flexibility and saponification resistance. However, the films are not weather resistance.

Polyurethane acrylates

Polyurethane acrylates are the product of the reactions between polyurethane prepolymers bearing terminal isocyanate groups and hydroxyalkyl acrylates (monoesters of acrylic acid and different diols). The product of the reactions contain terminal double bonds (see Figure IV-2.14), and can be crosslinked – mainly combined with reactive diluents – by UV curing.

The films exhibit excellent flexibility. The flexibility is supported by the hydrogen bonds formed from urethane groups. If the prepolymers consist of suitable compounds (polyester soft segments without aromatic structural elements, and with aliphatic or cycloaliphatic diisocyanates), the polyurethane acrylates offer excellent weather and chemical resistance. Due to the high reactivity and outstanding properties of films formed from polyurethane acrylates, they are used for high-quality coatings.

Unsaturated acrylic resins

The most important way of preparing unsaturated acrylic resins is to add acrylic acid to the epoxy groups of acrylic polymers that contain glycidyl methacrylate as co-monomer. The resultant binders are used in combination with reactive diluents for weather resistance and non-yellowing UV coatings.

Silicone acrylates

Silicone acrylates are prepared either by making polydialkyl siloxanes bearing terminal silanol groups react with hydroxyalkyl acrylates or by adding acrylic acid to polydialkyl siloxanes bearing terminal epoxy groups. The binders are used for non-stick coatings.

2.2.5 Reactive diluents for UV coatings

The UV systems described here do not contain any conventional solvent. The application viscosity of the paints is realized by adding so-called reactive diluents. These are compounds which act like solvents, but which can be incorporated into the crosslinking reaction. The unsaturated polyesters already described in Chapter IV-1.3 are also combined with reactive diluents (mainly styrene). For UV systems, the most important reactive diluents are monomers containing esters of acrylic acid. Due to their lower reactivity, esters of methacrylic acid are not considered. The type and amount of reactive diluents chosen significantly influence the viscosity and reactivity of the UV paints, followed by the crosslinking density and other related properties of UV cured films.

Monoesters of acrylic acid

Monoesters of acrylic acid are used if the crosslinking density after curing is relatively low. Low-molecular esters of acrylic acid evaporate relatively easily, are physiologically harmful or have an unpleasant odour. Therefore, the monoacrylates which are suitable for UV systems are esters of acrylic acid and higher-molecular monoalcohols, such as octyl, decyl, phenoxyethyl, narbonyl, and dicyclopentanedienyl acrylate. Hydroxyalkyl acrylates also serve as reactive diluents. Their residual hydroxyl groups allegedly support intercoat adhesion. All monoacrylates are good solvents; however, they act additionally as thinners that lower viscosity efficiently.

Acrylic esters of polyols

For a long time, the acrylic esters of polyols have been the most important reactive diluents for UV paints: hexanediol diacrylate (HDDA), trimethylol propane triacrylate (TMPTA), pentaerythritol triacrylate (PETrA), and pentaerythritol tetraacrylate (PETeA). They make it possible to strike an optimum balance of thinning effect and high reactivity. Films containing tri- and tetraesters offer outstanding hardness and scratch resistant. However, the greater the ester functionality, the less pronounced is the thinning effect. Acrylic esters of polyols have a relatively low vapour pressure at ambient temperatures, and so they should be quite harmless. However, on contact with skin, they can cause allergic reactions and cause sensitisation. For this reason, the use of these esters is restricted nowadays.

From health aspects, the esters of polyfunctional polyether polyols are less risky: diethylene diacrylate, dipropylene diacrylate, acrylic esters of ethoxylated polyols, such as glycerol, trimethylol propane, di-trimethylolpropane, pentaerythritol and di-pentaerythritol. The molecular mobility of ether groups confers optimum thinning properties on the products. Although the crosslinking density obtained with the use of these polyfunctional acrylates is high, the films are still flexible. However, the ether groups render their weatherability inadequate in some applications.

2.2.6 Properties and application of UV coatings

UV coatings are formed by copolymerization reactions between UV curing resins and reactive diluents. The molecular structure of such films is shown schematically in Figure IV-2.15.

Analytical studies show that the crosslinking density in cured UV coatings is generally higher than in most other crosslinked films. Since the network structure is formed mainly by C-C-bonds, there is excellent chemical resistance to acids and bases.

UV coatings are characterized by resistance to mechanical influences, and offer excellent scratch resistance. The flexibility of films can be adjusted by selecting more or less plasticizing molecular structural elements of resins and reactive diluents. This makes UV coatings suitable for plastic parts.

However, the most important application areas for UV systems are wood coatings for furniture, parquet sealers, and laminate sheets. The coating and curing process is especially suitable for these generally planar objects. The other key application area is the coating of papers and foils. There are also UV curing printing inks, printing sealers and laminates. Finally, there are can-coating and coil-coating applications.

It is really difficult to apply UV coatings to three-dimensional substrates. There are two main problems. On one hand, the viscosity of UV paints is not low enough for spray application. Recourse to conventional solvents to reduce the viscosity negates the advantage of solventless paints. On the other, the UV radiation does not reach all the parts of such objects uniformly, crosslinking proves to be irregular and this adversely affects the film properties.

Consequently, UV curing has not yet been introduced into automotive OEM coatings, even though its specific properties are required there, especially scratch resistant. But UV coating is used for coating of several automotive add-on pieces and for wheel rims.

Thin-film application does not present a problem. Thick layers require specific UV initiator combinations that work on the outer surface but also allow the UV light to penetrate into deeper layers to start crosslinking reactions.

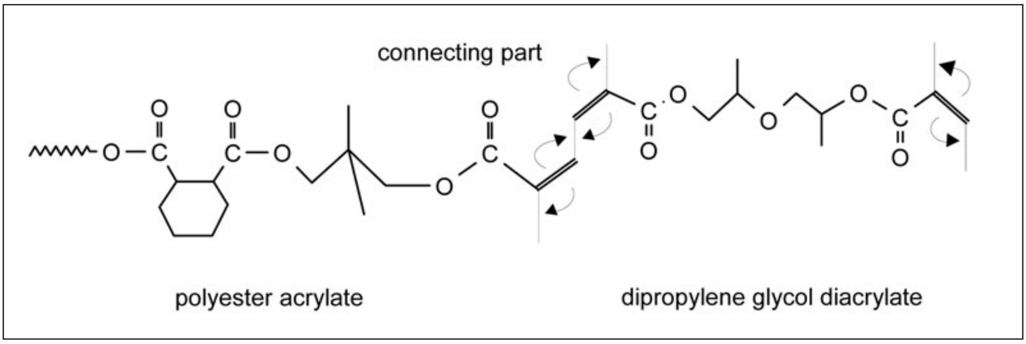


Figure IV-2.15: Schematic structure of molecules in UV coatings

Surprisingly, UV initiators can be combined with suitable UV absorbers (hydroxyphenyl triazines) and free-radical scavengers to confer weatherability on clear coats. Hardly any hindering of the crosslinking reaction occurs [5].

UV curing of pigmented systems is still a problem since several pigments absorb UV light [6, 7]. For these cases, the UV initiators selected permit effective penetration of UV light, and, additionally, can absorb light at wavelengths at which pigments reflect the UV light. Different pigments require individual initiator combinations and amounts for effective crosslinking.

To overcome the problem of application on three dimensional objects, so-called “dual-cure” systems have been developed. Besides UV curing, these products crosslink additionally by other reactions. Both curing processes seek to guarantee curing of all parts of the objects. Of course, this means that compromises have to be accepted on properties. Certainly, most dual-cure systems are no longer solvent-free.

Finally, there are also powder coatings which crosslink on exposure to UV light [8], see Chapter IV-3.4.2.4.5.

2.2.7 Typical UV coatings

The following examples are designed to aid an understanding of UV coating compositions.

UV clear coat for parquet sealing (roller coating)

For parquet sealing, a combination of a polyester acrylate and a trifunctional polyether acrylate is chosen [9]. The formulation contains a silica gel, a matting agent, and talc. The UV initiator is an α-hydroxyalkyl phenone. There is a trace of solvent (butanol). Details of the formulation are presented in Table IV-2.1.

The clear coat is produced in a dissolver.

The ratio of pigment versus binder and the PVC are calculated as follows.

Table IV-2.1: UV clear coat for parquet sealing

pos.	raw material	density [g/cm³]	formulation [wt.%]
01	polyether acrylate (trifunctional)	1.2*	74.7
02	polyester acrylate	1.2*	8.3
03	silica gel	2.1	8.3
04	matting agent	2.1	4.1
05	talc	2.7	2.1
06	UV initiator (β-hydroxyalkyl phenone)		2.1
07	butanol		0.4
sum			100.0

** densities are calculated on crosslinked binders*
pos. 01: Laromer LR 8945 (BASF)
pos. 02: Laromer LR 8799 (BASF)
pos. 03: Syloid 621 (Grace)
pos. 04: Acematt OK 607 (Evonik Degussa)
pos. 05: Micro-Talc AT 1 (Norwegian Talc)
pos. 06: Darocur 1173 (BASF Swiss, Ciba)

$$P/B = \frac{8.3 + 4.1 + 2.1}{74.7 + 8.3} = 0.17 / 1$$

$$PVC = \frac{8.3 / 2.1 + 4.1 / 2.1 + 2.1 / 2.7}{8.3 / 2.1 + 4.1 / 2.1 + 2.1 / 2.7 + 74.7 / 1.2 + 8.3 / 1.2} \cdot 100\% = 8.8\%$$

The product is applied to primed parquet panels by roller coating at an application rate of 8 to 12 g/m³. Crosslinking is effected by UV radiation, the speed of the conveyor belt is 5m/min, and the energy of the UV lamp is 120 W/cm.

Table IV-2.2: UV topcoat, pigmented, beige coloured

pos.	raw material	density [g/cm³]	formulation [wt.%]
01	polyester acrylate	1.2*	75.00
02	hexanediol diacrylate	1.2*	8.82
03	trimethylol propane triacrylate	1.2*	4.40
04	titanium dioxide, rutile	4.1	8.82
05	isoindoline pigment	1.9	0.98
06	UV initiator (bis-acyl phosphine oxide)		0.75
07	UV initiator (1-hydroxycyclohexyl phenone)		1.23
sum			100.00

** densities are calculated on crosslinked binders*
pos. 01: Laromer LR 8800 (BASF)
pos. 05: Irgazin yellow RTL (BASF Swiss, Ciba)
pos. 06: Irgacure 819 (BASF Swiss, Ciba), see Figure IV-2.9
pos. 07: Irgacure 184 (BASF Swiss, Ciba), see Figure IV-2.7

The resultant sealer offers excellent abrasion resistance and has a gloss measurement of 30% (Gardner measurement, 60°).

Beige pigmented UV topcoat

This pigmented topcoat consists of a polyester acrylate (resin) and hexanediol diacrylate and trimethylol propane triacrylate (reactive diluents). The pigments are titanium dioxide (rutile) and an isoindoline yellow pigment (CI pigment yellow 110). The mixture of UV initiators, optimized for pigmented UV systems consists of bisacylphosphine oxide and 2-hydroxycyclohexyl phenone. The formulation is presented in Table IV-2.2.

The ratio of pigment and binder compounds and the PVC are calculated as shown below:

$$P/B = \frac{8.82 + 0.98}{75.00 + 8.82 + 4.40} = 0.1 / 1$$

$$PVC = \frac{8.82 / 4.1 + 0.98 / 1.9}{8.82 / 4.1 + 0.98 / 1.9 + (75.00 + 8.82 + 4.40) / 1,2} \cdot 100\ \% = 3.5\%$$

The pigments are dispersed together with a portion of the mixture of resin and reactive diluents by the usual grinding methods. The paint is completed by adding the remaining portions of resin, reactive diluents, and the two UV initiators. After application by roller coating – the speed of the conveyor belt is 3 to 10 m/min – the coating is cured by UV radiation from two high-pressure mercury vapour lamps at an induced energy of 80 W/cm.

2.3 Electron beam curing

Electrons accelerated by voltages of 150 to 450 kV can generate free-radicals in organic film layers. The accelerated electrons react with the electrons of molecular bonds to form cations (cleavage of a bonding electron) or anions (adding an electron), followed by generation of free-radicals from the ions. Such electrons are also able to cleave double bonds into free-radicals.

The penetration depth of accelerated electrons is influenced by the voltage levels of the electron emitters. There are different types of electron emitters that generate different levels of energy. High voltage increases the penetration depth such that the accelerated electrons can form cascades of electrons in the coating material that also create ions and free-radicals in the deeper chapters of film layers.

For electron beam curing, the resin groups used for UV curing are suitable. Preferred are resin types which can avoid inhibition by oxygen. However, the electron beams are also able to activate saturated organic compounds to form free-radicals.

Electron beam curing does not need any initiators.

In comparison to UV curing, curing with electron beams presents no problems as regards effective crosslinking of thick layers and pigmented systems. The speed of the conveyor belts may be much higher than for UV curing.

Coatings prepared by electron beam curing show much better adhesion on plastic substrates. The reason is that the electron beams also trigger formation of free-radicals on the plastic surfaces. This may lead to grafting reactions. However, that can be a disadvantage since the plastic parts may be embrittled by such reactions and molecular decomposition might take place.

The main disadvantage of electron beam curing is that it has to be carried out in inert gas in the absence of oxygen, as otherwise crosslinking is inadequate. Additionally, there are many more problems associated with curing layers on three dimensional objects than with UV curing, which still suffers from some problems. Therefore, the installation of an electron beam curing system requires much more effort than its UV counterpart.

Electron beam curing is used in the production of some furniture (e.g. door coatings) and for plastic parts. It is estimated that it accounts for just 1% of all radiation curing.

2.4 References

[1] St. Davidson: Exploring the Science, Technology and Applications of U.V. and E.B. Curing, Sita Technology Ltd., London, 1999

[2] P. G. Garatt: Strahlenhärtung, Series: Technologie des Beschichtens, Publisher Vincentz Network, Hannover, 1996

[3] High-pressure mercury vapour lamps of IST, Type CK, for up to 120W/cm

[4] Data sheets of Ciba Spec. Chem.: Irgacure and Darocure

[5] A. Valet: Outdoor applications of UV curable clear coats - a real alternative to thermally cured clear coats, Progress in Organic Coatings, 35, (1999) 223-233, Elsevier

[6] A. Valet, T. Jung, M. Köhler: UV Härtung buntpigmentierter Lacke, 63. API-Conference Bonn, October 1997

[7] T. Jung: Eisenoxidpigmente und Pigmentruße, eine Herausforderung für die UV Härtung. Farbe & Lack 104, 12 (1998) S 81

[8] L. Misev, O. Schmid (Ciba Spec. Chem.) S. Udding-Louwrier, E. S. de Jong, and R. Bayards (DSM-Resins): Weather Stabilization and Pigmentation of UV Curable Powder Coatings, Journ. Coat. Technol. Vol 71 (891), p. 37-44, 1999

[9] Data sheets of BASF AG: Laromers

3 Powder coatings

3.1 Development of powder coatings

With a few exceptions, all polymers used for paint formulations have to be converted into an application form conducive to production and use. Such forms are solvent-borne and water-borne solutions and water-borne dispersions and solvent-borne dispersions (NADs, non-aqueous dispersions). However, there is another mobile phase that can be formed, namely an aerosol. Aerosols are composed of the finest distributions of powder particles in air. The conversion of coating materials into aerosols (powder coatings) offers a wide range of possible applications.

In the early 1950s, powder coatings were applied by the fluid bed sintering process ([1] 1952). That was the first step in eliminating the use of organic solvents for application by dipping and so avoiding the risk of fire and explosion. These systems were also the first paint products to meet the requirements of environmental protection. In the 1960s, electrostatic spray application was introduced for powder coatings ([2] 1965). Since that time, powder coatings have extended their fields of application into several areas.

The market for powder coatings is still growing. Market studies [2] expect the US market to enjoy 3.5% annual growth between 2010 and 2013 to a total of 445,000,000 lb, or 201,850 metric tons. After a trough in 2008, subsequent growth rates will exceed those between 2003 and 2007.

The requirements concerning avoidance of emissions and loss of organic materials are fulfilled by powder coatings in two ways. First, the powder coating materials are almost completely solvent-free. Second, powders can be recycled. The overspray from powder application is returned to the application process. This makes the transfer efficiency greater than in all other types of paint application. There are none of the problems of waste materials (paint sludge) that beset solvent-borne and water-borne paints.

3.2 Production of powder coating materials and general properties

Since powder coating are completely solvent-free, it makes sense to produce the powders without any process solvent. Thus, the powder is produced mainly in melt processes. The mixture of the components in melt – with relatively high viscosities – is carried out in a heated kneader. For continuous processes, extruders are preferred. For the extruder process, the ingredients, consisting of relatively fine particles, are brought together in a solid-materials mixer. If continuous extrusion is to take place, the ingredients have to be mixed beforehand. It is not easy to add liquid components for this process. Therefore, the liquid components are premixed with small portions of the resin in melt. This melt is crushed into particles which are then added to the solids mixer (masterbatch process). The components have to be homogenized effectively in the extruder in a melting-kneading process. Not only are the resin and crosslinker homogenized, but the pigments and extenders also have to be wetted effectively. Therefore powder coatings can have highly glossy surfaces. The extrusion

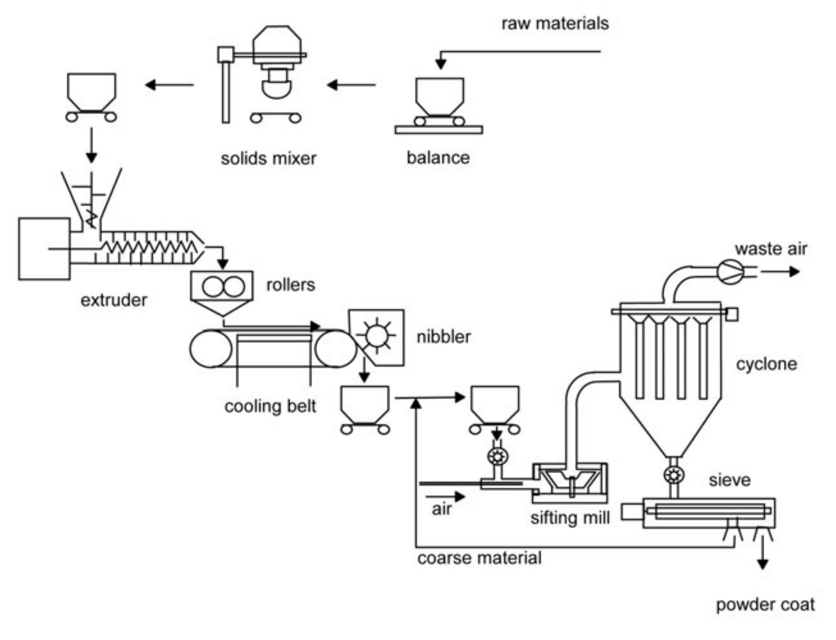


Figure IV-3.1: Process for the production of powder coatings

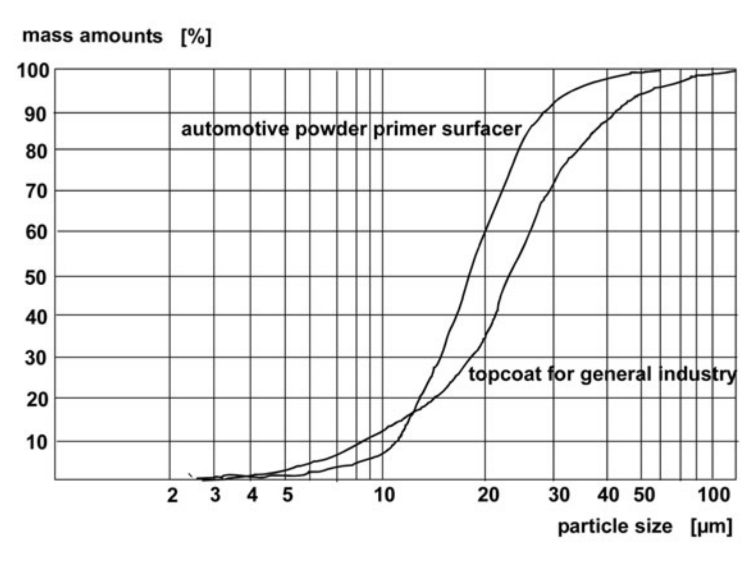


Figure IV-3.2: Typical particle size distributions of powder coatings

product passes through rolls and a cooling belt to form slabs, which are crushed by a nibbler. The powder coating material is then ground effectively in special mills. Suitable mills are of the impact and counter-current type. It is important to cool them. The resultant powder is separated by cyclones (to yield super-fine components) and by screens (coarse particles). The target is to produce powder with a narrow particle size distribution. In most cases, the separated materials are recycled into the process (super-fine components into the extruder, coarse particles back to the mill). So-called sifter mills combine the different process steps. A schematic diagram of the overall process is presented in Figure IV-3.1 [4].

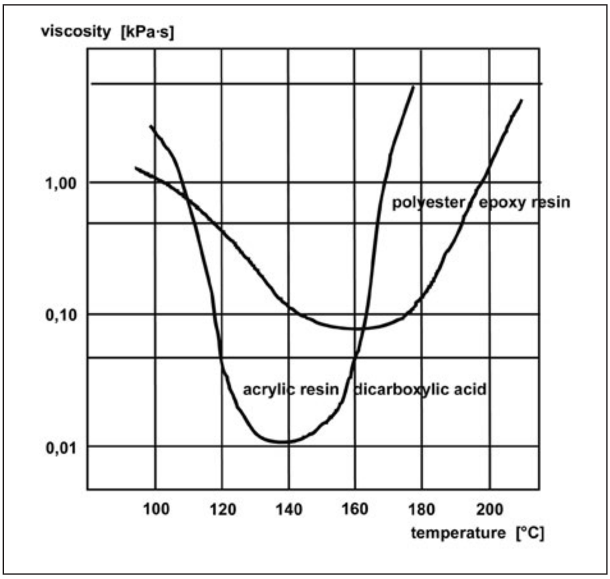


Figure IV-3.3: Melt viscosities of different powder coatings as a function of temperature

The average particle sizes of powders are between 18 and 80 μm. Studies are underway to produce much finer powders by means of special mills and separation processes. Since a current powder has an average particle size of 20 μm, it will contain significant amounts up to 50 μm in size. This makes it difficult – or impossible to prepare smooth and glossy films with thicknesses below 60 μm. This is a disadvantage over conventional paint materials. Figure IV-3.2 shows typical particle size distributions of powder coatings [4].

Since the goal is to apply thick films, this disadvantage proves to be an advantage. Powder coatings offer the possibility of preparing coatings in layers up to 600 μm thick. Unlike conventional paints, there are no problems with blistering or sagging.

The production process for powder coatings, and mainly the milling process, requires resin components with relatively high softening temperatures. The glass transition temperatures of the polymers have to be higher than 50 °C. Otherwise, the materials would fuse during milling. The choice of resins for powder coatings is therefore restricted. This property is also the reason that powder coatings are relatively hard (brittle). They therefore need to be crosslinked effectively in order that an optimum balance of hardness and flexibility may be obtained.

One more advantage of the high glass transition temperature is storage stability. Powder coating particles may not agglomerate (caking effect). It must be borne in mind that the finer the particles are, the higher are the effects of surface energy. In borderline cases, if the particles are very fine, some agglomerates will not be fluidised. That leads to the formation of specks and levelling defects in films. This is one reason to separate the finest particles during the production process of powder coating materials. On the other hand, it is the main reason for the restriction on minimum film thicknesses for powder coatings. Smooth and glossy films of powder coatings have minimum thicknesses of 55 μm (e.g. automotive powder clear coats).

Fluidisation can be supported by adding additives, for example by coating the particle surface with nanoparticles.

Film forming of powder coatings takes place by a melt process. In contrast to conventional paints, it is an advantage that the melt viscosity of films is low at the start of the stoving process. This is the best condition for optimum levelling. Therefore, the polymers chosen not only have high glass transition temperatures, but also low average molar masses. The melting temperatures of such resins are high, but the melt viscosities are low. If the solubility in organic solvent of resins for powder coatings do not play any role, it is possible to use semi-crystalline polymers. Such products have a relatively sharp melting temperature and low melt viscosities. This also applies to the various crosslinkers used in powder coatings. Melt viscosities of different powder coating materials are shown in Figure IV-3.3 [4].

However, there are also additives that facilitate flow and improve levelling and ventilation. The best known product, and one which is suitable universally, is benzoin (melting range 132 to 137 °C). The structure of benzoin is presented in Figure IV-3.4.

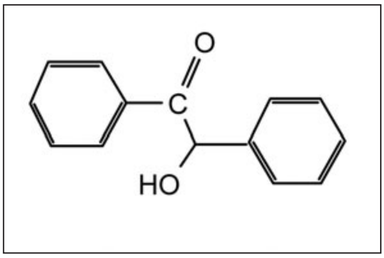


Figure IV-3.4: Structure of benzoin

There are special requirements on pigments that need to be suitable for powder coatings. First, they have to be wetted easily to meet the conditions in the heated extruder. Powder coatings are often cured at high temperatures and so the pigments must be heat-resistant. Both requirements are fulfilled by inorganic pigments. However, organic pigments must be selected carefully for effective wetting in the extrusion process and for their heat resistance [5].

Generally powder coatings and their applications offer the following advantages:

- Solvent-free, 100-% systems
- High transfer efficiency during application, in case of material recycling
- No need to clean exhausted air
- No paint sludge
- Most are physiologically safe
- Little or no fire hazard
- Work well as one-coat systems in many applications
- May be applied as thick films, without problems

But there are also some disadvantages:

- Production process is complex and expensive
- Special application equipment is required
- Smooth, glossy films need relatively high film thicknesses

However, the higher costs of raw materials and production – relative to conventional paint products – and of the application equipment are compensated by the high transfer efficiency during application, the elimination of exhaust-air cleaning, the absence of paint sludge, and the lower insurance costs. However, if high film thicknesses for high-quality coatings are required, the costs are relatively high.

3.3 Application of powder coatings

3.3.1 Fluid bed sintering

Since 1952, fluid bed sintering has been recommended as a replacement for the dipping processes of solvent-borne paints. No solvent vapours are emitted. The fluid bed is a tank with a porous metal sinter plate at the bottom. Compressed air fed through the sinter plate agitates the powder particles, forming an aerosol. The aerosol looks like a boiling liquid.

The objects to be coated are heated to temperatures above the melting point of the powder, and then dipped in the fluid bed. Particles of the powder that make contact with the surface of the object melt to form films. The thickness and quality of the films depend on the temperature and the heat capacity of the object, the melting temperatures, the particle sizes of the powder and the dipping duration. Coating can be readily controlled via all these parameters. After dipping, the object is returned to the stove for final film formation, which may also include a crosslinking reaction. The transfer efficiency is very high. The film layers formed by this process have thicknesses of 80 to 400 µm. Only heat-resistant objects (mainly metals) of a limited size are suitable for coating by fluid bed sintering.

3.3.2 Electrostatic spray application

Electrostatic spraying of powder coatings was introduced in the coatings industry in 1965. In this process, the powder is first fluidised in a closed container by compressed air. The aerosol formed thereby is transported by an injector to the spray gun. In the spray gun, the particles of the aerosol are charged electrostatically, and sprayed, often supported by additional compressed air, onto the object. The object is earthed. The electrostatic charging provides the transport to the object and is also the reason that the particles adhere to it.

Charging processes

There are basically two ways of charging powder particles for the spraying process. The first utilises ionisation (corona charging) and the second charges the particle stream itself as it passes through tubes of special materials (this is called kinetic or tribo-charging).

Corona charging happens when the powder particles pass through an electric field and remove the ions from the field. If the electric field is installed in the tube of a spray gun, the process is called internal charging. If charging takes place with the aid of electrodes parallel to the spraying, it is called external charging. Both methods lead to well defined charging states. The use of needle-like electrodes creates a field strength of 7 to 10 kV/cm. If a cylindrical condenser is used, the field strength can be up to 100 kV/cm. Of course, the electric field strength may not exceed the breakdown resistance of air, which is usually 1.0 to $3.0 \cdot 10^6$ A • s/g.

Kinetic charging takes place when the stream of particles passes through plastic tubes. Electron transfer happens by friction. In this case, the charging state is not so well defined, unlike the case for corona charging.

The object to be coated has to be electrically conducting and earthed. The powder particles following the electrical field to the earthed object are deposited on the surface. If discharging can be hindered, the particles adhere on the object for a long time. Finally, film formation is effected by stoving. The particles melt and flow to form a smooth film layer. Thicknesses are between 40 and 150 µm.

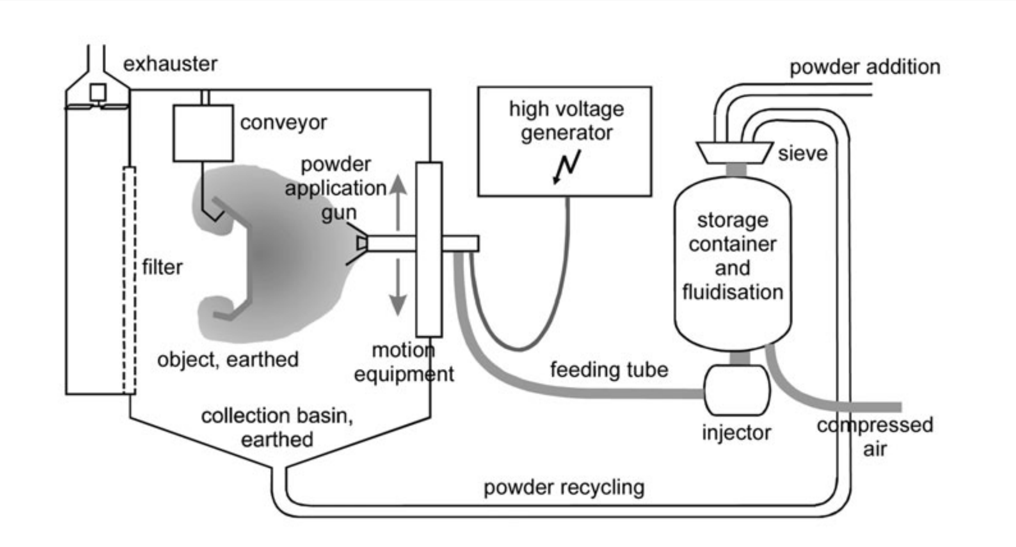


Figure IV-3.5: Equipment for electrostatic powder application

Like electrostatic application of wet paints, electrostatic powder spraying has relatively good throwing power. But cavities are not coated if they are Faraday cages. The primary transfer efficiency of roughly 50% is much lower than for wet paints applied electrostatically. However, the spray cabins are configured such that the overspray is recycled. These contain filters for the exhaust air and a basin for collecting the excess powder. When recycling is taken into consideration, the overall transfer efficiency is as high as 95%, which is the best value of all suitable paint systems. To reduce the level of recycling, the powder coating is fluidised by means of high-density fluidisation, in which the ratio of powder to air is reduced from 1 : 1 parts by weight to 1 : 1 parts by volume. This affords much greater control over the direction of spray dust. A schematic diagram of this application process is shown in Figure IV-3.5.

Although there is the advantage of recycling the overspray, there is also a risk. If the powder becomes contaminated, there is virtually no way to clean it, unlike the case for liquid paints. It can at best be screened to remove contaminants.

An additional disadvantage is the considerable effort involved in changing the paint colour during the application process. Complete cleaning of a powder spraying booth takes several hours. But more efficient processes are being developed in this regard.

Special application methods have been developed for radiation-curing powders (see Chapter IV-3.2.4.5).

3.4 Composition of powder coatings and special properties

3.4.1 Thermoplastic powder coatings

Resins for thermoplastic powder coatings are [1]:

- Polyethylene
- Polyvinyl chloride
- Polyamide
- Ethylene-vinyl alcohol copolymers
- Saturated polyesters

Thermoplastic powders are used for low-cost coatings. It must be remembered that thermoplastic powder coatings are not as resistant to chemicals and solvents as are crosslinked powder coatings. Thermoplastic powders are mainly used for internal coatings.

Polyethylene powders are the cheapest products. They are mainly applied by fluid bed sintering. They require film forming temperatures of 280 to 400 °C. For special substrates, an adhesion primer has to be applied first. The coatings are not weatherable.

Polyamide powders mainly consist of polyamide-12 (prepared from laurinlactam). They are also applied by fluid bed sintering and need film forming temperatures of 280 to 400 °C. The films are hard and relative chemically resistant. Their weather resistance is better than that of polyethylene powder coatings. However, polyamide powder coatings tend to become yellow and absorb relatively high amounts of humidity. Nevertheless, they are the most commonly used thermoplastic powder coatings.

PVC powder coatings consist of polyvinyl chloride and plasticizers. The films are relatively flexible, but are not yellowing resistant. PVC powders are inexpensive. They are applied by electrostatic spraying and form films at 160 to 200 °C. For many substrates, it is necessary to use an adhesion primer.

Powder coatings containing **ethylene-vinyl alcohol copolymers** are mainly applied by fluid bed sintering, and their film forming temperatures range from 200 to 400 °C. The films are distinguished by good adhesion and flexibility. They are relatively resistant to corrosion and weathering.

Polyester powder coatings consist of linear, high-molecular, aromatic polyesters. They are mainly applied by electrostatic spraying and form films at 200 to 240 °C. The films show good adhesion, high flexibility, and exhibit adequate resistance to water and weathering.

3.4.2 Crosslinkable powder coatings

3.4.2.1 Powder coatings from epoxy resins

Epoxy resins have been the most important resin group ever since powder coatings were first developed. Epoxy resins containing bisphenol A and terminal epoxy groups (oxirane rings) with more or less high molar masses are ideal for use in powder coatings. Epoxy resins for powder coatings have number average molar masses of 1,500 to 3,000 g/mol, glass transition temperatures of 50 to 65 °C and softening temperatures (Mettler measurement) of 80 to 100 °C [8, 9]. There are also solid epoxy resins prepared from bisphenol F and of novolak types [11].

Suitable epoxy resins are crosslinked by different hardeners. In all the crosslinking processes described, addition reactions occur. This is an advantage for forming films of high layer thickness without blistering and other film defects.

Suitable crosslinker are:

- Dicyandiamide and derivatives (also accelerated)
- Polyphenols
- Polyanhydrides

Dicyandiamide

Dicyandiamide (see Figure IV-3.6 for molecular structure) is a crystalline solid. It melts at temperatures of 209 to 212 °C and its NH equivalent mass is 21 g/eq. Due to its poor solubility, dicyandiamide has to be mixed into the composition in the form of a relatively fine powder. It is less reactive than amines and so catalysts have to be added. Some commercial products contain such accelerated dicyandiamide. But derivatives of dicyandiamide are more reactive, e.g. aryl bisguanamnides (Figure IV-3.6 shows the reaction of toluyl bisguanamide).

Stoving conditions for dicyandiamide are 15 to 30 min at 185 to 220 °C. Accelerated dicyandiamides and the substituted compounds need 10 to 15 min at 150 to 180 °C. The NH groups of dicyandiamide or of the derivatives react with oxirane rings of epoxy resins in an addition reaction, opening the oxirane ring. Although dicyandiamide contains five mobile hydrogen atoms attached to nitrogens, the effective crosslinking functionality is lower. However, dicyandiamide catalyses the self-crosslinking reaction of epoxy resins, with the secondary hydroxyl groups reacting with oxirane rings. It is therefore unnecessary to add stoichiometric amounts of dicyandiamide (calculated on NH equivalent mass) to the epoxy resin. Typical practical ratios of epoxy resins and dicyandiamide are 97 : 3 or 95 : 5.

Phenolic crosslinkers are polyphenols, e.g. bisphenol A or adducts of bisphenol A on epoxy resins. The adducts have principally the same molecular structure as the epoxy resins, but the chain ends bear phenolic hydroxyl groups in contrast to oxirane rings. Besides these products, novolaks are suitable for crosslinking epoxy resins. Novolaks are condensation products of phenols and formaldehyde that contain methylene ether bridges and phenolic hydroxyl groups. Due to the low reactivity of all the phenolic groups mentioned, crosslink-

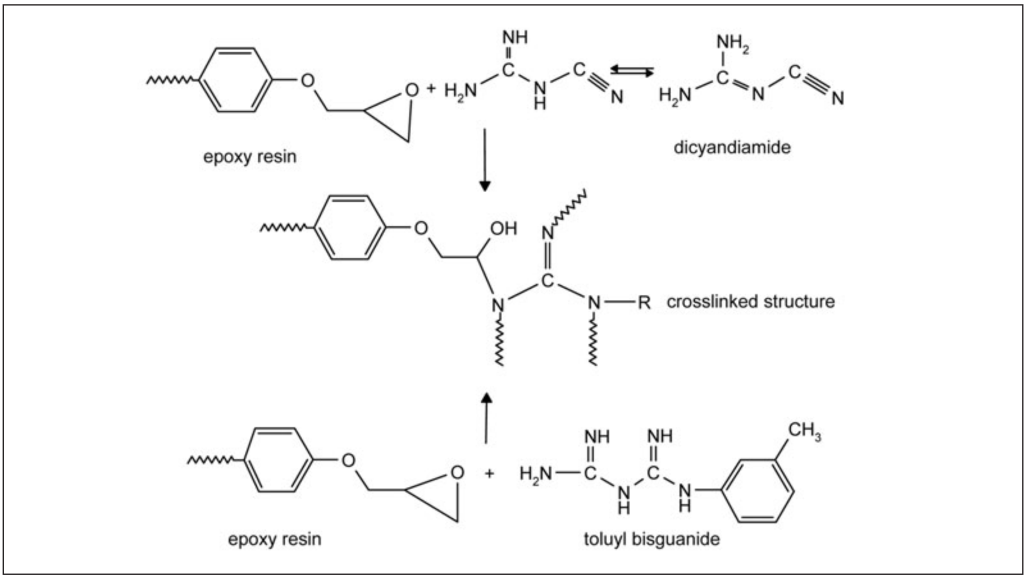


Figure IV-3.6: Crosslinking reactions between dicyandiamide and toluyl bisguanamide

ing of epoxy resins necessitates relatively high temperatures or catalysts. Effective catalysts include imidazoles (e.g. 2-methyl imidazole). Some commercial products of phenolic crosslinkers contain the requisite amounts of catalysts.

Stoving conditions for the resin systems are 10 to 20 min at 130 to 160 °C. The catalysts also support self-crosslinking by epoxy resins. The amounts of phenolic crosslinker to be added are therefore lower than the stoichiometric amounts. The crosslinking reaction is presented in Figure IV-3.7.

Anhydride hardeners for powder coatings start reacting by forming esters with the secondary hydroxyl groups of the epoxy resin and opening the anhydride rings to yield carboxyl groups. The second step is the addition reaction of these carboxyl groups and epoxy

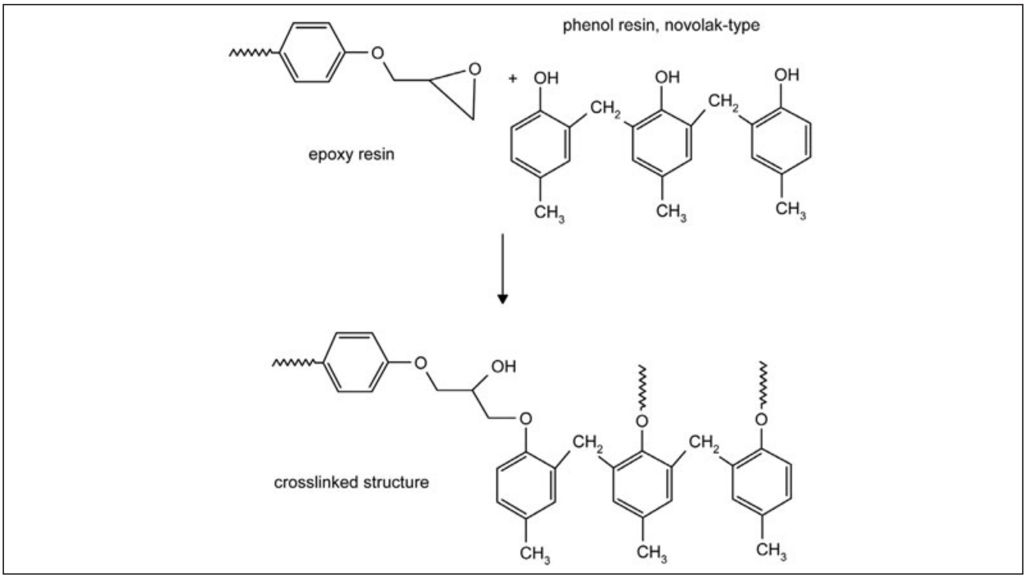


Figure IV-3.7: Crosslinking of epoxy resins with polyphenols

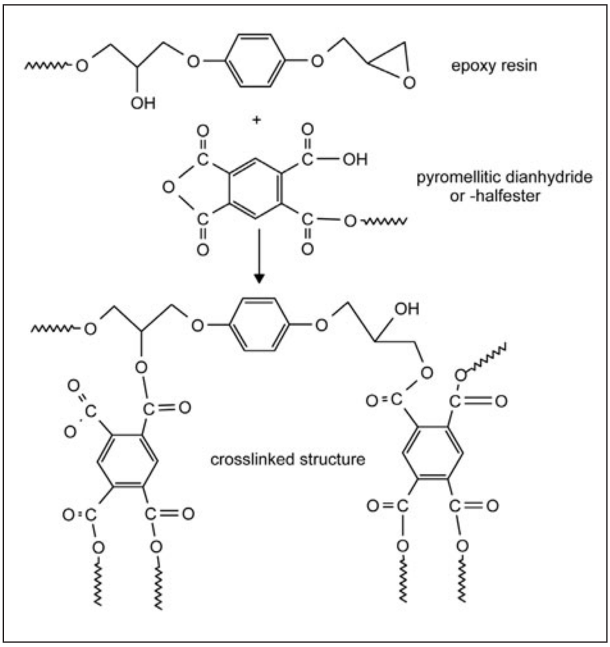


Figure IV-3.8: Crosslinking of epoxy resins with anhydride hardeners, as illustrated by pyromellitic dianhydride

groups. Both reactions lead to the formation of a three-dimensional molecular network. The reactions are presented in Figure IV-3.8.

The preferred anhydride hardeners are pyromellitic dianhydride and combinations of pyromellitic dianhydride and trimellitic anhydride. There are also diol esters of trimellitic anhydride with residual anhydride groups. Catalysts for the reaction are amines or amidines (e.g. 2-phenylimidazoline [10]). The catalysts act by forming salts in the first reaction step. Like the aforementioned crosslinking agents, for anhydrides, less than the stoichiometric amount is added.

Powder coatings from epoxy resins and the hardeners described show excellent adhesion on metallic substrates, confer very good corrosion protection, are adequately flexible and chemically resistant. They are not weatherable. On weathering, they become yellow and eventually exhibit matting and chalking. They are therefore used exclusively for interior coatings, for machine parts, metal furniture, domestic appliances, containers, tubes and for electrical insulation. The powder coatings are applied by electrostatic spraying, but they are also suitable for fluid bed sintering.

Formulation examples

Decorative powder coating for domestic appliance

Table IV-3.1: Decorative powder coat for domestic appliance

pos.	raw material	density $[g/cm^3]$	formulation [wt.%]
01	bisphenol-A epoxy resin (EW_{EP} 715 to 835 g/eq)	1.2	55.7
02	crosslinker: dicyandiamide derivate (EW_{NH} 38 g/eq)	1.2	2.8
03	levelling agent in epoxy resin (EW_{EP} 740 to 870 g/eq)	1.2	2.9
04	titanium dioxide, rutile	4.1	24.4
05	barium sulphate	4.3	12.7
06	calcium carbonate (natural)	2.7	1.5
sum			100.0

pos. 01: Araldit GT 7004 (melt temp. 65 to 75 °C [Huntsman])
pos. 02: Araldit HT 2844 (melt temp. 139 to 143 °C [Huntsman])
pos. 03: Araldit GT 2874 masterbatch of
Araldit GT 7004 (90%) and polyacrylate [Huntsman])

A decorative powder coating for domestic appliance [9] consists of an epoxy resin (epoxy equivalent mass of 715 to 835 g/eq), a derivative of dicyandiamide for crosslinking, a masterbatch of the mentioned epoxy resin and an acrylic polymer as levelling agent. The pigments are titanium dioxide and two extenders. The powder coating is prepared by the aforementioned production process. The composition is presented in Table IV-3.1.

The powder paint is applied by electrostatic spraying to panels that have been pre-treated with zinc phosphate. Stoving takes

8 min at 180 °C. The resultant film thickness is 80 to 100 µm. The coating has an indentation value (Erichsen) of 9.8 mm.

The mixing ratio of epoxy resin ($m_{epoxide}$) to hardener ($m_{hardener}$) is:

$$\frac{m_{epoxide}}{m_{hardener}} = \frac{55.7 + 2.6}{2.8} = \frac{95.4\%}{4.6\%}$$

The pigmentation level is:

$$P / B = \frac{24.4 + 12.7 + 1.5}{55.7 + 2.9 + 2.8} = \frac{38{,}6}{61.4} = 0.6 / 1$$

The PVC is:

$$PVC = \frac{24.4 / 4.1 + 12.7 / 4.3 + 1.5 / 2.7}{24.4 / 4.1 + 12.7 / 4.3 + 1.5 / 2.7 + 61.4 / 1.2} \cdot 100\% = 16\%$$

Powder coating for metal application with a phenolic hardener[11]

The chosen epoxy resin is a novolak (epoxy functionality 2.6, epoxy equivalent mass 500 to 560 g/eq, softening temperatures 89 to 97 °C). The hardener is a product of the reaction between bisphenol A diglycidyl ether and an excess of bisphenol A (hydrogen equivalent mass 240 to 270 g/eq, softening temperature 76 to 84 °C). The hardener additionally contains an accelerator and 2% polyacrylate, which acts as a levelling agent. The pigments are red iron oxide and barium sulphate (extender). A small amount of hydrophobic pyrogenic silica serves as an additive. Details of the formulation are listed in Table IV-3.2.

Table IV-3.2: Powder coat for metal application, phenolic hardener

pos.	raw material	density [g/cm³]	formulation [wt.%]
01	novolak epoxy resin (EW$_{EP}$ 500 to 560 g/eq)	1.2	46.0
02	phenolic crosslinker of epoxy resin and polyphenol with catalyst and levelling agent (EW$_{OH}$ 240 to 270 g/eq)	1.2	24.0
03	red iron oxide	5.1	12.0
04	barium sulphate	4.3	15.0
05	hydrophobic pyrogenic silicic acid	2.0	3.0
sum			100.0

pos. 01: D.E.R. 642 (melt. temp. 89 to 97 °C [Dow])
pos. 02: XZ 86798.02 (melt temp. 76 to 84 °C [Dow])
pos. 03: Bayferrox 180 M (Bayer)
pos. 04: EWO (av. particel size 3.5 µm [Alberti])
pos. 05: Aerosil R 972 (Evonik Degussa)

The molar crosslinking ratio of phenol (n_{phenol}) to epoxy (n_{epoxy}) is calculated from the mass amounts (m_{phenol} and m_{epoxy}) and the average equivalent weights (EW_{OH} of the phenol resin and EW_{epoxy} of the epoxy resin).

$$\frac{n_{phenol}}{n_{epoxide}} = \frac{m_{phenol} / EW_{OH}}{m_{epoxide} / EW_{epoxide}} = \frac{24 / 255}{46 / 530} = 1.1 / 1$$

There is an excess of phenol hardener.

The following equations show the pigment/binder ratio and the PVC:

$$P / B = \frac{12.0 + 15.0 + 3.0}{46.0 + 24.0} = \frac{30.0}{70.0} = 0.43 / 1$$

$$PVC = \frac{12.5 / 5.1 + 15.0 / 4.3 + 3.0 / 2.0}{12.5 / 5.1 + 15.0 / 4.3 + 3.0 / 2.0 + 70.0 / 1.2} \cdot 100\% = 11\%$$

3.4.2.2 Epoxy resin/polyester hybrid systems

Resin combinations

Hybrid systems consist of epoxy resins, which were described in the last chapter, and saturated polyesters, which contain free carboxyl groups. Like epoxy resins, the polyesters must have glass transition temperatures of more than 50 °C. They therefore consist mainly of aromatic polycarboxylic acids and polyols with short aliphatic chains. The crosslinking mechanism is presented in Figure IV-3.9.

Mixing ratios of polyesters and epoxy resins are between 70 : 30 and 50 : 50. The amount of polyester ($m_{polyester}$) necessary for crosslinking an epoxy resin (m_{epoxy}) in stoichiometric balance is calculated from the acid number (AN) of the polyester and the epoxy equivalent weight (EW_{epoxy}) of the epoxy resin.

$$\frac{m_{epoxide}}{m_{polyester}} = \frac{AN_{polyester} \cdot EW_{epoxide}}{56110}$$

Since, in addition to the carboxyl groups of the polyester, the secondary hydroxyl groups also participate in crosslinking by reacting with epoxy groups, it is recommended that excess epoxy resin be used. Catalysts for the crosslinking reaction of epoxy groups and carboxyl groups are phosphines, phosphonium salts, tertiary amines, and organic salts of heavy metals, which are known to catalyse the esterification reaction. The stoving temperatures are between 140 and 200 °C.

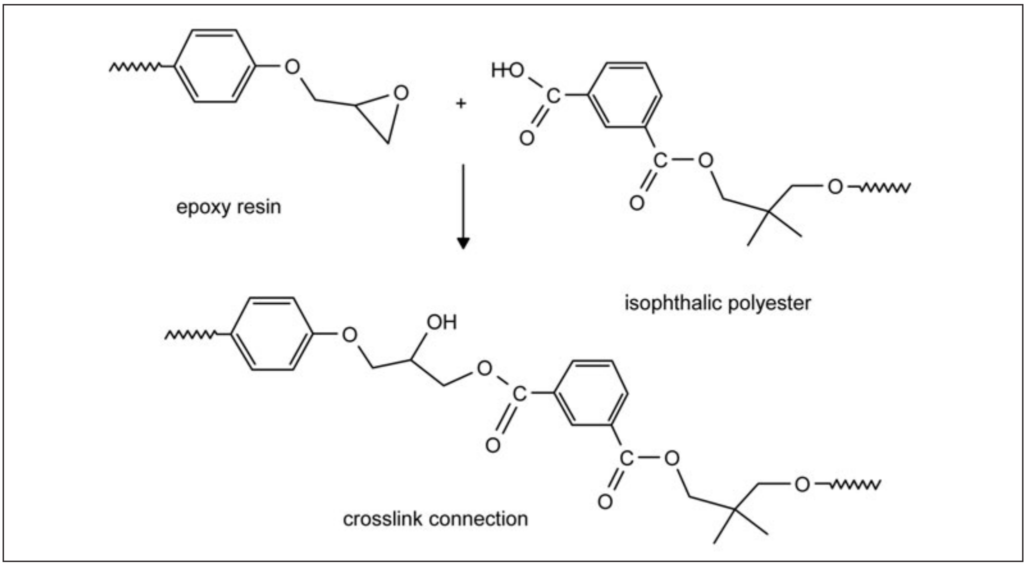


Figure IV-3.9: Crosslinking mechanism for epoxy resins and polyesters containing carboxyl groups

Properties and applications

In Europe, hybrid systems of epoxy resins and polyester resins are the most common powder coating resins. The preferred application method is electrostatic spraying. The resultant coatings have a balanced property profile. Although the level of corrosion protection and chemical resistance is not as outstanding as that described in the previous chapter, it is adequate. However, hybrid systems are more weatherable, and hard but flexible.

Hybrid systems therefore find application in exterior coatings, e.g. metal garden furniture and containers. Elsewhere, they are mainly used for domestic appliances, steel furniture, shelving, grids, and machine parts.

Formulation example

Decorative powder coating (polyester : epoxy resin = 60 : 40)

The decorative powder coating [11] consists of a saturated polyester with acid number 50 ± 3 mg KOH/g and an epoxy resin with epoxy equivalent weight of 730 to 820 g/eq. The mixture has softening temperatures of 95 to 106 °C. The pigments are titanium dioxide and barium sulphate (extender). The flow additive is benzoin and a polyacrylate serves as levelling agent. Details of the formulation are presented in Table IV-3.3.

This powder coating is produced as described above. The levelling agent can be incorporated by melting it in a portion of the epoxy resin (masterbatch).

Stoving conditions are 15 min at 180 °C.

Table IV-3.3: Decorative powder coat (polyester : epoxy resin = 60 : 40)

pos.	raw material	density [g/cm³]	formulation [wt.%]
01	polyester, containing carboxyl groups (AN 50 ± 3 mg KOH/g)	1.2	35.5
02	epoxy resin (EW$_{EP}$ 730 to 820 g/eq)	1.2	23.6
03	titanium dioxide, rutile	4.1	30.0
04	barium sulphate	4.3	10.0
05	levelling agent	1.2	0.6
06	benzoin		0.3
sum			100.0

pos. 01: Crylcoat 344 (Cytec, UCB)
pos. 02: D.E.R. 663 U (melt temp. 95 to 106 °C [Dow])
pos. 04: EWO (av. particel size 3.5 µm [Alberti])
pos. 05: Acronal 4 F (BASF)

The molar crosslinking ratio is calculated from the characteristic values defined above.

$$\frac{n_{\text{epoxide}}}{n_{\text{COOH}}} = \frac{m_{\text{epoxide}} / EW_{\text{epoxide}}}{m_{\text{polyester}} \cdot AN / 56110} = \frac{23.6 / 775}{35.5 \cdot 50 / 56110} = 0.96 : 1$$

After that, there is a small stoichiometric excess of polyester.

The pigmentation level and PVC are calculated as follows:

$$P / B = \frac{30.0 + 10.0}{23.6 + 35.5 + 0.6} = \frac{40.0}{59.1} = 0.67 / 1.00$$

$$PVC = \frac{30.0 / 4.1 + 10.0 / 4.3}{30.0 / 4.1 + 10.0 / 4.3 + (35.5 + 23.6 + 0.6) / 1.2} \cdot 100\% = 16\%$$

3.4.2.3 Polyester powder coatings

3.4.2.3.1 Polyesters containing carboxyl groups

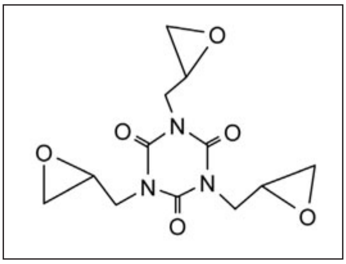


Figure IV-3.10: Triglycidyl isocyanurate (TGIC)

If polyesters, which have just been described in the last chapter (Chapter IV-3.4.2.2), are crosslinked with hardeners that have much lower equivalent weights than the epoxy resins described there, the resultant formulations are defined as polyester powder coatings, provided that polyesters are the main resin. For a long time, triglycidyl isocyanurate (TGIC; see Figure IV-3.10 for molecular structure) was the most important hardener component for these formulations [12 to 16].

Triglycidyl isocyanurate is much more reactive than the bisphenol A epoxy resins. The commercial product has an equivalent weight of 100 to 108 g/eq. For stoichiometrically balanced crosslinking of a polyester with acid number of 50 mg KOH/g, the mixing ratio of polyester to TGIC is 90 : 10 by mass.

Films of this combination are weather resistant and free of yellowing. They offer a good balance of hardness and flexibility, and adequate chemical resistance. They are preferred for exterior applications.

Hardener TGIC has now been classified as toxic and is no longer considered for new developments [16, 19]. Alternatives have been developed to replace it. These include glycidyl esters of aromatic polycarboxylic acids, e.g. the diglycidyl ester of terephthalic acid and the triglycidyl ester of trimellitic acid [17]. The molecular structures of these crosslinkers are presented in Figure IV-3.11.

These hardeners are less reactive than TGIC, but they confer nearly the same film properties as it does.

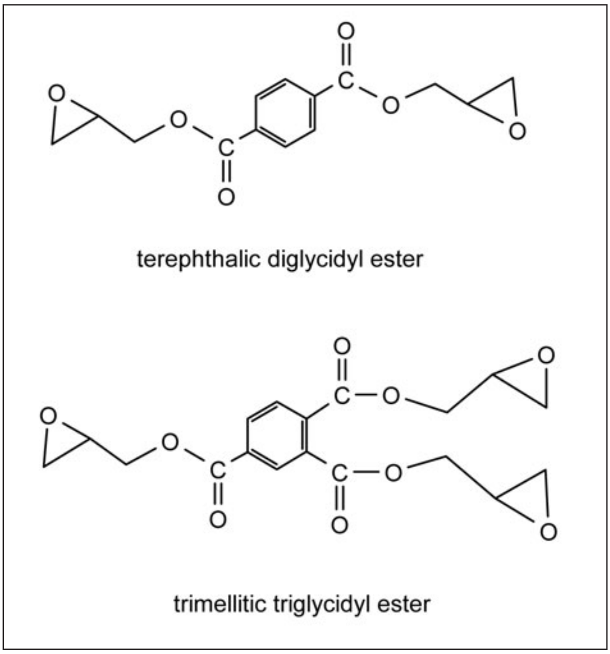


Figure IV-3.11: Molecular structures of glycidyl esters, hardeners for powder coatings

Another class of product suitable for crosslinking polyesters that contain carboxyl groups is that of β-hydroxy alkyl amides. These react more easily than normal alkanols with carboxyl groups to form ester groups, with cleavage of water. As amides, they have relatively high melting temperatures (about 120 °C). Commercial products include tetrakis-2-hydroxyalkyl adipic amides [18]. See Figure IV-3.12 for their molecular structures.

As the crosslinking reaction of these hardeners is a condensation reaction, with cleavage of water, it is important to ensure that the water can escape from the film during stoving without the formation of any film defects (e.g. blisters). The film thickness should therefore be restricted.

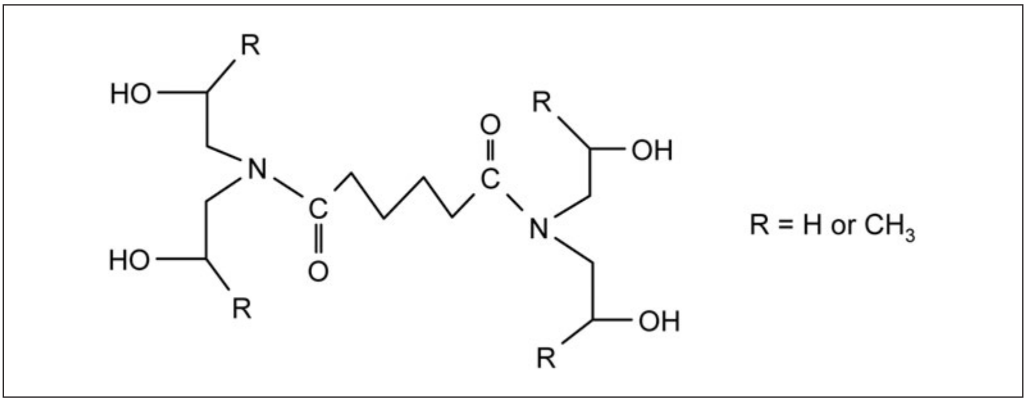


Figure IV-3.12: Molecular structures of tetrakis-2-hydroxyalkyl adipic amides

The hardeners are completely safe. The stoving conditions are 8 to 40 min at 150 to 200 °C. The resultant films are highly weatherable and their other properties are on a par with those of films made from polyesters and TGIC.

Formulation example

White topcoat for exterior metal coatings [20]

This formulation of a white topcoat for exterior metal coatings consists of a saturated polyester (acid number 32 mg KOH/g) and of tetrakis-2-hydroxyethyl adipic amide. The stoichiometric ratios are nearly balanced. The pigment is titanium dioxide. Additives are benzoin for flow, and a polyacrylate for levelling. The formulation is presented in Table IV-3.4:

Table IV-3.4: White topcoat for exterior metal coatings

pos.	raw material	density [g/cm³]	formulation [wt.%]
01	polyester, containing carboxyl groups (AN 31 to 36 mg KOH/g)	1.2	55.76
02	tetrakis-2-hydroxypropyl adipic amide (EW_H 86 to 102 g/eq)	1.2	3.25
03	titanium dioxide, rutile	4.1	40.00
04	levelling agent		0.80
05	benzoin		0.20
sum			100.00

pos. 01: Grilesta P 7612 (soft. temp. 80 to 90 °C [Ems Chemie])
pos. 02: Primid QM 1260 (melt temp. 120 to 124 °C [Ems Chemie])
pos. 03: Kronos 2160 (Kronos Titan)
pos. 04: Resiflow PV 88 (polyacrylate [Worlée])

All the ingredients are premixed and passed through a Buss-Ko kneader at 100 °C. The product is carried out, cooled, crushed, milled, and screened.

Properties of the powder coating

Storage stability:	Longer than 28 days at 40 °C
Gel time at 200 °C:	about 90 s

Application: Q-panel (type R-36, 0.8 mm), electrostatic spraying

Stoving conditions:	8 min at 200 °C to 40 min at 150 °C
Film thickness:	about 60 µm
Gloss:	93% (Lange, 60°)
Hardness:	91 (Buchholz), H (Pencil)
Adhesion:	Gt 0 (Cross-hatch)
Mandrel test:	Less than 2 mm: Pass
Condensation, salt spray tests (Kesternich):	Pass

The stoichiometric crosslinking ratio of hydroxyl groups (n_{OH}) in the amount of hardener ($m_{hardener}$) to carboxyl groups (n_{COOH}) in the polyester ($m_{polyester}$) is calculated from the hydroxy equivalent weight of the hardener (EW_{OH}) and the acid number of polyester (AN) as follows:

$$\frac{n_{OH}}{n_{COOH}} = \frac{m_{HAA} / EW_{OH}}{m_{polyester} \cdot AN / 56110} = \frac{3.25 / 94}{55.75 \cdot 33 / 56110} = 1.05 / 1$$

There is a small excess of hardener in the formulation example.

The pigmentation level and the PVC are calculated from the following equations:

$$P / B = \frac{40.00}{55.75 + 3.25} = 0.68 : 1$$

$$PVC = \frac{40.00 / 4.1}{40.00 / 4.1 + (55.75 + 3.25) / 1.2} \cdot 100\ \% = 17\ \%$$

3.4.2.3.2 Polyesters containing hydroxyl groups

The second group of powder coatings is based on polyester resins containing hydroxyl groups. In this case, the crosslinkers are blocked polyisocyanates. To decrease the amount of hardener, the polyesters have mainly low hydroxyl contents (hydroxyl numbers of 25 to 60 mg KOH/g). The stoving temperatures are relatively high, varying with the cleavage temperature of the blocked polyisocyanate. To achieve relatively high softening temperatures, the chosen polyisocyanate hardeners consist mostly of isophorone diisocyanate (IPDI). There are two ways of blocking isocyanate groups. The first consists in blocking with ε-caprolactam (see Chapter II, Figure II-2.17) and the second in producing polyuretdiones (see Figure IV-3.13).

Polyisocyanate adducts blocked with ε-caprolactam

Polyisocyanate adducts blocked with ε-caprolactamε react with hydroxyl groups of saturated polyesters at 160 to 180 °C to form crosslinked networks. Relatively high amounts of ε-caprolactam remain in the films, acting as plasticizer and supporting levelling. To accelerate the reaction rate, the usual catalysts (tin salts) are added. Tin salts are currently being replaced by other metal salts, in a manner similar to the formulations for solvent-borne paints containing blocked polyisocyanates.

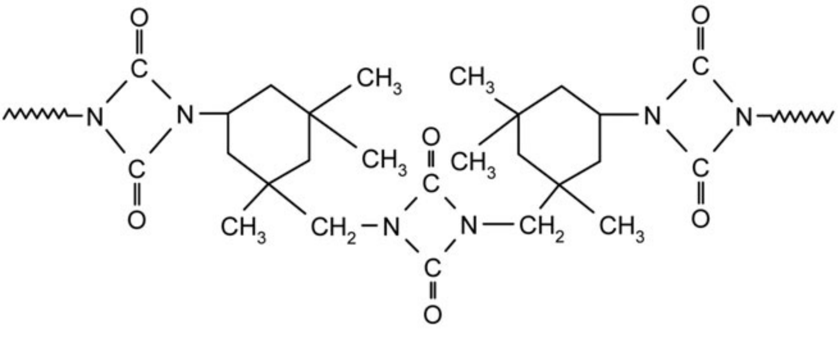


Figure IV-3.13: Polyuretdione of IPDI

The films of the systems offer excellent flexibility, are chemically resistant and weather resistance. Due to the high cost of the raw materials, these powder coatings are chosen for high-quality one-coat systems (see also Chapter II-2.4).

Polyuretdione crosslinking

Polyuretdione crosslinkers do not contain blocking agents (see Figure IV-3.13). At temperatures of around 170 °C, the products are cleaved into free polyisocyanates, which then react with hydroxyl groups of polyesters. Since no product is cleaved, there is no risk of blistering or other film defects. The properties of these systems are comparable with those of the other polyurethane groups containing coatings.

Formulation example

White, one-coat powder coating for exterior use [21]

This powder coating contains a combination of an aromatic polyester (hydroxyl number 45 to 55 mg KOH/g, acid number 8 mg KOH/g, glass transition temperature 51 °C) and a polyuretdione crosslinker containing IPDI (potential NCO content 13.5%, glass transition temperature about 49 °C). The stoichiometric ratio is well balanced. The pigment is titanium dioxide. Additives are benzoin for flow, and a polyacrylate for levelling. The catalyst is tin octoate. The formulation is presented in Table IV-3.5.

Table IV-3.5: One-coat powder coat, white, for exterior use

pos.	raw material	density [g/cm³]	formulation [wt.%]
01	polyester, containing hydroxyl groups (OHN 45 to 556 mg KOH/g)	1.2	48.6
02	cycloaliphatic polyuretdion (pot. NCO-content: 13.5%	1.2	13.4
03	levelling agent polyacrylate		1.5
04	catalyst tin-II-octoate		1.0
05	benzoin		0.5
06	titanium dioxide, rutile	4.1	35.0
sum			100.0

pos. 01: Alftalat AN 739 (glass transition temp. ~ 51 °C [Cytec, Surface Specialties, Vianova])
pos. 02: Crelan VP-LS 2147 (glass transition temp. ~ 49 °C [Bayer])
pos. 03: Modaflow Powder III (Cytec, Surface Specialties, Monsanto)
pos. 04: Desmorapid SO (Bayer)

The powder coating is produced and applied as described in the other examples.

The molecular crosslinking ratio of isocyanate groups (n_{NCO}) to hydroxyl groups (n_{OH}) is calculated from the amount of uretdione ($m_{uretdione}$) and polyester ($m_{polyester}$) and the potential isocyanate content (NCO-%) of uretdione and hydroxyl number (OH-N) of polyester.

$$\frac{n_{NCO}}{n_{OH}} = \frac{m_{NCO} \cdot \text{NCO-\%} \cdot 56110}{m_{polyester} \cdot \text{OHN} \cdot 4200} = \frac{13.4 \cdot 13.5 \cdot 56110}{48.6 \cdot 50 \cdot 4200} = 1/1$$

The pigmentation level and the PVC are calculated as follows:

$$P/B = \frac{35.0}{48.6 + 13.4} = 0.56/1$$

$$PVC = \frac{35.0/4.1}{35.0/4.1 + (48.6 + 13.4)/1.2} \cdot 100\% = 14\%$$

3.4.2.4 Acrylic resin powder coatings

3.4.2.4.1 Structure and production of acrylic resins for powder coatings

As resins for powder coatings should have high softening temperatures, adequate levels of monomers (acrylates and, more importantly, methacrylates) and comonomers with high glass transition temperatures are chosen for the production of acrylic resins. The use of methyl methacrylate (T_g = 105 °C) and styrene (T_g = 100 °C) is preferred. For crosslinking in powder coatings, the acrylic resins contain monomers bearing different functional groups: epoxy, carboxyl, and hydroxyl groups.

Optimum application properties of powder coatings are achieved by employing low-molecular acrylic resins with a view to achieving low melt viscosities. Such acrylic resins are produced by solution polymerization. Vacuum distillation is employed to remove the solvent and yield the solid resins. This is why acrylic resins for powder coatings are relatively expensive. A lot of study has gone into the production of low-molecular acrylic resins in bulk polymerization, but so far the trials have not been successful for acrylic resins containing functional groups, as most production measurements of this kind lead to side-reactions.

Acrylic resins for powder coatings are in competition with polyesters. As they are more expensive, their use is restricted to high-quality systems that must deliver outstanding chemical resistance (saponification resistance) and weather resistance (no yellowing).

3.4.2.4.2 Epoxy acrylic resins

Epoxy acrylic resins are copolymers that contain a significant amount of monomer with an epoxy group. The most commonly employed monomer is glycidyl methacrylate (see Figure IV-3.14).

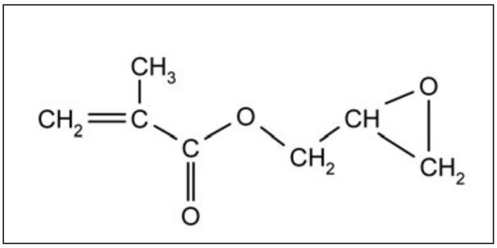


Figure IV-3.14: Molecular structure of glycidyl methacrylate

Epoxy acrylic resins are prepared by solution polymerization. The resultant resin solutions are vacuum distilled to yield the solid resin. The crushed solid resin is mixed with crosslinker, where necessary with pigments and additives. The mixture is extruded, crushed, ground, and screened.

Crosslinkers for epoxy acrylic resins are high-molecular polycarboxylic acids

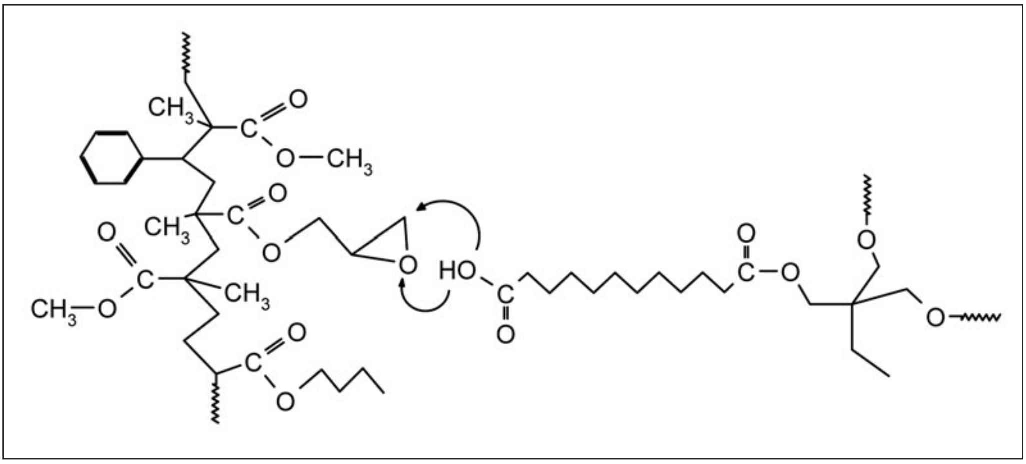


Figure IV-3.15: Crosslinking of epoxy acrylic resin with anhydride adduct (e.g. dodecanedioic acid, acelainic acid) and linear polyanhydrides. The polyanhydrides must first react with hydroxyl groups to form carboxyl groups (see the trimethylolpropane content in Table IV-3.6), which then react with the epoxy groups of the acrylic resin to form β-hydroxy esters. The hydroxyl group of the β-hydroxy ester can react again with residual anhydride. Additionally, it is possible that the resulting hydroxyl groups will react with the epoxy groups. The crosslinking of epoxy acrylic resins is shown in Figure IV-3.15.

The reactions described need relatively low temperatures of 140 to 160 °C. Therefore, the combinations are suitable for automotive OEM coatings, and especially for automotive clear coats. The higher stoving temperatures required for the other powder systems would adversely affect the other layers of an automotive coating system (known as over-curing).

Films of epoxy acrylic resins crosslinked by aliphatic or cycloaliphatic polyanhydrides or their derivatives offer excellent weather resistance, have high gloss and hardness and relatively good yellowing stability. They are mainly used in weatherable topcoats, e.g. automotive OEM clear coats as mentioned above.

Formulation example

Powder clear coat for automotive OEM coatings [22]

The chosen epoxy acrylic resin has an epoxy equivalent weight of 660 g/eq. The hardener is dodecanedioic anhydride with a potential carboxyl group equivalent weight of 106 g/eq. Trimethylolpropane as a co-reactant has a hydroxyl equivalent weight of 44.7 g/eq. The flow additive is benzoin. The other additives are a degassing agent, and – a must for all clear coats – a combination of light protection additives, an UV absorber and a free-radical scavenger.

Details of the clear coat composition are listed in Table IV-3.6.

The acrylic resin is milled to produce coarse particles and then mixed in a solids mixer with the other ingredients of the formulation. The mixture is passed through a Buss-Ko-kneader running at 60 rpm and a temperature of 90 to 110 °C. Then the product is cooled, crushed, and ground in an impact mill to yield a powder with average particle size after screening of about 22 µm.

Table IV-3.6: Powder clear coat for automotive OEM coatings

pos.	raw material	density [g/cm³]	formulation [wt.%]
01	epoxy acrylic resins ($\text{EW}_{\text{epoxide}}$ 660 g/eq)	1.2	73.3
02	dodecanedioic polyanhydride (EW_{COOH} 106 g/eq)	1.2	20.3
03	trimethylolpropane		1.6
04	benzoin		0.4
05	degassing agent		0.4
06	hydroxybenzo triazole		2.4
07	sterical hindered piperidine		1.6
sum			100.0

pos. 01: component A, example 1 of the patent DE 42 27 580 (methylmethacrylate, glycidyl methacrylate, styrene, butyl acrylate)
pos. 02: component B, example 2 of the patent DE 42 27 580
pos. 05: Perenol F 40 (BASF, Cognis)
pos. 05: Tinuvin 900 (BASF Swiss, Ciba)
pos. 06: Tinuvin 144 (BASF Swiss, Ciba)

The powder clear coat is applied by electrostatic spraying to a basecoat, which has been pre-dried for 10 minutes at 80 °C. The stoving conditions are 20 minutes at 160 °C. The resultant thickness of the clear coat is 50 to 60 µm. The clear coat has a good appearance, high gloss, fuel resistance, and excellent intercoat adhesion.

As mentioned above, crosslinking consists in the reaction of hydroxyl groups on the trimethylolpropane with the anhydride. The 1.6 wt.% trimethylolpropane (EW_{OH} = 44.7 g/eq) and the 73.3 wt.% epoxy resin (EW_{epoxy} = 660 g/eq, potential EW_{OH} = 660 g/eq) can generate a total of 0.258 moles hydroxyl groups. The 20.3 wt.%

dodecanedioic polyanhydride (potential EW_{COOH} = 106 g/eq) generates 0.1915 moles carboxyl groups. Thus, the equivalent ratio of epoxy acrylic resin to hardener is 0.74 : 1.

3.4.2.4.3 Acrylic resins containing carboxyl groups

Acrylic resins for powder coatings that contain carboxyl groups can be produced by bulk polymerization. The resultant resins have relatively high molar masses, the acid numbers are between 50 and 80 mg KOH/g, and the softening temperatures lie between 100 and 130 °C.

Like polyesters containing carboxyl groups, the acrylic resins may be combined for crosslinking purposes with TGIC, glycidyl esters of polycarboxylic acids, hydroxyalkyl amides or with epoxy resins [23]. As acrylic resins confer greater weatherability and yellowing resistance than polyesters containing aromatic structures, the preferred crosslinkers are the glycidyl esters and the hydroxyalkyl amides, which also support these properties.

Such combinations are recommended for exterior metal coatings. The required stoving temperatures of 170 to 200 °C are higher than for the epoxy acrylic resins and carboxyl derivatives.

3.4.2.4.4 Acrylic resins containing hydroxyl groups

Solid acrylic resins that have adequately high softening temperatures and contain hydroxyl groups can be crosslinked – as described above for hydroxyl polyesters for powder coatings – with blocked polyisocyanates (IPDI trimers blocked with ε-caprolactam) or polyuretdiones. Since they do not contain significant amounts of aromatic structural elements, they offer excellent weatherability, especially for clear coats. However, the products are very expensive.

3.4.2.4.5 Acrylic resins for radiation-curing powder coatings

As already described (see Chapter IV-2.2), coatings crosslinked by UV radiation are virtually 100% systems with no emissions of solvent or water. Hence, they are VOC-free systems and as such are classified as environmentally friendly. Nonetheless, powder coatings for UV curing have been developed.

The most important advantage of these systems is the fact that film-forming and crosslinking can be separated temporally. Consequently, films can be formed at rather low temperatures. This opens up scope for applying powder coatings to objects which are not really heat resistant. Such powder coatings are suitable for wooden objects.

For UV powder coatings, the resins are chosen so as to have a high glass transition temperature or softening temperature. Examples are epoxy acrylates and polyester acrylates. Standard UV initiators are used for such powder coatings.

The most important application field for UV powder coatings is that of MDF panels (medium density fiberboard). The powder coating is applied by continuously spraying the panels. Film-forming takes place on exposure to IR radiation. For this, the temperature is not much higher than 120 °C. Heating by IR radiation is mainly a surface process; the wooden object itself is protected against too much heat. After film formation, the panels are exposed to UV light. The resulting powder coatings offer excellent resistance to chemical and mechanical impact.

3.4.3 Future of powder coatings

Powder coatings are well suited to general industrial coatings. The next step must be to extend their use in high-quality coatings, mainly in automotive OEM. There are already isolated examples of the application of powder primer surfacers, powder clear coats, and topcoats in the automotive industry. Trials are underway to formulate special effect paints.

An important goal is to reduce the required film thicknesses, while still achieving smooth and glossy surfaces. The first step here is to produce powders with low particle sizes and narrow particle size distributions that are still readily amenable to fluidisation.

Powder coatings should also be suitable for substrates other than metal, namely wood and plastic. This would require a lowering of stoving temperatures, significantly An additional goal is to lengthen the weatherability of powder coating films. The production process for powder coatings also need to be optimized with a view to economising on both effort and costs.

3.5 References

[1] D. Stoye: Paints, Coatings and Solvents, Chapter 3.4; 7.2.3, VCH Verlagsgesellschaft, Weinheim, 1993
[2] B. D. Meyer: Umweltfreundliche Lackiersysteme für die industrielle Lackierung, Expert-Publisher, Kontakt und Studium, Vol. 271, p. 146 – 244; 1989
[3] Powder Coatings Daily Preview, 12/2001, Laurent Marais, AFTPVA/VILF Pulverlack-Symposium, Mulhouse, F, Juni 2001
[4] U. Poth, H. Wonnemann: Properties of Epoxy-Polyester-Powder-Primersurfacers for Automotive OEM, minutes of IBEC, Stuttgart 1997
[5] P. Thometzek et al: Pigmentierung und Pulverlackeigenschaften, Farbe & Lack 104 (1998) Nr. 2, S. 22-30,
[6] A. Goldschmidt, B. Hantschke, E. Knappe, G.-F. Vock: Glasurit-Handbuch, 11. Edition, Chapter III-2.4, S. 384; Publisher Vincentz Network, Hannover, 1984
[7] Report of BMW, Praxis Forum, Bad Nauheim, März 2002
[8] Data sheets of Shell-Resolution
[9] Data sheets of Ciba
[10] Data sheets of Evonik Degussa
[11] Data sheets of Dow
[12] M. Budnowski: Herstellung u. Eigenschaften der diastomeren Triglycidylisocyanurate, Angew. Chemie 80 (1968)
[13] H. Kittel, Lehrbuch der Lacke und Beschichtungen, Volume 2, Chapter 2.2.2.3.5, S. Hirzel, 1998
[14] D. Stoye, Paints, Coatings and Solvents, Chapter 3.4; VCH, Weinheim, 1993
[15] D. Stoye, W. Freitag: Lackharze - Chemie, Eigenschaften und Anwendung, Chapter 7.2.6, Publisher C. Hanser, 1996
[16] Technical and safety data sheets of Araldit PT 810 (BASF-Ciba)
[17] Technical and safety data sheets of Araldit PT 910 (BASF-Ciba)
[18] Primid XL-552 and Primid QM-1260 (Ems Chemie)
[19] Th. Brock: Farbe & Lack, 106 (2000), Nr. 2, S 38-45
[20] Technical data sheet of Primid QM-1260 (Ems Chemie)
[21] Technical data sheet of Crelan VP-LS 2147 (Bayer)
[22] Example of the Patent DE 42 27 580 (BASF Coatings GmbH) 1992
[23] D. K. Moran, J. M. J. Verlaak (S. C. Johnson Polymer): Acid-Functional Acrylic Resins in Acrylic Hybrid Powder Coatings, Modern Paint and Coatings, June 1993

General Literature

To facilitate access to paint and coatings technology for beginners, some recommended standard books are listed below. This list is inevitable incomplete. Further literature is cited at the end of each chapter.

Paints and coatings

- Z. W. Wicks, F. N. Jones, S. P. Pappas, Organic Coatings – Science and Technology, 2nd ed., Wiley 1999
- D. Stoye, W. Freitag, Paints Coatings and Solvents, 2nd ed., Wiley-VCH 1998
- Goldschmidt, H. J. Streitberger, BASF Handbook on Basics of Coatings Technology, Vincentz Network 2003
- Th. Brock, M. Groteklaes, P. Mischke, European Coatings Handbook, 2nd ed., Vincentz Network 2010
- J. M. Oyarzún, Pigment Processing – Physico-chemical Principles, Vincentz Network 2000
- U. Meier-Westhues et al., Polyurethanes: Coatings, Adhesives and Sealants, Vincentz Network 2007
- R. Baumstark, M. Schwartz, Waterborne Acrylates, Vincent Network 2001
- U. Poth, Automotive Coatings Formulation, Vincentz Network 2008
- H. J. Streitberger, K. F. Dössel, Automotive Paints and Coatings, Wiley-VCH 2008
- P. G. de Lange, Powder Coatings – Chemistry and Technology, Vincentz Network 2004
- D. Satas, A. D. Tracton, Coatings Technology Handbook, 2nd ed., Marcel Dekker 2001
- P. Glöckner et al., Radiation Curing, Vincentz Network 2008

Raw materials

- B. Müller, Understanding Additives, Vincentz Network 2010
- J. Bieleman, Additives for Coatings, Wiley-VCH 2000
- W. Herbst, K. Hunger, Industrial Organic Pigments, 2nd ed., Wiley-VCH 2004
- G. Buxbaum, Industrial Inorganic Pigments, 2nd ed., Wiley-VCH 1998
- E. B. Faulkner (Ed.), R. J. Schwartz (Ed.), High Performance Pigments, 2nd ed., Wiley 2009
- U. Poth, R. Schwalm, M. Schwartz, Acrylic Resins, Vincentz Network, 2011
- U. Poth, Polyester und Alkydharze, Vincentz Network 2005

For advanced studies

- T. C. Patton, Paint Flow and Pigment Dispersion, Wiley 1979
- G. D. Parfitt, Dispersions of Powder in Liquids, Applied Science Publishers 1981
- D. Myers, Surfactant Science and Technology, VCH 1988
- D. Myers, Surfaces, Interfaces and Colloids, VCH 1990
- D. H. Solomon, D. G. Hawthorne, Chemistry of Pigments and Fillers, Wiley 1983
- D. H. Everett, Basic Principles of Colloid Science, RSC Paperbacks 1988

Journals

- European Coatings Journal (Vincentz Network)
- Journal of Coatings Technology (Federation of Societies for Coatings Technology, Blue Bell, USA)
- Surface Coatings International – JOCCA (Oil and Colour Chemists' Association, Wembley, England

Internet platform

- www.european-coatings.com (Vincentz Network)
- www.specialchem4polymers.com
- www.resinweb.com
- www.paintquality.co.uk (Paint Quality Institute)
- www.coatingsworld.com

Prof. Dr. rer. nat. Bodo Müller was born in 1954. He was responsible for developing water-borne metallic coatings and later adhesives and sealants. Since 1990 he has been professor for Coatings Technology in Stuttgart/Germany. Since 1996 he has joined in Esslingen/Germany the University of Applied Sciences. Currently, he is Head of Studies of Chemical Engineering.
He has published more than 100 papers and three books.

Dipl.-Ing. Ulrich Poth, born in 1941, underwent training at Herberts (now DuPont Performance Coatings) where he worked on developing electro-insulation coatings and resins, and powder coatings. He studied at the University of Applied Science Niederrhein, Krefeld/Germany, graduating as an engineer. In 1971 he joined BASF Coatings, Münster/Germany, where he worked in research & development, and on the production of resins for industrial coatings applications, with special emphasis on resins for automotive coatings. He ultimately held a managerial position. In 1995, he assumed responsibility development and production operations of automotive topcoats and clear coats in the OEM business unit of BASF Coatings. Although he retired in 2002, he still works on projects, provides consulting services, and is a lecturer.

Index

BUYERS' GUIDE

Binders

Acrylic resins, unspecified

Lehmann & Voss & Co. KG
Alsterufer 19, D-20354 Hamburg
Tel. +49 40 44197-0
info@lehvoss.de, www.lehvoss.de

Silicone copolymers

SILICONI COMMERCIALE S.P.A.
Via Francia 4
36053 Gambellara (Vicenza)
ITALY
TEL. +39.0444.649766
FAX +39.0444.440018
sales@siliconi.it
www.siliconi.it
SILICONI
COMMERCIALE SPA

Colorants and Pigments

Ultramarine blue

nubiola
our passion your colors
www.nubiola.com

Chromium oxide and hydrate green

NUBIOLA
Gran Via C.C., 648, 1°, Bcn, Spain
T +34 933 435 750 - F +34 933 435 766
nubiola@nubiola.com - www.nubiola.com

Red iron oxide, synthetic

nubiola
our passion your colors
www.nubiola.com

Ultramarine violet

nubiola
our passion your colors
www.nubiola.com

Bismuth vanadate/molybdate pigments

NUBIOLA
Gran Via C.C., 648, 1°, Bcn, Spain
T +34 933 435 750 - F +34 933 435 766
nubiola@nubiola.com - www.nubiola.com

Yellow iron oxide, synthetic

nubiola
our passion your colors
www.nubiola.com

Black iron oxide, synthetic

nubiola
our passion your colors
www.nubiola.com

Aluminium pigments

ECKART GmbH
Guentersthal 4
91235 Hartenstein/Germany
info.eckart@altana.com
www.eckart.net

Bronze pastes

ECKART GmbH
Guentersthal 4
91235 Hartenstein/Germany
info.eckart@altana.com
www.eckart.net

Metallic pigments

ECKART GmbH
Guentersthal 4
91235 Hartenstein/Germany
info.eckart@altana.com
www.eckart.net

Pearlescent pigments

ECKART GmbH
Guentersthal 4
91235 Hartenstein/Germany
info.eckart@altana.com
www.eckart.net

Merck KGaA
Pigments/Coatings
64293 Darmstadt, Germany
T +49 6151 72-2127, F +49 6151 72-7684
www.effects-for-coatings.com

Special-effect pigments, unspecified

ECKART GmbH
Guentersthal 4
91235 Hartenstein/Germany
info.eckart@altana.com
www.eckart.net

Merck KGaA
Pigments/Coatings
64293 Darmstadt, Germany
T +49 6151 72-2127, F +49 6151 72-7684
www.effects-for-coatings.com

Phosphate pigments

NUBIOLA
Gran Via C.C., 648, 1°, Bcn, Spain
T +34 933 435 750 - F +34 933 435 766
nubiola@nubiola.com - www.nubiola.com

Anti-corrosive pigments, unspecified

ECKART GmbH
Guentersthal 4
91235 Hartenstein/Germany
info.eckart@altana.com
www.eckart.net

Conductive pigments

Merck KGaA
Pigments/Coatings
64293 Darmstadt, Germany
T +49 6151 72-2127, F +49 6151 72-7684
www.effects-for-coatings.com

Functional pigments, unspecified

Merck KGaA
Pigments/Coatings
64293 Darmstadt, Germany
T +49 6151 72-2127, F +49 6151 72-7684
www.effects-for-coatings.com

Fillers

Barium sulphate, natural

Seitz + Kerler GmbH & Co. KG
D-97816 Lohr
Tel. + 49 9352 8787-0
Fax +49 9352 878711
www.seilo.de

Calcium sulphate (gypsum)

Seitz + Kerler GmbH & Co. KG
D-97816 Lohr
Tel. + 49 9352 8787-0
Fax +49 9352 878711
www.seilo.de

Hollow microspheres

Lehmann & Voss & Co. KG
Alsterufer 19, D-20354 Hamburg
Tel. +49 40 44197-0
info@lehvoss.de, www.lehvoss.de

Silica

HOFFMANN MINERAL GmbH
Muenchener Str. 75
86633 Neuburg (Donau), Germany
Phone: + 49 (0) 8431 53-0
info@hoffmann-mineral.com
www.hoffmann-mineral.com

Talc (hydrated magnesium silicate)

Luzenac Europe SAS
T +32 4 95 51 09 11
coatings.europe@luzenac.com
www.luzenac.com

Fillers, unspecified

HOFFMANN MINERAL GmbH
Muenchener Str. 75
86633 Neuburg (Donau), Germany
Phone: + 49 (0) 8431 53-0
info@hoffmann-mineral.com
www.hoffmann-mineral.com

Additives

Algicides

LANXESS Deutschland GmbH
Material Protection Products
51369 Leverkusen, Germany
MPP-eBusiness@lanxess.com
www.protectedbypreventol.com

Anti-blocking additives

KEIM-ADDITEC Surface GmbH
Tel. +49 (0) 6763 93 33-0
www.keim-additec.de

SILCONA GmbH & Co. KG
Tel. +49 (0) 6724 60 22 45
www.silcona.de

Anti-foam additives

SILICONI COMMERCIALE S.P.A.
Via Francia 4
36053 Gambellara (Vicenza)
ITALY
TEL. +39.0444.649766
FAX +39.0444.440018
sales@siliconi.it www.siliconi.it

SILICONI
COMMERCIALE SPA

SILCONA GmbH & Co. KG
Tel. +49 (0) 6724 60 22 45
www.silcona.de

Anti-fouling compounds

LANXESS Deutschland GmbH
Material Protection Products
51369 Leverkusen, Germany
MPP-eBusiness@lanxess.com
www.protectedbypreventol.com

Bactericides

LANXESS Deutschland GmbH
Material Protection Products
51369 Leverkusen, Germany
MPP-eBusiness@lanxess.com
www.protectedbypreventol.com

Blueing protective additives

LANXESS Deutschland GmbH
Material Protection Products
51369 Leverkusen, Germany
MPP-eBusiness@lanxess.com
www.protectedbypreventol.com

Dispersing additives

SILCONA GmbH & Co. KG
Tel. +49 (0) 6724 60 22 45
www.silcona.de

Fungicides

LANXESS Deutschland GmbH
Material Protection Products
51369 Leverkusen, Germany
MPP-eBusiness@lanxess.com
www.protectedbypreventol.com

Leveling additives

SILCONA GmbH & Co. KG
Tel. +49 (0) 6724 60 22 45
www.silcona.de

Lubricants

KEIM-ADDITEC Surface GmbH
Tel. +49 (0) 6763 93 33-0
www.keim-additec.de

SILCONA GmbH & Co. KG
Tel. +49 (0) 6724 60 22 45
www.silcona.de

Matting additives

KEIM-ADDITEC Surface GmbH
Tel. +49 (0) 6763 93 33-0
www.keim-additec.de

Preservatives

LANXESS Deutschland GmbH
Material Protection Products
51369 Leverkusen, Germany
MPP-eBusiness@lanxess.com
www.protectedbypreventol.com

Release additives

KEIM-ADDITEC Surface GmbH
Tel. +49 (0) 6763 93 33-0
www.keim-additec.de

Rheological additives

Lehmann & Voss & Co. KG
Alsterufer 19, D-20354 Hamburg
Tel. +49 40 44197-0
info@lehvoss.de, www.lehvoss.de

ROCKWOOD
Clay Additives GmbH

Optigel® TIXOGEL®
OPTIFLO® CLAYTONE®

Stadtwald Str. 44 · 85368 Moosburg, Germany
Phone: +49 8761 72 150-315
Fax: +49 8761 72 150-334
rheo@rockwoodadditives.com
www.rockwoodadditives.com

Sandability improvers

KEIM-ADDITEC Surface GmbH
Tel. +49 (0) 6763 93 33-0
www.keim-additec.de

Soft-feel additives

KEIM-ADDITEC Surface GmbH
Tel. +49 (0) 6763 93 33-0
www.keim-additec.de

Thickeners

ROCKWOOD
Additives Limited

Optigel® TIXOGEL®
OPTIFLO® CLAYTONE®

Widnes, Cheshire WA8 3AA, UK
Phone: +44 151 495-2222
Fax: +44 151 420-4088
info@rockwoodadditives.com
www.rockwoodadditives.com

Thixotropic additives

Lehmann & Voss & Co. KG
Alsterufer 19, D-20354 Hamburg
Tel. +49 40 44197-0
info@lehvoss.de, www.lehvoss.de

Water repellents

KEIM-ADDITEC Surface GmbH
Tel. +49 (0) 6763 93 33-0
www.keim-additec.de

SILCONA GmbH & Co. KG
Tel. +49 (0) 6724 60 22 45
www.silcona.de

SILICONI COMMERCIALE S.P.A.
Via Francia 4
36053 Gambellara (Vicenza)
ITALY
TEL. +39.0444.649766
FAX +39.0444.440018
sales@siliconi.it www.siliconi.it

Waxes

KEIM-ADDITEC Surface GmbH
Tel. +49 (0) 6763 93 33-0
www.keim-additec.de

Wetting additives

SILCONA GmbH & Co. KG
Tel. +49 (0) 6724 60 22 45
www.silcona.de

Additives, unspecified

KEIM-ADDITEC Surface GmbH
Tel. +49 (0) 6763 93 33-0
www.keim-additec.de

SILCONA GmbH & Co. KG
Tel. +49 (0) 6724 60 22 45
www.silcona.de

Testing and Measuring Equipment

Colour matching booths

Konica Minolta Sensing Europe B.V.
81829 München
Tel. +49 89 4357 156 0
info.germany@seu.konicaminolta.eu
www.konicaminolta.eu

Colorimeters

Konica Minolta Sensing Europe B.V.
81829 München
Tel. +49 89 4357 156 0
info.germany@seu.konicaminolta.eu
www.konicaminolta.eu

Film applicators

TQC B.V.
Developers and manufacturers of
paint test equipment
www.tqc.eu

Gloss meters

Konica Minolta Sensing Europe B.V.
81829 München
Tel. +49 89 4357 156 0
info.germany@seu.konicaminolta.eu
www.konicaminolta.eu

TQC B.V.
Developers and manufacturers of
paint test equipment
www.tqc.eu

Software for testing and measuring equipment

Konica Minolta Sensing Europe B.V.
81829 München
Tel. +49 89 4357 156 0
info.germany@seu.konicaminolta.eu
www.konicaminolta.eu

Spectrophotometers

Konica Minolta Sensing Europe B.V.
81829 München
Tel. +49 89 4357 156 0
info.germany@seu.konicaminolta.eu
www.konicaminolta.eu

Transmittance/haze meters

Konica Minolta Sensing Europe B.V.
81829 München
Tel. +49 89 4357 156 0
info.germany@seu.konicaminolta.eu
www.konicaminolta.eu

Services

Servicing companies, unspecified

We develop and realize surfaces
www.coatings-science-lab.de
Tel. +49 (0) 202 4795-123
contact@coatings-science-lab.de

The Mission: A single book covering the practical and scientific basics underpinning the strategic formulation of modern paint and coatings systems – from physicochemical concepts to the recipes themselves. This book explains and elaborates in some depth on the key principles of coatings formulation. Indispensable for formulators.

The Audience: Trainees, students and newcomers to the profession who are seeking to acquire a solid grounding in coatings formulation, along with experienced formulators wishing to deepen, extend or refresh their knowledge. A knowledge of chemistry and basic knowledge of binders, pigments and additives are required.

The Value: Coatings formulation explained step by step. The book opens with a look at the composition of coatings, placing special emphasis on the base binder in each type. Advice on specific formulations is then given before formulation guidelines are analysed. Throughout, the focus is on coatings formulation and how to arrive at the final recipe. A special feature of the book is its detailed index, which allows the reader to conduct targeted searches for specific aspects of coatings formulation.

ISBN 978-3-86630-891-6

VINCENTZ
Providing Professional Information