Meier-Westhues + Danielmeier + Kruppa + Squiller

POLYURETHANES

COATINGS, ADHESIVES AND SEALANTS

2nd Revised Edition

EUROPEAN COATINGS library

VINCENTZ

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Foreword

A world without polyurethanes is hard to imagine these days. Polyurethane chemistry has become an established technology worldwide in various industrial applications. For innovative coatings, adhesives and sealants, it plays a significant role and has been in many cases the key to new technology implementation. Polyurethanes enable innovation and technological advancement and help to develop products that meet market needs, devising efficient and environmentally friendly manufacturing processes and asserting a position in the global competitive environment.

In 2007 the first edition of the textbook Polyurethanes for Coatings, Adhesives and Sealants was published with the purpose to give a comprehensive overview of the potential offered by polyurethane chemistry. It was a time, when the significance of solvent-free, water-borne or UV-cured systems had steadily increased and reached a considerable importance. While solvent-borne formulations occupied center stage for many years before, polyurethane chemistry suddenly demonstrated that environmental improvements, better quality and economy were not mutually exclusive, but could be synergistic.

The book became an established standard work for professionals and students in technical and commercial areas, who desired the know-how and background of polyurethane related topics for coatings, adhesives and sealants.

Now, 11 years later, we once more deal with this topic and analyze the current role of polyurethane chemistry for coatings, adhesives and sealants, taking the development within the past decade into account. Based on our findings we updated the book, added new technical developments, extended the global view and included increasingly important topics such as sustainability and digitalization. Additionally, we refreshed citations and reduced content in areas deemed to be less relevant as they had been eleven years ago.

Polyurethane chemistry appears to have become even more established in the last decade and has continued to develop. Some of the trends foreseen in the previous edition have come to fruition, e.g., the trend towards water-borne systems. Furthermore, new, even more specialized systems and application technologies have been developed. This widened the applications fields and pushed the performance of the PU technology even further. Examples include the first bio-based PU raw materials which are entering the market, new catalyst systems which have been developed, or the digital printing process as new application technology that makes its way into the market place. Due to the adaptability of polyurethanes, modern systems are able to address the more stringent market, legislation and sustainability demands of today, and it is anticipated that polyurethanes will be able to do this in the future. The enormous diversity and possible combinations of polyurethane raw materials result in an impressive breadth of properties enabling the development of specific, customized solutions. The potential of further development is by no means exhausted.

Although the book has been revised, we took care to maintain the original intent of providing a comprehensive overview that allows newcomers to the industry an understanding of the principles and the potential of the polyurethane chemistry in the applications of coatings, adhesives and sealants, as well as, give the experienced specialist the option to refresh their knowledge and inspire the interested reader to think about how new innovations in polyurethanes can solve the problems of the future. The book opens with an introduction to polyurethane chemistry and technology, followed by a discussion of the many different applications, their current significance and their future prospects. Like the first edition of the book, the second one was also created in a global team approach involving experts in their respective fields for each chapter including experts of the Covestro group of companies, as well as, partners from universities and institutes. We would like to thank all of them for their contribution and patience. The book would not have been possible without their commitment and dedication to the PU technology.
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Leverkusen, Germany, January 2019

Ulrich Meier-Westhues
Karsten Danielmeier
Peter Kruppa
Edward P. Squiller

Contents

1 Introduction

1.1 Historical aspects

Coating, bonding and sealing are techniques that humankind has used for many centuries. For a long time, only natural resins, oils and fats were used for these purposes.

Shellac, a natural resin secreted by the scaly lac insect, has been used in India as a weather-resistant coating for surfaces. The word *lacquer* in English is derived from the Sanskrit word *laksha*, which means one hundred thousand and describes the unimaginably large number of insects required to produce shellac lacquers. Later it was learned that lacquer resins could also be obtained from other sources, e.g. by boiling down wood oil.

Animal tissue, especially bones and hide, were the basis for glues and adhesives in many applications for a long time. The makers of high-quality glues were called *Kellepsos* in ancient Greece. During the Middle Ages development was largely static. The invention of the printing press by *Johannes Gutenberg* then led to a new and rapidly growing need for adhesives in the emerging bookbinding industry.

The development of synthetic resins began in the early 20th century driven by the oil industry and the emerging downstream industry with their related products. This laid the foundation for the production of coatings, adhesives and sealants of vastly improved quality and in volumes. Polyurethanes were discovered in 1937 when *Heinrich Rinke* produced 1,6-hexamethylene diisocyanate (HDI) and *Otto Bayer* developed the diisocyanate polyaddition process[1–3]. Initial research in this new field of polymer chemistry in the 1940s focused on polyurethane fibers, while the first polyurethane foams were produced a little later.

Fifty years ago, the first polyurethane coatings were developed. Otto Bayer and his team discovered that the technical properties of alkyd resins could be improved through modification with diisocyanates. However, the real conquest of the coatings sector by polyurethanes only began with the development and industrial use of low-monomer polyisocyanates. The first products were based on

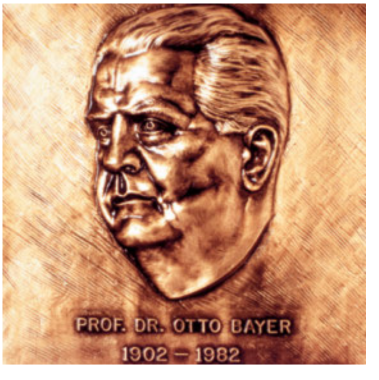

Figure 1.1: Otto Bayer – Inventor of polyurethane chemistry [4]

toluene diisocyanate. Due to the aromatic nature of the base isocyanate, these tend to yellow on exposure to light and can therefore only be used for interior applications or in primers.

The range of applications was broadened later with the introduction of products based on aliphatic diisocyanates, initially hexamethylene diisocyanate. "Desmodur" N was the first product of this type and was launched in the early 1960s by Bayer AG. Gradually, the two-component (DD) coatings prepared by combining polyisocyanates ("Desmodur") with polyols ("Desmophen") replaced the traditional alkyd coatings, first in the coating of large vehicles. The driving force was the quality of the coatings which, even when dried under mild conditions, matched the performance of coatings which had been baked. This is important when coating large vehicles (airplanes, rail wagons and buses) as their size makes baking impossible.

In the 1970s, it was found that the quality of automotive refinish coatings could be substantially improved with the help of polyurethane chemistry. By adding polyisocyanates based on isophorone diisocyanate (IPDI) to the medium oil-based alkyd resins mainly used at that time, the hardness, overcoatability and gasoline resistance of the resulting coatings could be improved significantly. Today, two-component polyurethane coatings have almost completely replaced alkyd resin chemistry in this segment.

The broad range of applications for polyurethanes in coatings was quickly recognized. Other examples of applications include wood finishing, corrosion protection and construction, as well as textile coating. Another advance has been the development of two-component metering technology. The breakthrough in automotive OEM finishing occurred in the mid-1980s, and since this time, plastic coatings have become a further domain for polyurethanes.

Polyurethane adhesives came onto the market in the 1950s with the development of the hydroxyl polyurethanes and the first trifunctional isocyanate crosslinker, "Desmodur" R. The early 1960s also saw the development of plasticizer-resistant hydroxyl polyurethanes, which laid the foundation for the success of these products in shoe manufacture.

Solvent-free polyurethane reactive adhesives have been used since the 1970s, first in automotive production, and then in the manufacture of laminated films and sandwich elements. They were later joined by reactive sealants. Since the 1990s, polyurethane-based reactive and waterborne adhesives have gained significant market share in automotive, construction, furniture and shoe production.

The process of substituting traditional technologies in coatings, adhesives and sealants with polyurethane is ongoing, and can be observed occurring around the world. Against a background of increasingly demanding quality requirements, ever more stringent environmental legislation, and cost optimization of the end-product manufacturing processes, there has been growth in the use of low-solvent, solvent-free, waterborne and radiation-curing formulations of one- and two-component polyurethane systems[5–9]. Bearing in mind current concomitant developments, polyurethanes will continue to gain further importance. Their spectrum of use will thus expand beyond the established applications into other new areas.

1.2 Definition of scope

This book describes the use of polyurethane raw materials for coatings, adhesives and sealants in selected application areas. Topics covered include applications in the wood and furniture industry, the automotive sector, construction, the broad area of metal coatings including corrosion protection, the shoe industry, and plastic coating and bonding. Also discussed are the manufacture of laminated films and the coating of textiles, leather, glass and paper. In addition to describing the chemical and technical principles involved, the issues of occupational hygiene and sustainability associated with the handling of polyurethane coatings, adhesives and sealants are covered. The broad spectrum of applications is evidence of one key property of polyurethanes: the versatility resulting from their chemistry which is also exploited in segments other than coatings, adhesives and sealants.

For example, polyurethane raw materials are used in the manufacture of foams: rigid foams for insulation (construction industry, refrigerators) or energy-absorbing components in automobile interiors (instrument panels); integral skin foams, e.g. for furniture and medical applications; flexible foams for upholstery, mattresses and packaging materials. Other applications for polyurethanes are found in the manufacture of versatile elastomers for the footwear and electrical industries, thermoplastic urethanes, e.g. for sports and leisure equipment, and polyurethane elastic fibers for stretch fabrics.

This book does not intend to address all these applications. Detailed information can be found in other sources[10–12].

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2 Economic aspects and market analysis

2.1 Introduction and definitions

When looking at the economic importance of coatings, adhesives, and sealants, there is a significant market of formulated products with 64 million tons or 170 billion € globally in 2017 (see Figure 2.1). The formulated product always describes the ready to use material as it will be applied to the end product – being it a wall, car or industrial good. The formulated product contains the so called resin, binder or film forming component and further additives, pigments, fillers and organic solvents or water. This market is split roughly 75:25 for coatings versus adhesives and sealants with 49 versus 15 million tons of material (see Figure 2.1).

With regard to the resin within the formulated product, several market studies and also the authors of this book refer to the resin supply form. This includes not only the mon-

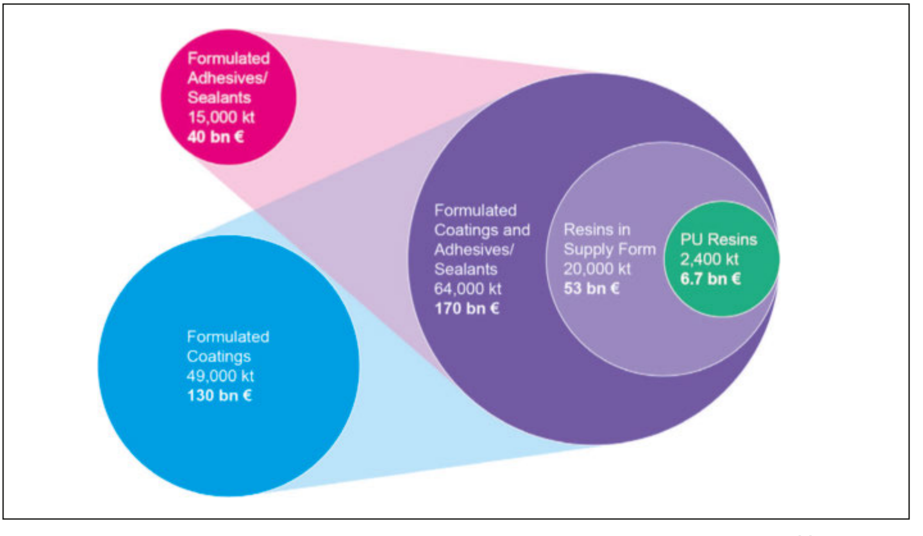

Figure 2.1: Overview world consumption 2017 for coatings, adhesives and sealants [1]

omeric, oligomeric or polymeric resin material itself, but also a certain share of organic solvent or water that is usually included in the commercially available products.

Other market data sources use the term of dry resin to describe only the active resin material without any solvents that will eventually evaporate in the final film forming process during application of the formulated product.

Within this book the term polyurethane (PU) chemistry is used to describe markets, which comprise all resin materials that are crosslinked by urethane or urea groups. In addition, the term also covers all materials that are indirectly based on isocyanates or the reaction products thereof. This means, that the isocyanate is not necessarily reacted in the last crosslinking step, but might be used as a precursor (see Chapter 3). In general, polyurethane resins consist of aliphatic polyisocyanates, aromatic polyisocyanates, prepolymers, polyurethane dispersions (PUDs), polyols and specific diamines.

Based on these definitions, polyurethane based resins have a market size of 2.4 million tons or 6.7 billion €. This represents a 12 % share of the overall resins market in supply form. Therefore, polyurethane chemistry is usually recognized as a specialty market where the final application demands for increased performance, e.g. durability or quality of appearance.[1]

2.2 Coatings

The world consumption of coatings for industrial and architectural applications (i.e. the total production of formulated coating products sold) amounted to 49,000 kilotons in 2017 (see Figure 2.2). This represented global consumption of 16 million tons of coating resins in supply form, corresponding to a value of 44 billion €. Polyurethane resins account for 1.6 million tons representing roughly 10 % of the overall resins market in supply form.[2]

2.2.1 Fields of application

There are two general fields of application for coatings in the world: The architectural applications account for approximately 66 % by volume, including dispersions for architectural coatings, whereas the general industrial coatings make up approximately 34 % (see Figure 2.3).

The architectural market is dominated by interior wall applications, i.e. wall emulsions/dispersions with 51 %. This segment is followed by exterior wall coatings with 24 %. After wood coatings with 15 %, floor coatings (8 %) and roof coatings (2 %) hold the smallest share (see Figure 2.3). Within this market, polyurethane technology only holds a very small share and thus the architectural applications are not further considered within this book with regard to market data.

The industrial market accounts for 34 % of the coating market and can be divided into seven different fields (see Figure 2.4, see page 25) with the largest, named metal, representing roughly 40 % of the market share. This application is followed by protective and marine with 22 %. Industrial wood and automotive account for 14 % and 13 %, respectively. They are followed by agricultural, construction, earthmoving equipment (ACE) and plastics with 4 % each. The smallest segment is transportation with 3 %.[4] Other markets include textile, leather, glass and paper coating. The market size for textile and leather coating sums up to approximately 5,100 kilotons of resins in supply form, of which 50 % is based on polyurethane technology.[5] This market is not reflected in the following graphs but will be discussed in detail in the respective chapter.

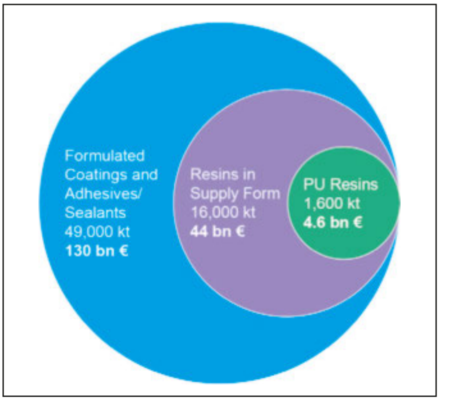

Figure 2.2: Overview world consumption 2017 for industrial and architectural coatings[2]

The weighting is different if one compares polyurethane coatings to the total formulated industrial coatings market

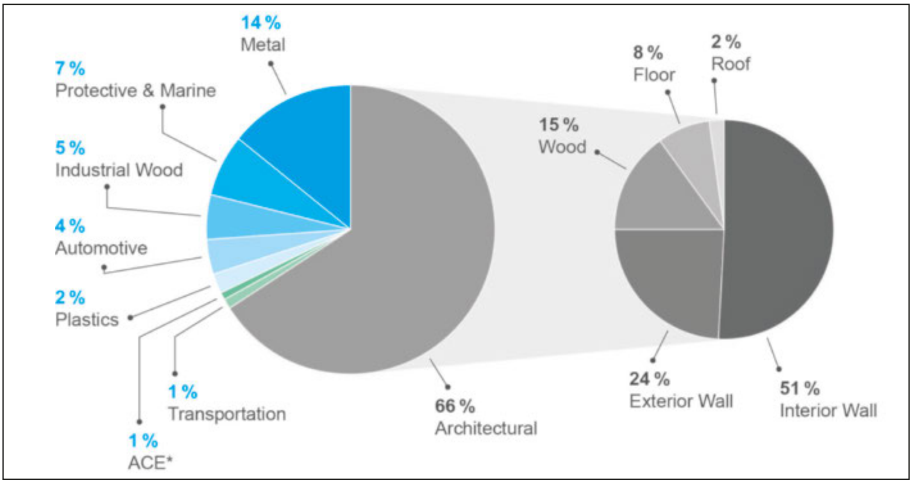

Figure 2.3: Formulated coatings volumes per application 2017 (industrial and architectural): 49,000 kt in total[3]

**ACE: Agricultural, Construction, Earthmoving Equipment*

Table 2.1: Formulated polyurethane coatings volume per application vs. the total formulated industrial coatings market[4]

Application	Total industrial coatings market per application [%]	Polyurethane industrial coatings market per application [%]
Automotive	13	21
Transportation	3	8
Industrial wood	14	24
Protective & marine	22	16
Plastics	4	15
Agricultural, construction, earthmoving equipment	4	6
Metal	40	10
	100	**100**

(i.e. the sum of all coatings types) in terms of share of technologies (see Table 2.1): Industrial wood, automotive, plastics, and ACE have a higher or even significantly higher market share in the polyurethane market compared to the total formulated industrial coatings market. This clearly shows that high-quality polyurethane resins are preferred for applications with more demanding requirements in terms of quality and durability – and these are found accordingly in a higher price segment.

2.2.2 Chemistries and regions

The world consumption for industrial coatings is distributed unequally (see Figure 2.5). More than half of the industrial coating demand is consumed in the Asia-Pacific (APAC) region, while slightly more than one quarter is used in EMEA, namely Europe (21 %) and the Middle East and Africa (4 %), and just under one quarter is going to the Americas (NAFTA and LATAM) with 23 %. It should be emphasized here that APAC's share of global industrial coatings consumption has grown in the last five years (2012 to 2017) to more than 50 % and is expected to continue to rise.

The volume of formulated solvent-borne coating products summed up to 65 % over all technology classes (see Figure 2.6), whereas water-borne coatings, including electrocoats for cathodic electrodeposition (CED), make up 17 % of the formulated coatings market. The remaining share is distributed among powder coatings (14 %), UV coatings (3 %), and others (1 %).

The volume distribution by chemistry type shows that the traditional systems, such as alkyd resins, acrylics, and polyesters, including others, are still of great importance (see Figure 2.7). In 2017, these product groups accounted for just over 51 % of world consumption. Polyurethane coatings have a market share of 20 %.

The main components of polyurethane coating resins are polyisocyanates, polyurethane dispersions, and other polyurethane materials, such as prepolymers and polyols based on polyacrylates, polyesters, polyethers as well as specific diamines. The 1.6 million tons of polyurethane coating resins used worldwide are distributed as shown in Table 2.2 (see page 26):

The key isocyanates used in coatings resins are polyisocyanates, prepolymers and further derivatives. Aliphatic materials are based on hexamethylene diisocyanate (HDI), isophorone

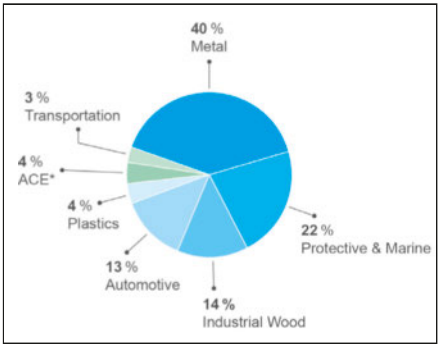

Figure 2.4: Formulated industrial coatings volume per detailed areas of application in 2017, around 17,000 kt[4]

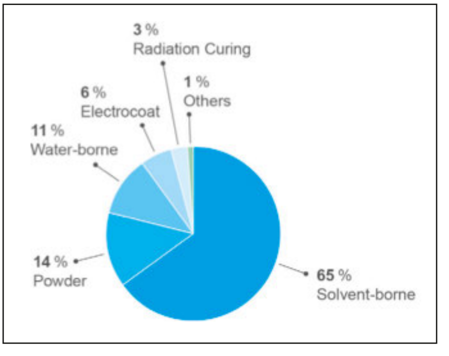

Figure 2.6: Formulated industrial coatings volumes per technology 2017, around 17,000 kt[4]

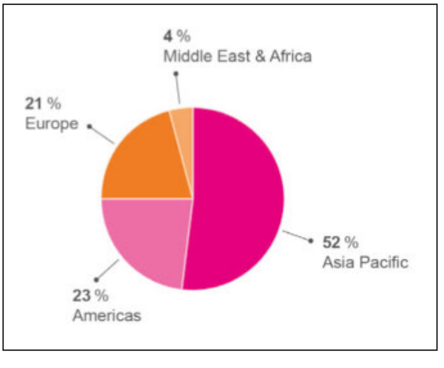

Figure 2.5: Formulated industrial coatings volumes per region 2017, around 17,000 kt[4]

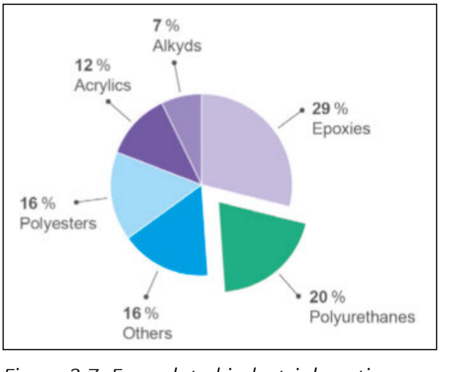

Figure 2.7: Formulated industrial coatings volumes per chemistry 2017, ~ 17,000 kt[6]

Table 2.2: Components of polyurethane coating resins in supply form (volumes in kt)[7]

	Resins in supply form [kt]	Relative share [%]
Aliphatic polyisocyanates	210	13
Aromatic polyisocyanates	130	8
Polyurethane dispersions	170	11
Polyols and prepolymers	1,090	68
Polyurethanes total	**1,600**	**100**

diisocyanate (IPDI) or dicyclohexylmethane diisocyanate (H_{12}MDI). Aromatic isocyanates are based on toluene diisocyanate (TDI) or diphenylmethane diisocyanate (MDI).

2.2.3 Market forecasts

For the coming years (2017 to 2021), annual market growth of 3.1 % is forecasted for formulated industrial coatings, which represents a higher growth rate than the 2.1 % observed from 2012 to 2017. It is expected that growth in APAC will be above global average at 4.1 %, whereas the European and American markets are expected to grow at around 1.8 % and 2.1 % respectively.

The market growth of formulated industrial coatings for different coating technologies reveals that water-borne coatings and electrocoats grew above regional market average in the past five years (2012 to 2017). This trend is expected to continue for APAC and Americas. For Europe, electrocoats should continue to grow above average, while water-borne coatings will grow at average market rates.

Polyurethanes are expected to experience an increasing annual growth of approximately 2.7 % in the upcoming years (2017 to 2021) compared to the past (2012 to 2017), which grew at 2.2 %. This is driven by APAC and Middle East and Africa with roughly 4 % annual growth. For polyurethanes, the market growth was driven by different technologies, depending on the region. Most of the growth was accounted for by solvent-borne and powder coatings in APAC, while in Europe water-borne and UV coatings posted stronger growth. In the Americas, UV and solvent-borne coatings grew above average.[4]

2.3 Adhesives and sealants

In 2007, the world adhesives and sealants industry had a volume of approximately 11.8 million tons and was worth some 30 billion €.[8] After a decrease of about 4 % during the financial crisis in 2008/2009 and the subsequent economic recovery in the following years the volume and value growth in this industry sector averaged around 3 %. In 2017, world demand of formulated adhesives and sealants reached approximately 15 million tons,