RESINS FOR WATER-BORNE COATINGS
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Jaap Akkerman + Dirk Mestach et al.

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Resins for
Water-borne Coatings
Foreword

There is no doubt that water-borne resins for coatings have a bright future. The environmental and health related issues have caused a slow but unstoppable change from solvent-borne resins and coatings to water-borne. It started slowly with some pioneering countries in Europe in the 1980s and became more imbedded in legislation when the solvent emission directives were introduced in 2007 and 2010. In the last decade other stricter regulations appeared that in general led to the increasing preference for water-borne resins and coatings. In fact, the change can be called a “solvent-to-water-transition” similar to the “energy transition” that we are facing to reduce CO₂ emission.

Simultaneously the legislation on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) highly influenced the resins and coatings market, not only for water-borne but for all resins and coatings. One could even say that the water-borne resins and coatings technologies even suffer more from REACH than solvent-borne for two simple reasons: water-borne resins and coatings use far more additives and these additives cannot easily replaced by alternatives that are not phased out by REACH.

What are the largest problems to overcome during the “solvent-to-water-transition” in the coming decennia? We mention a few but not by necessarily in order of priority.

First there is the overall performance of the water-borne alternatives for solvent-borne paints. There are more obvious and more well-developed transitions in, for instance, joinery and furniture coatings whereas spraying, heating, radiation curing, or two-component systems are currently used with much success. The transition in the automotive OEM industries is happening as well, but strongly depends on investments into new production lines suitable for the use of water-borne coatings. In this market segment, the conditions are favourable for water-borne coatings as the application can be controlled easily and higher temperature curing is often used. In both examples the performance of water-borne coatings is up to par or even better.

In other markets such as architectural or vehicle-refinish coatings, the transition is also happening but is not so obvious since water-borne coatings have different performance and not always up to par, when it comes to the performance.

The second problem is the presence of water in coatings where conditions such as relative humidity and temperature affect drying. When it rains outside, coating walls or wood is not possible and can only be overcome by excluding outdoor conditions, such as scaffolding with rain cover and a heater.

The third problem is the pseudoplastic rheology of water-borne paints especially in architectural paints. This is not only the case in the can, but also during application, resulting in poor open time and in the final film formation leading to limited flow. Water-borne paints often still suffer from limited flow and gloss and this may lead to inferior appearance. “Telegraphing” is an often-occurring problem as this copying the surface roughness
is caused by a lack of change in surface tension as described by Filip Oosterlinck et al. in Surface Coatings International in 6/2009. For these reasons, professional painters often still use the alternative high solids solvent-borne alkyd paints for application and aesthetic reasons.

The fourth problem is the sustainability of water-borne resins and paints when compared to solvent-borne types. Especially, in the choice between water-borne acrylics and alkyds. The use of renewable raw materials and life cycle analysis have not clearly steered the resin development in one clear direction.

The fifth problem with water-borne resins and coatings is the relatively low solid content leading to the need to apply more layers. As a consequence, this requires more application work and also road transport of more paint. And therefore, this can have a negative influence on the life cycle analysis.

All these issues will be discussed with the best of our know-how, however, not always supported by hard evidence. Resin producers and paint makers know the stodgy reality where some phenomenon or problems cannot be understood and only be solved by hard trial and error efforts with often unexplained solutions (“don’t ask me why but it works”). The so-called “tacit” know-how is often our day to day reality. Because of this issue the writing of this book was a challenge and may lead to disagreement with other specialists. We absolutely liked this challenge.

If one overlooks the last 40 to 50 years, the “solvent-to-water-transition” had a large impact of the research and development budgets of resin and paint companies. A lot, if not most developments have been done to keep-up with the evolving legislation.

We wish you a pleasant and instructive reading on behalf of all co-authors.

Jaap Akkerman and Dirk Mestach

Goes and Bergen op Zoom, The Netherlands, January 2021
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1 A brief introduction

The discussion on water-borne resins and their application in coatings immediately leads to a division in chapters on resin technologies. This is also the approach in the present book. Every resin technology is very often specifically used in a specific application area. Per resin technology the important application areas are discussed and wherever possible guidelines for formulation of the paint including starting point formulations are supplied. Comparison of performances to the alternative solvent-borne are made and shortcomings as well as better properties are discussed.

Important for any formulator of paints is to understand the resin technology he or she is using. For that reason, it is even important to know how the resins are made including all chemistry that is used and the physics transforming a hydrophobic resin into a water-borne resin. If this is not known, the formulator cannot ask the important and correct questions to the resin company’s technical support staff. Then the wrong resins or the wrong raw material components may be used in the paint. Attention is paid to the must-have information that a paint formulator needs to receive from the resin technical service people.

In Chapter 2 the history of water-borne resins and coatings is discussed. The various businesses and their importance in the market are shown. Next to that the most important definitions are reviewed critically.

In Chapter 3 water-borne dispersions are discussed. Important is the definition of dispersion polymers in comparison with emulsion polymers (discussed in Chapter 6). They use completely different technologies, production processes and even monomers. The process will influence for instance the morphology or surface of the dispersed particle. It is also important to understand that the dispersed particles, whether in the form of a dispersion or emulsion, will only lead in a perfect film if coalescence is possible during the application and drying of the film. The various chemically based classes of dispersion polymers are discussed: their chemical composition almost directly will lead to the application area. It can happen that a “dispersion” polymer actually proves to be an emulsion polymer. It is also important to realize that not all resin suppliers use the same definition. This may lead to incorrect choice of the resin that you will use to start the development of a paint formulation.
A brief introduction

Chapter 4 focuses on water-borne alkyds. They are divided into three categories: dissolved, externally emulsified and internally emulsified alkyds. Each of these will be discussed in detail, including the demand on the resin properties, the different requirements and possibilities regarding resin functionalization and processing technology. Also, recipes and applications are presented.

In Chapter 5 water-borne epoxies will be reviewed. An overview of properties and application areas and their relationship to the structure and crosslinking of epoxy resins is followed by a summary of emulsification methods for the preparation of anionic-, cationic- and non-ionic epoxy resin dispersions. The use of electrophoretic dip coating as the sole application method for water-borne epoxy resins in the automotive industry is described. The chapter ends with a discussion of future trends in the area of water-borne epoxy resins with an emphasis on the benign replacement of bisphenol A (BPA) and examples of bio-based epoxy resins.

In Chapter 6 water-borne polyurethane (PU) paint formulations are discussed that use PU dispersions (one and two-component) or hydroxyl functional emulsion resins that are cured with polyisocyanate crosslinkers (two component). PU dispersion resins often have very special applications and in most cases are used in combination with other resins, as will be shown in application examples. Attention will be paid to their various and complex production processes. The well and broadly used two component hydroxyl functional emulsion resins cured with polyisocyanates are subsequently discussed and illustrated with several guideline formulations in a variety of applications.

In Chapter 7 silicone resins and their use in silicone resin emulsion paints and plasters are described. The key features of silicone resin-based coatings are low water absorption and at the same time high water vapour permeability. With these physical principles the coatings are extremely durable and last for decades. Guide formulations for paints and plasters are presented and the performance is discussed. Aside of the silicone resins other silicone components are presented which are used in coatings for special effects e.g. anti-scratch or easy-clean.

In Chapter 8 soluble silicates and their properties are discussed. Soluble silicates, also commonly known as water glass or alkali silicates, are the only type of glasses, which are soluble in water again. The different production routes as well as the different structures in solution and types of water glass are shown, which have an influence on the chemical properties of the products. By curing, they form very stable inorganic covalent bonds, which match especially with inorganic fillers, pigments and substrates. Different curing methods are presented, as well as the broad range of different applications where soluble silicates are the means of choice. Especially in combination with organic emulsions they show a very high potential for versatile hybrid coatings.

In Chapter 9 melamine resins as the most important type of amino resins are presented. Formulations of water-borne stoving enamels with melamine resins in combination
with alkyds, polyesters and acrylics are discussed and formulation examples for different applications are given.

In Chapter 10 the REACH situation and other regulations will be discussed. During the last twenty years several important regulations have been implemented, which have had and continue to have a direct impact on the coating sector in Europe. Among these we may indicate the European Directives to reduce the emissions of volatile organic compounds (VOC), the 'REACH' regulation for the control of chemical substances and the European Regulation on biocidal products. Other topics are currently on European or national authorities' agendas, like the nanomaterials, the emissions of dangerous substances into the indoor air in buildings and sustainable development.

The closing Chapter 11 will take you through an outlook in the future. What problems – as described in the foreword – need to be solved, are there still solvent-borne resins and what new resin technologies or chemistries will appear on the horizon.

This book does not cover in detail all the individual coating raw materials required to produce a good coating. Only if the coating raw material is essential and specifically critical in interaction with the resin, it is discussed.
2 Water-borne resins and coatings: history, markets and definitions

Jaap Akkerman and Dirk Mestach

This chapter deals with the history of water-borne resins and its coatings. In order to understand water-borne resins that are used in the water-borne coating formulations, not only the history is important, but also the markets and application areas in these markets.

In order to use the same language, the definitions used in Europe and the deviating ones used elsewhere are discussed.

2.1 History of water-borne coatings and resins

2.1.1 The past

Paint made its earliest appearance about 40,000 years ago. It was one of the earliest inventions of mankind as it truly can be traced to the dawn of history, to artefacts from pre-historic humans, and all cultures. Tribes in Europe, Australia, and Indonesia painted images of hunters and herders on cave walls and had expanded their colour palette to include many colours. Some cave paintings drawn with red or yellow ochre, hematite, manganese oxide, and charcoal were made by early Homo sapiens as long as 40,000 years ago[1]. They used eggs, blood, milk or tree sap as “resins” in order to improve the adhesion and durability. Water was the only solvent available at that time. They then applied the paint with fingers, brushes, or by blowing them through hollow bones, very much like today’s airbrushes.

Ancient coloured walls at Dendera, one of the best-preserved temple complexes in Egypt, which were exposed for years to the elements, still possess their brilliant colour, as vivid as when they were painted more than 2,300 years ago. The Egyptians mixed their colours with a binding substance, such as casein, egg whites, bees wax and vegetable gums such as Gum Arabic, the hardened sap of various species of the acacia tree and applied
them separately from each other without any blending or mixing them. They appear to have used only six basic colours: white, black, blue, red, yellow, and green. First the area was covered entirely with white, then the design was traced in black, leaving out the lights of the ground colour.

The Egyptians continued the advancements and began painting on fresh lime plaster, where the pigments became fixed by carbonization and drying of the lime. Greeks and Romans expanded upon these techniques, to create a painting style not matched till the Renaissance – when Italian artists made paint with plant oils to create works of astonishing colour and depth that still captivate viewers today. The Greeks also developed lead white paint, which was the most popular white paint in use until titanium dioxide replaced it in the nineteenth century. White lead is the basic lead carbonate, 2PbCO₃·Pb(OH)₂⁴[2] and occurs naturally as a mineral. Lead-based paint has been the source of health issues for painters and others for centuries.

Before the industrial revolution “whitewash” also known as calcimine, kalsomine, calamine, or just lime paint, a type of paint made from slaked lime (calcium hydroxide, Ca(OH)₂ or chalk calcium carbonate, (CaCO₃), was one of the main paint types used. Whitewash cures through a reaction with carbon dioxide in the atmosphere to form calcium carbonate in the form of calcite, a reaction known as carbonization. It was usually used for exterior applications, however, it has been also applied for interior applications, for example in kitchens. Whitewash could be tinted for decorative use however it can rub off to a small degree. Various materials were added to the lime to improve the quality of the coating. Portland cement was added to improve the durability in harsh environments. Casein, a protein extracted from milk, was added to improve adhesion and durability. Actually, the origins of modern water-borne paints begin with these casein paints.

At the onset of the industrial revolution, in the mid-18th century, paint was being ground in steam-powered mills, and an alternative to lead-based pigments had been found in a white derivative of zinc oxide. Interior house painting increasingly became the norm as the 19th century progressed, both for decorative reasons and because the paint was effective in preventing the walls being affected by moisture. Linseed oil was also increasingly used as an inexpensive “resin”. The paint and coatings industry, however, had to wait for the industrial revolution before it became a recognized element of the economy.

The first US paint patent dating from 1865 to Flinn (US 50,068), covers a composition based on zinc oxide, potassium hydroxide, resin, milk and linseed oil. In 1867, Averill of Ohio patented the first prepared or “ready mixed” paints in the United States. In the mid-1880s, paint factories began springing up in populated and industrial centres across the nation. In 1886, Sherwin-Williams in the United States started as a large paint-maker and invented a paint that could be used directly from the tin without additional preparation.

The casein paints were continually improved. By the 1930s they contained pigments with a high refractive index (high covering power), similar to those used in oil paints. The
casein paints were traded as a powder or in the form of a paste. In order to trade the paste form, it was necessary to protect the paint against hydrolysis and infestation by micro-organisms. A major advantage of casein binders was their low cost. The paints were easy to apply and provided covering in one layer. A disadvantage of the casein paints was, that they are porous and therefore easily fouled. Adding drying oils resulted in a more compact film and improved durability as well. A drawback was that the drying process became slower. When the amount of oil in the paint was increased, the casein paint evolved into an "emulsion paint". In the 1920s, however, alkyd resins were first developed\cite{9,15}. In many cases, the drying oil was partially or completely replaced by an alkyd to accelerate the drying of the paint film. The role of the casein in the paint shifted from "resin" to emulsion stabilizer and thickener. The drying oil and the alkyd became the real binders.

\subsection*{2.1.2 The present: from polymer science to resins}

The development of modern paint is closely associated with the event of polymer science. However, as early as the 1830s people like Bacroonnot and Schönbein developed derivatives of the natural polymer cellulose such as celluloid and cellulose acetate. In 1844, Goodyear, amongst others, discovered that adding sulphur to natural rubber, polyisoprene, transformed the material from a flexible, non-sticky material to a hard solid ("ebonite")\cite{8}, depending on the amount of sulphur used. In 1907 Baekeland invented the first synthetic polymers: phenol-formaldehyde condensation resins called Bakelite\cite{7} and Novolac\cite{8}.

Despite advances made, the molecular nature of polymers was not well understood until the work of Staudinger in 1922\cite{9}. He was the first to propose that polymers consisted of long chains of atoms held together by covalent linkages. He presented this at a meeting of the Swiss Chemical Society, coinig the term "macromolecules"\cite{10}. He was awarded the Nobel Prize for this in 1953.

Meanwhile, also the very first inventions were made that would eventually lead to the development of water-borne paints. In 1912 Gottlob patented the dispersion polymerization of isoprene (German patents 254 & 255), using egg albumin or starch as emulsifier. Polyvinyl acetate was patented by Klatte and Rollet in Germany in 1914. Rather than using naturally occurring stabilizers, the first synthetic surfactants developed in Germany during World War I (WWI) were used. These were short-chain alkyl naphthalene sulfonates, similar to the materials are still used today.

It was not until the end of the World War I, when a lot of paint raw materials such as linseed oil were in short supply, that artificial resins became available on the market. In 1920 Kienle of General Electric develops unsaturated alkyls\cite{11} that were commercialized under the name "Glyptal" resins (from glycercor phthalate). A patent is applied for, but the patent is ruled invalid in 1935 due to existing prior art, which enables other companies to produce and sell alkyls (after 1935). Kienle was probably responsible for the combination
of the word alkyd – from the condensation of alcohols and acids. Alkyd modified oil paints and then alkyd paints were eventually used on cars and household appliances.

In 1929 Carothers (DuPont) publishes papers on linear polyesters[12], He is generally credited with formalizing the concept of functionality, although Kienle had almost certainly been thinking along the same lines. By 1930 Flory[13] starts work on molecular weight distributions (experimentally and theoretically) and shows that step-growth polymerizations follow the Gaussian distribution for molecular weight. In the years leading up to the second World War, a range of additional synthetic resins was appearing.

In 1933 Schläk patents the first epoxy resins: diglycidyl ethers made from epichlorohydrin and bisphenol A[14]. Also, Castan (Switzerland) and Greenlee (USA) file patents on epoxy resins. Epoxies resins only became commercially available in about 1947. They impart outstanding resistance properties and find many applications, including one- and two pack air drying systems. The latter includes a polyamine, polyamide or polyamino-amide as a crosslinker. This results in durable and resistant films used in heavy duty coatings.

Urea formaldehyde resins started to be combined with alkyd resins. Several US automobile producers, such as Ford and Chrysler, started using alkyd enamel topcoats. Urethane resins produced by Bayer for elastomers and foams are first being introduced in 1937. Later on, polyurethane paints were produced by Bayer based on solvent-borne polyols (“Desmophen”) and polyisocyanates (“Desmodur”), often referred to as “D-D” coatings, for example on German military planes. In 1939 DuPont introduced thermosetting acrylics developed by Strain[15].

During the years of the second World War, there were a couple of important developments in the field of water-borne paints. In the US, the classic cheap interior wall paints based on casein were improved by combining them with both drying oil and alkyd resin. The acid number of the resin was high enough to be neutralized with ammonia in order to make them dispersible in water. In order to obtain fast drying it was necessary that the binder had a high molecular weight (degree of polymerization). The first drying was caused by the evaporation of the water in the paint. The through-drying was due to the oxidative crosslinking of the alkyd resin and the drying oil. A disadvantage of this type of paint was the fact that only low gloss coatings could be made, limiting the use to interior wall paints. In Germany in the meantime, due to the shortage of linseed oil, polyvinyl acetate and polyvinyl propionate latexes were used for the preparation of wall paints.

One of the most important developments was the emulsion polymerization process for the synthesis of styrene-butadiene latexes. Even though in Germany, Luther and Hück patented a method for making a styrene-butadiene dispersion already in 1932[16], the biggest progress was made in the US. Being cut off from their supplies of natural latex by the occupation by Japan of big parts of south-east Asia, a project was set-up that was the second largest in the US during WW2, after the Manhattan project aimed at developing
the atomic bomb. The so-called GR-S (government rubber styrene), was developed originally for the production of car tires and tracks used for military vehicles. GR-S according to the “Mutual Recipe” consisted of 75% butadiene, 25% styrene with a rosin soap as emulsifier and a small amount of mercaptan. At the end of WWII, it was found that the production capacity that was installed could also be used for paint applications, mainly in the US. Later, polyvinyl acetate dispersions became available which were also increasingly used. In 1953 the first all-acrylic dispersion was introduced commercially under the trade-name “Rhoplex” AC-33 in the USA or “Primal” AC-33 in Europe.

In the 1970s, satin gloss latex paints were introduced. For these paints, new types of fine-particle size polymer dispersions were developed. These were combined with new coalescing agents. In recent years, a large variety of high-quality acrylic dispersions have been introduced on the market, including types with a controlled particle morphology or types that contained functional groups for (self) crosslinking. At the end of the 1960s, the first polyurethane dispersions were patented[18] by Bayer although it would at least take until the 1980s before they saw widespread use.

For several years, alkyd emulsions have also made a “come-back”. In the 1950s, water-reducible alkyd paints were introduced for industrial applications[18]. These alkyd paints contained both alkyd resins in dispersed and dissolved form and were combined with amino-formaldehyde resins for thermo-setting applications. Vianova, a heritage company of the current Allnex, pioneered the use of “core-shell” alkyd emulsions under the trade-name “Resydrol”, where the alkyd core was stabilized by an acrylic carboxylic acid functional shell. Also, other internally stabilized types of alkyd emulsions appeared on the market. One particular driver was that alkyls are easily produced from renewable oils or fatty acids. Also, other alkyd building blocks, such as the polyols or polacids can be derived from sustainable building blocks.

The following chapters will discuss the different aspects of modern resins for water-borne coatings.

2.1.3 The present: water-borne resins and coatings

The modern development of water-borne resins and coatings may be roughly divided in the years before 1970, the years between 1970 and 1990 and the years after 1990. This choice is maybe arbitrary, since this differs depending on the end use application and region.

Before 1970, water-borne coatings and resins were only applied in those areas and applications where they performed better than solvent-borne paints, be it on performance or on cost. Performance wise there are not many examples except for the widely used interior and exterior wall paints. Here classical acrylic, styrene or styrene-butadiene dispersions were used in formulations with a low binder content. Chalk and water-glass binders
and coatings are other well-known examples used in both interior and exterior wall paints. Other main application of early water-borne coatings is the electrophoresis coatings used in industry: both in automotive OEM as well as industrial metal coatings.

In the years between 1970 and 1990, environmental awareness resulted in a slow but steady reducing of the amounts of organic solvents. Solvent emissions could be avoided either by lowering the content of volatile organic solvents (VOC) such as high solids coatings or using water-borne or solvent-free solutions such as radiation cured or powder coatings. Legislation initiatives started in Europe around 2000, amongst others in the Netherlands. The KWS2000 ("KoolWaterStoffen" or hydrocarbon) decree was an initiative to reach a reduction of 100 KT/year solvent emissions, by transfer from low or medium solid solvent-borne coatings to water-borne or high solid coatings in the architectural paint markets[19]. In spite of these initiatives, it took until 2007 to 2010 before a VOC legislation was implemented in the European Union[20]. During this period frantic research efforts were initiated in most resin and paint companies as well as in Universities and Research Institutes. The many disadvantages of the older generation water-borne resins and paints still had to be overcome. This will be discussed in Chapter 3.

The results of these efforts can be observed in the next period starting from 1990. If we focus on architectural paints, a continuous stream of new water-borne resins and paints appeared on the market with for instance for water-borne trim paints VOC’s of 120 to 150 g/l (incl. water) as from 1990 till recently VOCs of 30 to 50 g/l (incl. water). This was also the case for high solids resins and paints and has led to low VOC alkyd paints for instance with VOCs of 250 to 300 g/l (a 300 g/l VOC became the limit for trim paints in 2010). For wall paints, the VOCs can be as low as close to 0 g/l for interior application and up to 5 to 30 g/l (incl. water) for high resistance or outdoor wall paints where the limit is 30 g/l (incl. water).

For automotive coatings – from primer to topcoat – the choice between water-borne and high solid resin technology strongly depends on the production lines that are able to use water-borne coatings. The market is still in transition depending on the characteristics of these production lines. On most automotive OEM production lines, a water-borne cathaphoretic electro deposition (CED) coating is applied to new car bodies. Use of water-borne base coat application is state of the art though the VOCs of these coatings can still be quite high (420 g/l excl. water). Solid colour topcoats are water-borne in a number of automotive OEM factories. Clear coats are less commonly using water-borne technology, though some car producers have water-borne production lines. Clear coats are in most cases still solvent-borne (ultra) high solids (<VOC 420 g/l).

For vehicle refinish coatings, water-borne technology is more common than in automotive, though clear coats and solid colours tend to be more solvent-borne high solids than water-borne. Base coats are almost all water-borne based on acrylic or polyurethane dispersions or combinations thereof with a VOC from 350 to 400 g/l excl. water (limit 420 g/l excl. water).
2.1.4 The future

The recent years of 2010 to 2020 have shown a further increase of low emission paints with a move to either water-borne or high solids, depending on the specific end-use application. Additionally, the sustainability as well as life cycle analysis (LCA), carbon footprint and use of renewable and recycled raw materials, has strongly influenced the developments over the last years.

These trends do not always match with the move to water-borne or high solids. Earlier published results from the 1980s of LCA studies[21] in the Netherlands show at least that water-borne acrylic dispersions are not more LCA friendly as the then actual high solid alkyd paints. More recent investigations show comparable results, when parameters that are used in the calculations are correctly used and peer reviewed. The dominant contribution on all segments in the LCA calculations is by far the titanium oxide (when used in the formulation, however most coatings are using TiO₂). Another trend is the carbon footprint calculation that is more focused on one – very important – parameter and thus only partly sustainable. If one adds bio-based to the equation, the situation becomes even more complicated. It may favour alkyds, both high solids as well as alkyd emulsions[22].

Another recent trend in resin chemistry is the focus on either bio-based alternatives for existing monomers used as drop-in in the resins or new bio-based building blocks (having different chemical structures) that can be alternatives when providing similar performance in the paint. However, a main obstacle remains the high raw material cost of these bio-based alternatives and the uncertainty of supply.

The near future may also have surprising events ahead that can lead to the ban or limitation in use of certain raw materials or even cause major transitions in application of water-borne or high solid paints or even more vital raw materials. The use of titanium dioxide – at the moment of writing this book – is under pressure, being registered as a carcinogenic raw material. This may in worst case lead to a radical change in use of colour in any paint application. Chapter 10 is addressing all H&S issues in the coatings and resin world.

This book ends with a special chapter on the coming innovations and outlook for the coming decades.

2.2 Markets and applications

2.2.1 The market for water-borne coating resins

Since the early days of water-borne coatings, the coating resins used and their applications have come a long way. The substitution of solvent-borne coatings by water-borne equivalents was mainly due to legislation on the emissions of organic solvents (Clean Air Act[23], U.S. Environmental Protection Agency-EPA[24], the solvent emissions directive – SED[25]).
Table 2.1: Estimated global value of paints and resins, based on several sources

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Global coatings market**</td>
<td>99.6</td>
<td>115.2</td>
<td>1.8%</td>
</tr>
<tr>
<td>Global resins market***</td>
<td>28.8</td>
<td>36.0</td>
<td>4.7%</td>
</tr>
<tr>
<td>Global water-borne coatings market****</td>
<td>60.7</td>
<td>80.3</td>
<td>5.7%</td>
</tr>
<tr>
<td>Global water-borne resin market*****</td>
<td>24.0</td>
<td>37.0</td>
<td>5.3%</td>
</tr>
</tbody>
</table>

* based on several sources and years
** www.decisiondatabases.com/ip/5588-paint-maker-industry-market-report
# stated CAGR (compound annual growth rate)

Nevertheless, in some market-segment, solvent-borne coatings are still the dominant technology (only 22% of all coatings in Europe are water-borne).

Automotive, protective and wood coating applications are important growth areas for water-borne coating resins. In Europe and North America, however, it is estimated that the growth will be moderate due to strong regulations for coating resins. The Asia Pacific water-borne coatings market, however, is projected to witness the highest growth. Factors such as huge and increasing population, rapidly growing construction activity, and increase in the number of automobiles, wooden furniture, and electronic appliances are driving the growth. Acrylic resins are the fastest-growing class of coating resins. They are used in a wide range of applications for their chemical and mechanical characteristics and aesthetic properties. Currently, the strongest demand for water-borne acrylic coating resins comes from the automotive, architectural and construction markets. Next to acrylics, also water-borne epoxy and polyurethane coating resins are high growth segments in the resins market.

The market size data of the global market for water-borne coating resins was estimated to be 24,000 million euros and forecasted to reach over 37,000 million euros in 2025, growing at a CAGR of 5.3% from 2019[28]. The estimated breakdown[27] going from the global paint volume – CACR (compound annual growth rate) of 1.8% – to the global water-borne coating resins volume (24% of the total value and a CACR of 5.3%) – shows the substantial value of the water-borne resins and their high growth rate (Table 2.1).

Table 2.2 shows the spread of the global volumes over the different regions. Asia Pacific (mainly China) produced in 2017 (in volume) by far the most water-borne coatings: 24.6 billion Euros. This region also shows the largest growth both in sales volume as well
Table 2.2: Spread of global water-borne coatings and their growth, market size, by region in 2017 and 2022

<table>
<thead>
<tr>
<th>Region</th>
<th>EUR billion 2017</th>
<th>% of global 2017</th>
<th>EUR billion 2022</th>
<th>% of global 2022</th>
<th>growth [%]</th>
<th>CACR [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asia-Pacific</td>
<td>24.6</td>
<td>39 %</td>
<td>34.3</td>
<td>41 %</td>
<td>39 %</td>
<td>6.6 %</td>
</tr>
<tr>
<td>Europe</td>
<td>18.5</td>
<td>30 %</td>
<td>22.0</td>
<td>27 %</td>
<td>19 %</td>
<td>3.2 %</td>
</tr>
<tr>
<td>North America</td>
<td>11.4</td>
<td>18 %</td>
<td>15.8</td>
<td>19 %</td>
<td>39 %</td>
<td>6.4 %</td>
</tr>
<tr>
<td>South America</td>
<td>3.5</td>
<td>6 %</td>
<td>5.3</td>
<td>6 %</td>
<td>51 %</td>
<td>8.6 %</td>
</tr>
<tr>
<td>Middle East &amp; Africa</td>
<td>4.4</td>
<td>7 %</td>
<td>5.3</td>
<td>6 %</td>
<td>20 %</td>
<td>3.4 %</td>
</tr>
<tr>
<td>Total</td>
<td>62.4</td>
<td>100 %</td>
<td>82.7</td>
<td>100 %</td>
<td>33 %</td>
<td>5.4 %</td>
</tr>
</tbody>
</table>

as in 6.6% CACR. The growth of water-borne coatings is substantially slower in Europe and the Middle East & Africa.[28]

The global market of water-borne coatings is spread across all market-segments as can be seen in Figure 2.1. The most important segment for water-borne coatings and resins is the architectural coatings market, more specific in both interior as well as exterior wall or façade paints. This market dominates the total global sales as well as volume (Table 2.1) by over 60% in paint sales and 40% in resin sales. Water-borne wall paint types started to appear over 50 years ago, qualities as well as application areas were and are differing strongly per country. For instance, in France interior wall paints have for a long time been solvent-borne – see for example the VOC values for solvent-borne wall paints (Chapter 2.3.3) – and the PVC (pigment volume concentration) of both interior as well as exterior wall paints vary largely depending on the country and application: for example in the Netherlands the high end wall paints have substantially lower PVC than in the neighbouring countries. Another application in architectural coatings are the trim paints used in the USA. In Europe the use of water-borne trim paints is of more recent date. Recently architectural coatings are divided in wall paints and deco/DoItYourself (Do-it-yourself) or trim paints. Deco paints are trim paints for professional painters and DIY obviously for the Do-it-yourself painter. Often similar or almost similar brands are sold in deco via warehouses or company-shops whereas the DIY paints are sold under different brands in shops and outlet stores.

Second largest business segment is automotive coatings with a substantial percentage of 9% in value of water-borne coatings. It is a fast-growing market due to mainly expansion of car production in Asia, more specifically in China.

If one looks at the global spread of resin types or technologies the figures are almost evenly divided over the technologies. The biggest part is “others” which suggests that there
Table 2.3: Volumes of deco/DIY paints in Europe in 2016, breakdown for architectural in total and water-borne

<table>
<thead>
<tr>
<th>Segment</th>
<th>Overall [t]</th>
<th>Segment share [%]</th>
<th>Water-borne [t]</th>
<th>Water-borne share/total [%]</th>
<th>Water-borne share [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interior wall</td>
<td>3,275,000</td>
<td>56 %</td>
<td>3,105,000</td>
<td>95 %</td>
<td>66 %</td>
</tr>
<tr>
<td>Exterior wall</td>
<td>1,305,000</td>
<td>22 %</td>
<td>1,180,000</td>
<td>90 %</td>
<td>25 %</td>
</tr>
<tr>
<td>Wood/trim</td>
<td>1,255,500</td>
<td>22 %</td>
<td>440,000</td>
<td>35 %</td>
<td>9 %</td>
</tr>
<tr>
<td>Totals, tonnes</td>
<td>5,835,500</td>
<td>100 %</td>
<td>4,725,000</td>
<td>81 %</td>
<td>100 %</td>
</tr>
</tbody>
</table>

Source: European Coatings Journal 11/2017, p. 12-14

are a lot of smaller polymer technologies present in the water-borne resin market. Most water-borne technologies will be discussed in this book and not discussed here. It is important to realize that the global market technologies mentioned in Figure 2.2 are clusters of applications.

So far, the sales of water-borne resins have been discussed. The comparison of volumes is as important, especially if a technological comparison is made. Tables 2.3, 2.4 and 2.5
Table 2.4: Volumes of industrial and OEM paints in Europe in 2016, breakdown for OEM and industrial coatings in total and water-borne

<table>
<thead>
<tr>
<th>Segment</th>
<th>Overall [t]</th>
<th>Segment share [%]</th>
<th>Water-borne [t]</th>
<th>Water-borne share/total [%]</th>
<th>Water-borne share [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Automotive OEM</td>
<td>281,250</td>
<td>9 %</td>
<td>175,000</td>
<td>62 %</td>
<td>24 %</td>
</tr>
<tr>
<td>Automotive refinish</td>
<td>190,500</td>
<td>6 %</td>
<td>44,000</td>
<td>23 %</td>
<td>6 %</td>
</tr>
<tr>
<td>Other transportation</td>
<td>87,500</td>
<td>3 %</td>
<td>22,000</td>
<td>25 %</td>
<td>3 %</td>
</tr>
<tr>
<td>Protective &amp; marine</td>
<td>736,000</td>
<td>23 %</td>
<td>45,500</td>
<td>6 %</td>
<td>6 %</td>
</tr>
<tr>
<td>Industrial wood</td>
<td>522,000</td>
<td>16 %</td>
<td>130,500</td>
<td>25 %</td>
<td>18 %</td>
</tr>
<tr>
<td>Agricultural, construction &amp; earthmoving (ACE)</td>
<td>110,000</td>
<td>3 %</td>
<td>38,000</td>
<td>35 %</td>
<td>5 %</td>
</tr>
<tr>
<td>Precoated metal (Coil)</td>
<td>190,000</td>
<td>6 %</td>
<td>3,500</td>
<td>2 %</td>
<td>0 %</td>
</tr>
<tr>
<td>Metal packaging (Can)</td>
<td>201,500</td>
<td>6 %</td>
<td>80,500</td>
<td>40 %</td>
<td>11 %</td>
</tr>
<tr>
<td>Other (general metal and plastic)</td>
<td>920,000</td>
<td>28 %</td>
<td>176,500</td>
<td>19 %</td>
<td>25 %</td>
</tr>
<tr>
<td>Totals, tonnes Industrial and OEM</td>
<td>3,238,750</td>
<td>100 %</td>
<td>715,500</td>
<td>22 %</td>
<td>100 %</td>
</tr>
</tbody>
</table>

Source: European Coatings Journal 11/2017, p.12–14

Table 2.5: Combination of Tables 2.3 and 2.4

| Total and water-borne volumes of deco/DIY, industrial and OEM coatings in Europe in 2016 |
| Totals, tonnes deco/DIY                     | 5,835,500 | 64 % | 4,725,000 | 81 % | 87 % |
| Totals, tonnes industrial and OEM           | 3,238,750 | 36 % | 715,500   | 22 % | 13 % |
| Total European volumes in tonnes            | 9,074,250 | 100 %| 5,440,500 | 60 % | 100 %|

show available data of 2016 volumes for Europe, both as total and as water-borne systems. As can be seen, the volume percentage of water-borne paints in architectural coatings is substantial, up to 81%. The high levels for architectural systems come from the dominance of water-borne wall paints. Trim paints account only for 35% of the water-borne coatings. The highest growth rate for water-borne will probably occur in this segment as some of the application issues are solved.

The volume percentage of water-borne paints in the segments industrial and automotive OEM coatings are as low as 22% (Table 2.4). For industrial applications, only automotive OEM has a high score, most probably due to the full water-borne sub-segment electrophoreses coatings. All other segments score low levels of water-borne paint (2 to 40%).
Water-borne resins and coatings: history, markets and definitions

Table 2.6: Global markets and their detailed applications (based on author’s experience and estimates)

<table>
<thead>
<tr>
<th>Markets in review (see Figure 2.1)</th>
<th>Main applications</th>
<th>Applications used in this book</th>
<th>Present in water-borne coatings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Architectural</td>
<td>decorative</td>
<td>deco</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>Do-it-yourself/DIY</td>
<td>DIY</td>
<td>medium</td>
</tr>
<tr>
<td></td>
<td>trimpaints or wood coatings</td>
<td>trim paints</td>
<td>medium</td>
</tr>
<tr>
<td></td>
<td>wall or façade paints</td>
<td>wall paints</td>
<td>full</td>
</tr>
<tr>
<td></td>
<td>plaster</td>
<td>wall paints</td>
<td>full</td>
</tr>
<tr>
<td></td>
<td>plastic, concrete and metal</td>
<td>plastic, concrete or metal</td>
<td>medium</td>
</tr>
<tr>
<td></td>
<td>new vehicles</td>
<td>automotive</td>
<td>limited</td>
</tr>
<tr>
<td></td>
<td>electrophoresis car bodies</td>
<td>automotive</td>
<td>high</td>
</tr>
<tr>
<td></td>
<td>car refinishes</td>
<td>car refinishes</td>
<td>medium</td>
</tr>
<tr>
<td></td>
<td>plastic coatings (OEM parts)</td>
<td>automotive</td>
<td>limited</td>
</tr>
<tr>
<td></td>
<td>OEM original equipment manufacturing</td>
<td>automotive</td>
<td>limited</td>
</tr>
<tr>
<td>Automotive</td>
<td>marine</td>
<td>protective</td>
<td>limited</td>
</tr>
<tr>
<td></td>
<td>protective</td>
<td>protective</td>
<td>limited</td>
</tr>
<tr>
<td></td>
<td>anti-corrosion</td>
<td>protective</td>
<td>limited</td>
</tr>
<tr>
<td></td>
<td>metal coatings</td>
<td>metal coatings</td>
<td>medium</td>
</tr>
<tr>
<td></td>
<td>ACE coatings</td>
<td>metal coatings</td>
<td>limited</td>
</tr>
<tr>
<td></td>
<td>glass coatings</td>
<td>glass coatings</td>
<td>limited</td>
</tr>
<tr>
<td></td>
<td>OEM original equipment manufacturing</td>
<td>metal coatings</td>
<td>medium</td>
</tr>
<tr>
<td>General industrial</td>
<td>plastic coatings</td>
<td>plastic coatings</td>
<td>medium</td>
</tr>
<tr>
<td></td>
<td>coil coatings</td>
<td>coil coatings</td>
<td>limited</td>
</tr>
</tbody>
</table>

Overall the score is only 22%. Combining Tables 2.3 and 2.4 gives the European volume of architectural, industrial and automotive OEM coatings, it adds up to 9.0 billion kilos of coatings of which 5.4 billion kilos (60%) are water-borne (Table 2.5). Unfortunately, for the global volumes no comparable data are available.

Table 2.6 shows a breakdown of the most important sub-segments, classified in the various main segments. The presence in water-borne is in this case an estimate of the au-


### Markets and applications

#### Table 2.6 (continue)

<table>
<thead>
<tr>
<th>Markets in review (see Figure 2.1)</th>
<th>Main applications</th>
<th>Applications used in this book</th>
<th>Present in water-borne coatings</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Wood</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>industrial wood</td>
<td>joinery</td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td>joinery</td>
<td>joinery</td>
<td>full</td>
<td></td>
</tr>
<tr>
<td>kitchen cabinets</td>
<td>kitchen cabinets</td>
<td>medium</td>
<td></td>
</tr>
<tr>
<td>flooring, parquet</td>
<td>flooring</td>
<td>medium</td>
<td></td>
</tr>
<tr>
<td><strong>Packaging</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>packaging</td>
<td>packaging</td>
<td>limited</td>
<td></td>
</tr>
<tr>
<td>interior can coatings</td>
<td>can coatings</td>
<td>limited</td>
<td></td>
</tr>
<tr>
<td>exterior can coatings</td>
<td>can coatings</td>
<td>limited</td>
<td></td>
</tr>
<tr>
<td><strong>Other</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>aircraft and aerospace coatings</td>
<td>aerospace coatings</td>
<td>limited</td>
<td></td>
</tr>
<tr>
<td>paper coatings</td>
<td>paper coatings</td>
<td>high</td>
<td></td>
</tr>
<tr>
<td>intumescent coatings</td>
<td>fire retarding coatings</td>
<td>medium</td>
<td></td>
</tr>
</tbody>
</table>

Deco and DIY involve in most cases the same resins and formulations except for legislative matters.
Only then the applications are mentioned
When possible, OEM is not used since it involves many different industries

Several sub-segments appear in different segments due to totally different applications of the same technologies.

Not the least important issue is to mention the most important resin producers that are leading producers in water-borne resins and their specific resin technologies (Table 2.7, p. 28).

### 2.2.2 Coatings market definitions

Coating market definitions are as varied as there are countries or continents. Instead of using larger segments as presented below, more specific applications to focus the application are used. Table 2.6 illustrates the used terminology in this book.

#### Wall paints

Wall paints can be divided into exterior and interior wall paints.

Exterior wall paints are also called façade paints. They are applied on the outside of façades of brick walls, masonry, concrete, PVC and other plastic panels or metal cladding, as well as plastering. Depending on the type of surface they need different performance...
<table>
<thead>
<tr>
<th>Company</th>
<th>Water-borne resins technologies</th>
<th>Most important brand names</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alberdingk Boley</td>
<td>acrylate dispersions types AC and AS, PUD type U</td>
<td>Alberdingk, Albudur, Albolink</td>
</tr>
<tr>
<td>Allnex</td>
<td>acrylics, epoxies, alkyds, polyurethanes, acrylic-polyurethane hybrids, cationic electro deposition, amino resins</td>
<td>Setaqua, Resydrol, Acropol, Ucecoat</td>
</tr>
<tr>
<td>Arkema</td>
<td>acrylics</td>
<td>Encor, Synaquana</td>
</tr>
<tr>
<td>Axalta</td>
<td>acrylics</td>
<td>PercoHyd, Standox, Lucite</td>
</tr>
<tr>
<td>BASF</td>
<td>acrylics</td>
<td>Propiofan, Acrional, Joncryl, Styrofan, AQAGloss, Glascol, Luhydran</td>
</tr>
<tr>
<td>Covestro</td>
<td>acrylics, polyurethanes, acrylic-polyurethane hybrids, alkyds</td>
<td>Bayhydrol types U, UH, PAC, PU etc., NeoCryl, NeoPac, Haloflex, NeoRez, NeoRad, Uradil</td>
</tr>
<tr>
<td>DIC</td>
<td>acrylics, epoxies, polyurethane</td>
<td>Watersol, Burnock</td>
</tr>
<tr>
<td>DOW Chemical Company</td>
<td>acrylics, polyurethanes</td>
<td>Primal, Rosfield, Rhoplex, Avance, Aquaset</td>
</tr>
<tr>
<td>Evonik Corp.</td>
<td>epoxies, silanes</td>
<td>Ancarex, Dynasilan,</td>
</tr>
<tr>
<td>Hexion</td>
<td>epoxies</td>
<td>EPI-REZ, Epicote</td>
</tr>
<tr>
<td>Huntsman Corp.</td>
<td>epoxies</td>
<td>Araldite</td>
</tr>
<tr>
<td>King Industries</td>
<td>water-thinned resins</td>
<td>K-Flex</td>
</tr>
<tr>
<td>Lubrizol</td>
<td>acrylics, PUD, polyvinylidene chloride PVDC dispersions</td>
<td>Carboset, Aptalon, Permax</td>
</tr>
<tr>
<td>Reichold</td>
<td>acrylics, epoxies, alkyds</td>
<td>Beckosol, Kelsol, Urotuf, Arolon</td>
</tr>
<tr>
<td>Specialty Polymers</td>
<td>acrylics, styrene acrylics</td>
<td>RayCryl, RayFlex, RayCote</td>
</tr>
<tr>
<td>Worlée</td>
<td>alkyds, acrylic</td>
<td>WorléeSol, WorléeCryl</td>
</tr>
</tbody>
</table>

parameters. Very important, especially in warm, humid climates is resistance to dirt-pickup and bacterial growth. Also important are aesthetics where the wall paint is able to hide formation of small cracks of the substrate.

For interior wall paints, the focus is mainly on low cost, as well as on hiding and dirt resistance or easy cleaning. The substrate can be concrete, plaster or wall paper. Both interior
and exterior wall paints are mainly applied with rollers, large brushes and spray guns. Main critical factors are the pigment volume concentration (PVC), levelling and the possibility to use point-of-sale colouring, using mixing machines. Formulations should be economic since large surfaces are involved as well as there is fierce competition in this market-segment.

Trim paints
Trim paints are applied by professional or non-professional painters on all “fittings on a building” such as panels, doors, window frames. The substrate being the full range of wood types, plastics, concrete and metal.

Main critical factors: very broad area of country-specific applications, mixing machines, colouring, colour acceptance, formulations, huge variation of quality and performance due to VOC limits based on “ready for use” amongst other things.OEM coatings

OEM coatings
(original equipment manufacturer; e.g. automotive coatings) are coatings used at the original equipment manufacturer and are applied under very well controlled conditions. Application can be by automated spray robots or by dipping in electrophoresis baths, followed mostly by curing at elevated temperatures often referred to as baking or stoving. Substrates are metal and plastic. Important application areas are the automotive as well as automotive related industries such as bumpers and fenders.

Vehicle-refinish coatings
Vehicle-refinish coatings are all coatings used for the repair of damaged cars: fillers, primers, metallic base coats, solid colour topcoats and clear coats. Main substrates are metal, aluminium, repair-putties and plastics. Main critical factors for water-borne topcoats is the fact that it is still difficult to obtain excellent appearance unless the VOCs are still substantial.

Industrial wood coatings
Industrial wood coatings are industrially applied. Main application areas are window and door frames (often referred to as joinery) and parquet flooring. Windows and door frames are mainly coated by means of spraying, flow coating or dipping. The changeover to water-borne in the joinery segment is almost completely realized. The drying conditions can be from primitive to complete high speed lines under controlled conditions.

Industrially finished parquet coatings are almost always applied and dried on high speed lines using radiation cured coatings. Individual layers are water-borne, the topcoat however is almost always a 100 % solid UV-curing coating. Many “parquet” materials are not at all based on solid wood but on foils that are printed and glued to an MDF or other fibre-board like substrate. In most case a thick clear coat is then applied on the printed foil to protect it from abrasion.
Protective coatings

Protective coatings are the cluster of marine, metal constructions and other applications where anti-corrosion applications are important. Substrates can be steel, aluminium or other metal substrates. The change to water-borne coatings in this segment is still limited or in a transfer phase. Recently air-drying polyurethane dispersions and very hydrophobic acrylic dispersions have entered the market and they have an acceptable performance.

Industrial coatings

Industrial coatings, sometimes also referred to as general industrial coatings, are basically the collection of coatings that do not fit in the previously described segments. End-use applications are for instance metal machines, agricultural construction and earthmoving equipment (ACE), kitchen appliances or household equipment and anti-corrosion applications. The British Coatings Federation (BCF)[31] defines this market segment as follows: “An industrial coating is a paint or coating defined by its protective, rather than its aesthetic properties, although it can provide both.” The most common use of industrial coatings is for corrosion control of steel or concrete. Overall the change to water-borne coatings is still limited or in a transition phase. Most water-borne coatings still have substantial to high VOC.

Plastic coatings

Plastic coatings are often a sub-segment of automotive OEM coatings. A very well know application are bumpers and wheel covers. The pretreatment of polypropylene plastics is far more critical if water-borne coatings are used. The sub-segment plastic coatings for equipment (TV, mobile phones etc.) is often put under industrial coatings.

Packaging coatings

Packaging coatings are defined as a means to give functional as well as aesthetic properties to various products related to consumer goods, personal care, healthcare, food & beverages, and other such industries[32]. It is a large mixed bag of coatings and applications and will only be discussed on specific known applications. One of the main areas is can coatings: both interior and exterior. Often this segment is not included in market overviews. An example of the complexity of these coatings is the coating of multicolour printed plastic food bags such as for crisps. For direct or indirect food contact coating, ingredients must meet the FDA regulations and in addition migration tests need to be done by the end-user (formulated and applied, cured coating) to determine migration of certain ingredients from the coating into the food.

Other coatings

Other coatings businesses are certainly not less important. Figure 2.1 shows the substantial market share they have of 16%. Main areas are aerospace coatings, intumescent coatings, resin flooring coatings, paper coatings, etc. It becomes visible that these market-seg-
ments tend to look for water-borne resins, developed for other applications and then adapt these resins for their specific use. For paper coatings, for example, a lot of styrene butadiene dispersions are being used. Aerospace coatings on the other hand use both one- and two-component water-borne systems for the interior (coatings and fillers). The exterior coating is expected to remain solvent-based for a longer period of time.

2.3 Definitions

This paragraph discusses various definitions of terms like applications, markets and parameters used that are prone to discussion or sometimes used inappropriately. Nevertheless, some have more than one definition or are not the same in various countries. The definitions that are used in this book need to be crystal clear in order to keep the subject and information the same for all readers. Whenever possible also the alternative definitions or accuracy of a definition will be mentioned. The combination of defined paints and the defined resins that lead to the proper product and performance is discussed in the forthcoming chapters.

2.3.1 Definitions of water-borne paints

The definition of water-borne paint seems to be straightforward. It could very well be the following one:

“A water-borne paint is a paint containing and using water in order to apply the mixture of solid materials such as pigments, resin, hardener and additives, in order to form a proper wet and dry film and leading to the performance that is required when applied and dried”[33]

Some critical remarks.

"...using water...": almost all water-borne paints need still limited to considerable amounts of solvent be it cosolvents, coalescing agents, plasticizers or other solvent. Meaning they still emit solvents and therefore have a VOC value. The function of these solvents is critical to the formation of a proper film after evaporation of the water. Water is in fact the carrier of the paint for the application and not taking part in the actual film formation. Exceptions are real water dissolved resins, their use is rare. In that case water acts as a solvent.

"...containing water..." is too limited, we should add a proper and accurate definition of the amount of water. Since water is not to be seen as a classical solvent and its function to dilute the resin/paint to the proper viscosity, it is depending on the application “excluding water” or “including water” in the VOC calculation.

There are well known examples of a classical solvent-borne alkyd paint that is diluted with water until the VOC requirements are met. The water actually forms a water in oil emulsion. They still emit the same large amount of solvent when applied in the proper layer
thickness. Another example may be the water-borne base coat formulations used in metallic automotive paints that have very high VOCs (over 400 g/l, excluding water) and are in fact high solid metallic paints containing water.

Taking this into account the definition should be sharper:

“A water-borne paint is a paint containing water and only contains other volatile components such as solvents, to a level that meets the actual and local volatile emission legislation. Additional to that the water-borne paint, when applied at the proper and final layer thickness/solids, must also lead to a legally acceptable emission. Exempt solvents as are used in the USA should be part of the emitting solvents.”

Note: The second sentence of the definition covers the practice and fact that VOC legislation may largely miss its objective. If multiple layers need to be applied to have the proper amount of solid and dried film on the substrate. It is well known in architectural water-borne paints, having a VOC of 120 g/l (incl. water) has a total emission that equals that of a high solid alkyd paint with a VOC of 250 g/l simply because of the fact that the volume solid of the high solid alkyd paint is a factor of 1.8 to 1.9 higher than the water-borne paint[34]. Several alternative terms for water-borne are used in the literature and communication, such as water-based, water-dilutable and water-reducible. In this book water-borne is the preferred terminology. This is well motivated by Martens: a resin as well as a paint is based on the main functional component of the resin/paint. A resin or paint is for instance acrylic- or alkyd-based and not borne.

The main and very important component is not water or solvent – it is there to apply the paint – but the generally accepted chemistry of the binder. Martens writes: “This (the water-based coating) is a misnomer in that the base is normally the binder. … It is recommended that the term “water-based” be dropped. … Calling a coating water-based is equivalent to calling a coating toluene (note by authors: it should be xylene-borne) based or mineral-spirits based ….”
2.3.2 Definitions of water-borne resins

“A water-borne resin is a polymer diluted, emulsified or dispersed in water and not containing volatile organic materials such as solvents. It should not contain non-volatile materials such as monomer residuals not incorporated in the polymer, higher than the allowed levels, according to the local legislation.” [33]

Volatile materials may be solvents or additives used during production that are not or not completely removed during production. Examples are for instance the remaining solvents such as N-methyl pyrrolidone or N-ethyl pyrrolidone present in older polyurethane dispersions. Neutralizing agents such as triethyl amine that has an unfavourable labelling are not allowed in various Eco-labels. Higher boiling point amines such as di isopropyl ethyl amine serve a similar function but are not yet regulated to the extent of triethyl amine.

Water-borne resins are basically made in three different processes (Figure 2.3): water-borne dispersions, water-borne emulsions and water-borne solutions.

Water-borne resin dispersions are made in situ by addition polymerization of the selected monomer mix in water with the help of a stabilizing additives (emulsifiers) or polymer stabilizers. Water-borne resin emulsions are made in two steps by first making the resin both by addition polymerization or polycondensation using organic solvents and then either adding water called primary emulsification (phase-inversion) or adding the hot resin in water called secondary or direct emulsification. Water-borne resin solutions are resins made really dissolved in water with the help of ionic or non-ionic functionalities build into the polymer backbone followed in the case of ionic polymers by neutralization. These resins are only used in specific areas such as electrophoresis in metal treatment and some other automotive coatings.

2.3.3 Volatile Organic Compounds

Volatile organic compounds or contents (VOC) regulations and definitions differ between USA, Europe, China and other countries or continents[36]. The following part focuses on the European situation.

The VOC is defined as follows:

“Volatile organic compound means any organic compound having an initial boiling point less than or equal to 250 °C measured at a standard pressure of 101.3 kPa”.

The present European VOC legislation is complicated and can be misleading since it uses two VOC definitions[35]. A VOC value expressed in g/l excl. water is used for vehicle refinishing coatings and a VOC value expressed in g/l incl. water or g/l ready to use is used for architectural coatings. For industrial coatings there is no VOC legislation, but here the emissions of solvent and carbon dioxide are regulated.
Table 2.8: VOC directive for architectural paints per application area, Directive 2004/42/CE: "ready for use"

<table>
<thead>
<tr>
<th>Category type</th>
<th>Type</th>
<th>Phase 1 (2007) VOC\textsubscript{\textsc{max}} content [g/l]</th>
<th>Phase 2 (2010) VOC\textsubscript{\textsc{max}} content [g/l]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paints for interior walls and ceilings</td>
<td>water-borne</td>
<td>75</td>
<td>30</td>
</tr>
<tr>
<td>Ibid (Gloss &lt;25 @ 60\textdegree)</td>
<td>solvent-borne</td>
<td>400</td>
<td>30</td>
</tr>
<tr>
<td>Paints for interior walls and ceilings</td>
<td>water-borne</td>
<td>150</td>
<td>100</td>
</tr>
<tr>
<td>Ibid (Gloss \geq25 @ 60\textdegree)</td>
<td>solvent-borne</td>
<td>400</td>
<td>100</td>
</tr>
<tr>
<td>Paints for exterior walls of mineral substrates</td>
<td>water-borne</td>
<td>75</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>solvent-borne</td>
<td>450</td>
<td>450</td>
</tr>
<tr>
<td>Interior and exterior paints for wood or metal, trim and cladding</td>
<td>water-borne</td>
<td>150</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td>solvent-borne</td>
<td>400</td>
<td>300</td>
</tr>
<tr>
<td>Interior and exterior transparent coatings and varnishes, semi-transparent</td>
<td>water-borne</td>
<td>150</td>
<td>130</td>
</tr>
<tr>
<td>coatings, stains and wood stains and opaque wood stains for wood &amp; metal</td>
<td>solvent-borne</td>
<td>500</td>
<td>400</td>
</tr>
<tr>
<td>Interior &amp; exterior minimal build wood stains</td>
<td>water-borne</td>
<td>150</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td>solvent-borne</td>
<td>700</td>
<td>700</td>
</tr>
<tr>
<td>Primers for use on wood, walls and ceilings</td>
<td>water-borne</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>solvent-borne</td>
<td>450</td>
<td>350</td>
</tr>
<tr>
<td>Binding primers to stabilise substrates or impart hydrophobic properties</td>
<td>water-borne</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>solvent-borne</td>
<td>750</td>
<td>750</td>
</tr>
<tr>
<td>One-component coatings (performance)</td>
<td>water-borne</td>
<td>140</td>
<td>140</td>
</tr>
<tr>
<td></td>
<td>solvent-borne</td>
<td>600</td>
<td>500</td>
</tr>
<tr>
<td>Two-component reactive coatings (performance)</td>
<td>water-borne</td>
<td>140</td>
<td>140</td>
</tr>
<tr>
<td></td>
<td>solvent-borne</td>
<td>550</td>
<td>500</td>
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<tr>
<td>Multi-coloured coatings</td>
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<td>150</td>
<td>100</td>
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<tr>
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<td>solvent-borne</td>
<td>400</td>
<td>100</td>
</tr>
<tr>
<td>Decorative effect coatings</td>
<td>water-borne</td>
<td>300</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>solvent-borne</td>
<td>500</td>
<td>200</td>
</tr>
</tbody>
</table>