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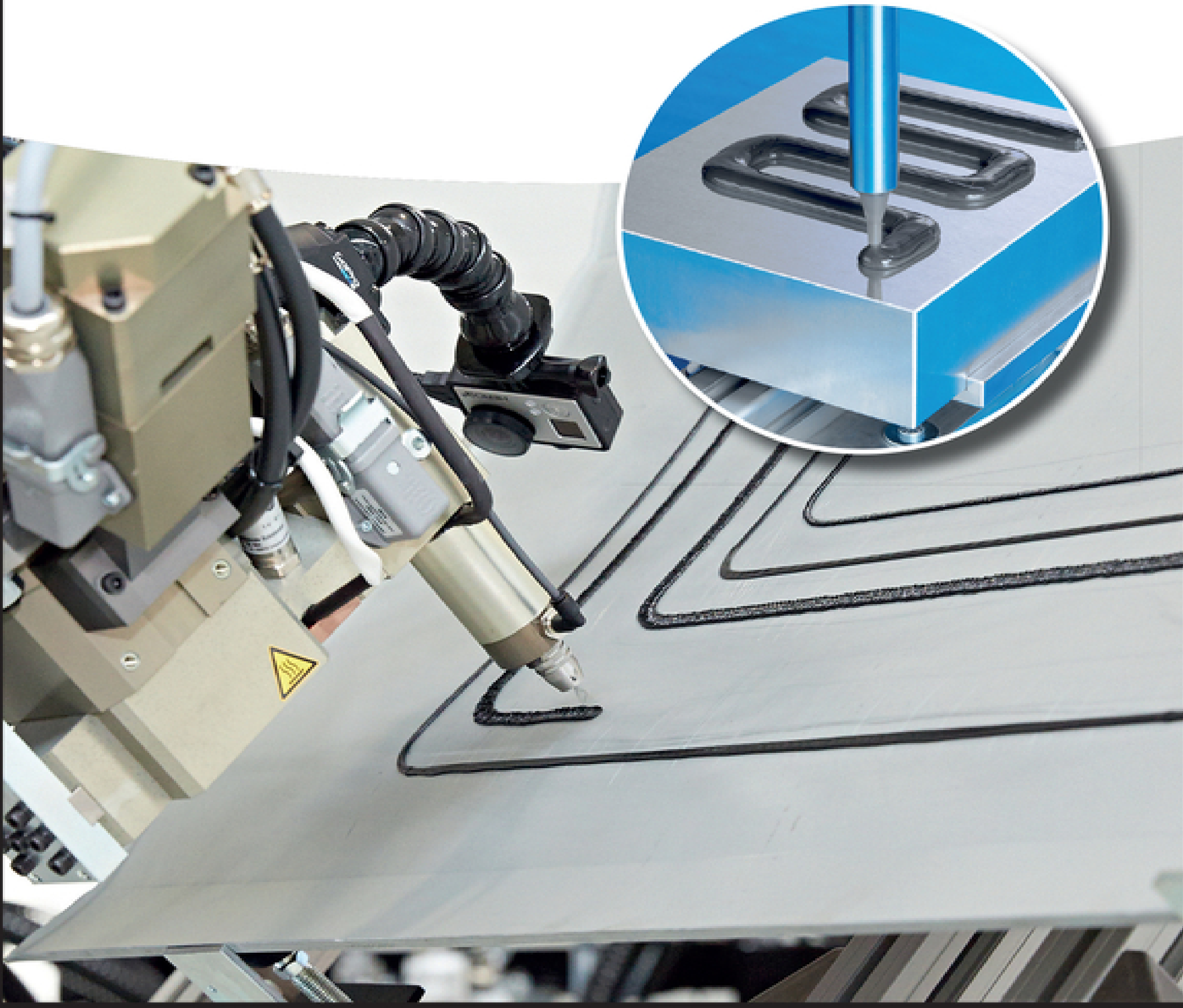
Jürgen Klingen

Adhesive Bonding in Five Steps

Achieving Safe and High-Quality Bonds



Adhesive Bonding in Five Steps

This book is dedicated to Prof. Dr. Walter Brockmann, a great scientist, teacher, and promoter of adhesive-bonding technology, who unfortunately passed away far too early in June 2011 at the age of 72.

In various positions, Prof. Brockmann significantly advanced the corresponding research and application engineering activities in Germany and Europe over decades. Before his death, he had headed the Materials and Surface Engineering Group (AWOK) at the University of Kaiserslautern, Germany, since 1990. Prior to that, he worked for more than 20 years as a scientist and department head at the Fraunhofer Institute for Applied Materials Research (IFAM) in Bremen, Germany.

As a co-founder of the "European Adhesion Conference" (EURADH), he has significantly promoted European and international cooperation in the field of adhesive-bonding technology and with his significant involvement in the initiation of the "World Congress on Adhesion and Related Phenomena" (WCARP) Prof. Brockmann strongly supported the globalization of research in adhesive-bonding technology.

His open, uncomplicated, and friendly manner, coupled with his boundless knowledge and experience, has enabled Prof. Brockmann to convey the many aspects and advantages of adhesive-bonding technology to me and many others, including R&D managers, scientists, students, and users in industry. In my case, he triggered a great enthusiasm for this technology that remains unbroken to this day.

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Preface

There is no doubt that adhesive-bonding technology is one of the key technologies for manufacturing products in the twenty-first century. The reasons for this are the need to simplify production processes, implement modern and innovative design concepts, reduce costs in the manufacture of products, and make greater use of lightweight construction methods to save energy.

However, the bonding process is a "special process" that cannot be inspected without destroying the products it creates, the bonded components. In addition, its design is decisively, indeed almost exclusively, responsible for the quality of the bonded joint. The reason is that in adhesive bonding, unlike alternative joining processes such as welding, screwing, and riveting, the joining agents used here – the adhesives – are not present in their final form, but are physically and/or chemically modified by the user during the manufacture of the components. To guarantee the required product quality, the process used for this purpose must be developed in a detailed, careful, and resilient manner, from the initial assessment of the materials involved to the successful completion of the bonded joints.

This book is intended for engineers, chemists, scientists, technicians, foremen, and students who are charged with the development of such a process or who, for other reasons, would like to inform themselves about the necessary prerequisites and measures for the production of an optimally bonded component. It describes in detail the steps required to set up an adhesive-bonding process to produce a high-quality component. This is done with the help of a specially developed 5-step project management system tailored to adhesive-bonding technology, which accompanies the development team from the initial idea for the adhesive-bonding process to its successful introduction into production. The requirements of DIN 2304 – a standard developed specifically for adhesive-bonding technology – are observed and ensure the establishment of suitable organizational structures in the manufacturing plant, the design of the environment required for adhesive-bonding technology, a high-quality production facility, and execution in line with quality standards. The tools and quality techniques required for planning and executing the 5-phase management process are provided by the Six Sigma methodology.

When working through the reading, the reader is taken by the hand, so to speak, and guided step by step through this process. Right at the beginning of the book – in the concept stage – the necessary basic knowledge of adhesive-bonding technology, technical information about the substrates used, the methods for treating their surfaces, and knowledge about the properties and behavior of adhesives are provided in detail. This enables the reader to outline bonding concepts as a basis for the further development steps.

In the subsequent feasibility demonstration step, practical work begins in the laboratory, initially focusing on the production and testing of laboratory samples of all outlined concepts. The aim here is to identify the most suitable candidate and then validate it after preparation and intensive testing of the corresponding practical components. At the end of the feasibility step, a concept validated for the stresses occurring in practical use is available, which is described in detail by the substrates to be used, the required surface treatment, the most suitable adhesive, and the necessary manufacturing steps for producing the bonded component.

The goal of the development step following the feasibility stage is to establish a robust process for manufacturing the already-validated bonded component. To this end, once the manufacturing process suitable for production scale has been outlined, its suitability in principle must be demonstrated by appropriate pilot runs using statistical methods. Subsequently, after the standards for production and quality control have been developed and the personnel performing the work on the production machines have been trained and instructed, production of the bonded component can be started.

This book is intended to help strengthen the already-outstanding status of adhesive-bonding technology as a modern joining method. To this end, it enables users in industry and the trades to plan the process of bonding components systematically and thus to make it highly efficient. Thus, the application of the proposed management system enables the reproducible production of safe and high-quality bonded joints.

I would like to thank Wiley-VCH for their willingness to publish the book and for their great help in realizing it. I would also like to thank Prof. Dr. Paul Ludwig Geiß, head of the Materials and Surface Engineering Group in the Department of Mechanical Engineering (AWOK-Arbeitsgruppe Werkstoff- und Oberflächentechnik) at the University of Kaiserslautern, for the interesting and stimulating discussions on the conception of the book. I hope that it will be of great help to many users in industry and trade in the development of appropriate bonding processes and thus make a significant contribution to the further positive development of bonding technology in the twenty-first century.

Schwalmtal, Germany *Dr. Jürgen Klingen*
January 2022

Author Biography

Dr. Jürgen Klingen studied chemistry at the University of Duisburg, Germany, and received his doctorate from Prof. Robert Gillard at the University of Wales (Department of Applied Chemistry) in the field of crosslinking of polyisoprene-based adhesives.

For more than 35 years, he held various positions in research, development, and application engineering for the company 3M Deutschland GmbH, 1 year in corporate research in St. Paul, Minnesota, USA, where he worked on new high-performance adhesive systems for the European market. He received the 3M Corporate Circle of Technical Excellence Award for his research in this area. From 1996 to 2017, Dr. Klingen headed 3M's European Corporate Materials and Process Laboratory in Neuss, Germany, where he was responsible for technology development of new adhesives, tapes, films, coatings, and polymer processing for Europe.

Since the end of 2017, he has been working as a consultant for the development of bonding processes in industry and trade. Dr. Klingen is co-author of two technical books and sole author of one technical book as well as holder of several patents in the field of adhesive-bonding technology.

1

Introduction

1.1 The *Art* of Adhesive Bonding

In a broader sense, the word *art* means any developed action based on knowledge, training, perception, imagination, and intuition as on the initiative to perform it. This description also applies to adhesive bonding, since the development of a safe and high-quality bond also requires similar attributes such as appropriate knowledge, creativity, experience, and innovative strength. It is therefore permissible and appropriate to apply the term *art of adhesive bonding* to the creation of a safe and high-quality adhesive bond (Figure 1.1).

The classic joining technologies such as screwing, riveting, and welding are used today in numerous applications in industry and trade. However, there are some side effects, such as weakening of the materials involved, uneven stress distribution, and a high probability of corrosion, which the user has to accept. In contrast, adhesive-bonding technology, which can be used to join almost all different engineering materials, offers considerable advantages. Thus, in the early phase of component development, the designer enjoys the design freedom desired through the use of adhesive-bonding technology. And later, after the development of the bonding system has been completed, engineers in the manufacturing plant can easily implement it in existing production processes for individual and series production. The use of adhesives to join materials is characterized by the fact that identical or different substrates are joined over a large area by an organic material (the adhesive), and the resulting system (the bonded joint) is capable of transferring the acting forces from one substrate to the other. A special feature here is that the bond cannot be detached without destroying it.

1.2 Adhesives

Adhesives are nonmetallic organic materials with sufficient internal strength (cohesion) that are capable of bonding materials through intermolecular interactions occurring at substrate surfaces (adhesion) and transferring forces from one material to another.

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Figure 1.1 The creation of safe and high-quality adhesive joints through knowledge, creativity, experience, and innovation.

Two basic requirements must be met for a functioning adhesive, which are accomplished by appropriate adjustment of the chemical composition and physical properties:

- *good adhesion* – provided by sufficient molecular interactions with the material surfaces.
  During the bonding process, the adhesive must behave like a liquid, with a relatively low viscosity and the ability to wet the surface of the substrate to establish intermolecular interactions. This allows the molecules of the adhesive to approach the nanometer-scale molecular regions of the substrates.
- *good cohesion* – provided by sufficient molecular interactions within the cured adhesive layer.
  In application, the cured adhesive layer must behave like a strong solid with low-molecular flexibility. This is necessary for the transfer of tensile, shear, and peel forces from one substrate to another and to resist environmental influences. Therefore, for good cohesion, the adhesive chemistry must be adjusted to allow molecular interactions within the adhesive layer.

1.3 Adhesive Bonds

An adhesive bond is a two-dimensional connection of similar or dissimilar materials with the help of an organic material that adheres well to the surface of the two substrates to be joined. After the bonding has been prepared and the bonded component is in use, the task of the adhesive bond is to transfer forces from one substrate to the other.

In industry and craft usually, the following materials are used for the creation of an adhesive bond:

- metals,
- plastic materials,
- glasses, and
- wood.

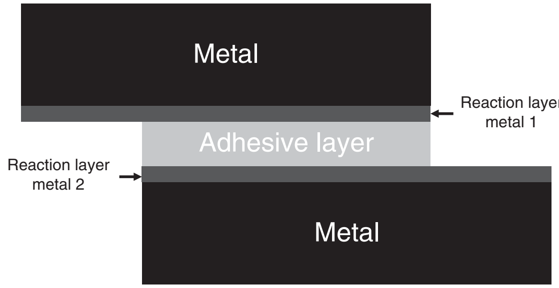

Figure 1.2 Structure of an adhesive bond with metal substrates, in which the adhesive is applied directly to the reaction layer.

1.3.1 Metal Bonds

When bonding to metal, it should be noted that contact is not usually made with the bare metal. Provided that the substrates are cleaned and, if necessary, surface-treated, a – so-called – reaction layer remains, which has been created by the reactions of the metal surface with the environment. This layer usually consists of reaction products of the materials with gases in the air such as oxygen, carbon dioxide, or even water. If the adhesion of this layer to the base material of the substrate and additionally its cohesion is sufficient, the adhesive can be applied directly to this layer (Figure 1.2).

Compared to plastics and glasses, the surface structure of metals is relatively complex and consists of:

- base metal material,
- interface layer (2000–5000 nm) with modified physical and/or mechanical properties, caused by the forming process during the production of the material,
- reaction layer (1–50 nm) formed by chemical changes at the interface and representing the actual adhesion layer,
- adsorption layer (0.1–1 nm), with adhering *non-material* molecules such as water and gases, and
- impurity layer, with solid materials such as dust or liquid contaminants such as oils, greases, or moisture.

In any case, for good adhesion, both the adsorption layer and the contamination layer must be removed by suitable cleaning and/or surface treatment methods before the adhesive is applied to the material surface (Figure 1.3). As already discussed, bonding is then usually carried out on the reaction layer. Examples for this case are aluminum and copper. In a normal atmosphere, aluminum always has an up to 50 nm thick porous oxide layer (reaction layer) that forms spontaneously in air. This surface can be bonded directly if no extreme high demands are made on long-term resistance. If this is the case, as often in the aerospace industry, however, this oxide layer must be removed from aluminum components. In the case of copper, a resistant brown copper oxide layer forms after a few hours in air and adheres well to the substrate. After months, this layer transforms by reaction with the CO_2 in the air to green basic copper(II) carbonate, the so-called patina, which additionally contains sulfate and/or chloride anions. Adhesive bonds of good quality can be

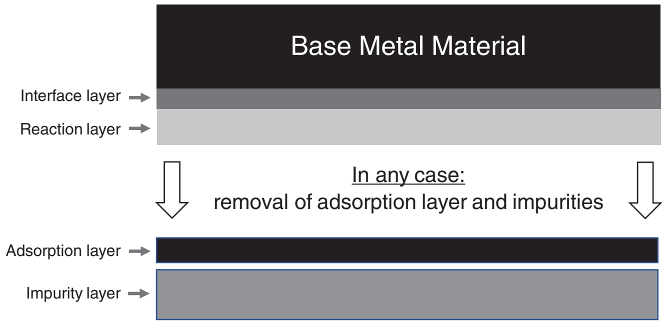

Figure 1.3 Detailed structure of a metal surface and removal of the adsorption layer/impurities to expose the reaction layer before bonding.

produced on both the brown copper oxide and the green copper carbonate layers. Therefore, the reaction layer does not have to be removed here either.

These are cases where, after cleaning the surfaces, adhesives can be applied directly to the reaction layer. However, this is not always the case. If the cohesion of the reaction layer is low and/or its adhesion to the base material is insufficient, it is necessary to remove the reaction layer from the surface as well. This is the case with low-alloyed or unalloyed steels, because the reaction layer (rust) does not adhere sufficiently to the base material. Another reason for such a measure may be the poor influence of the reaction layer on the aging resistance of the bond, as in the case of galvanized (zinc-coated) steel. Also, in this case, the reaction layer should also be removed from the surface before bonding. Zinc oxide initially forms on galvanized steel surfaces, which then reacts further with carbon dioxide in the air to form resistant zinc hydroxide/carbonate reaction layers. These layers bond very well with the base material even under the influence of temperature, but their hydrophilic (water-attracting) character leads to a negative influence on the quality of the bond, which is why they should be removed.

1.3.2 Plastic Bonds

As with metals, plastics are often not bonded to the pure material. In the case of softened plastics, for example, plasticizers can diffuse to the surface after some time, leading to a drop in strength and thus to failure of the bond. This effect occurs, for example, with polyvinylchloride (PVC) or ethylene-propylene-diene rubber (EPDM) materials and cannot be completely avoided by surface treatment. Therefore, when selecting materials for bonding, care should be taken to ensure that the parts to be bonded do not contain such substances or that these are crosslinked and thus chemically anchored in the polymer.

1.3.3 Glass Bonds

When bonding glass, the adhesive is usually not applied to the pure glass surface either, but finds a layer covered with OH groups generated by hydrolysis. These are created by so-called *glass corrosion*, in which the metal oxides contained in the glass are dissolved in water adsorbed on the surface. This increases the OH ion concentration on the glass surface and the pH value rises. Thus, glass corrosion has a considerable negative influence on the formation of adhesive forces on the glass surface and, especially in the case of glasses with a high alkali content, the surface energy is significantly reduced. For this reason, the surfaces of glass should be treated with suitable adhesion promoters, especially if the glass composites are required to have high resistance to aging.

1.3.4 Wood Bonds

Due to its pronounced pore structure, which offers the possibility of mechanical anchoring of the adhesive film in the structure, wood is a grateful substrate for bonding. In addition, the chemical structures of the main constituents of the wood matrix (cellulose and lignin), which to a large extent contain hydroxyl and other polar functional groups, result in numerous opportunities for the formation of hydrogen bonds and even covalent chemical bonds in the adhesive layer. However, the behavior of the adhesive at the boundary layer is strongly influenced by the wood density, which depends on the wood species, but within the wood species also on whether it is early or late wood. Since wood in practice always has a residual moisture content of 6–15%, the adhesive used must have a certain compatibility with water and water vapor, both during application and in continuous use.

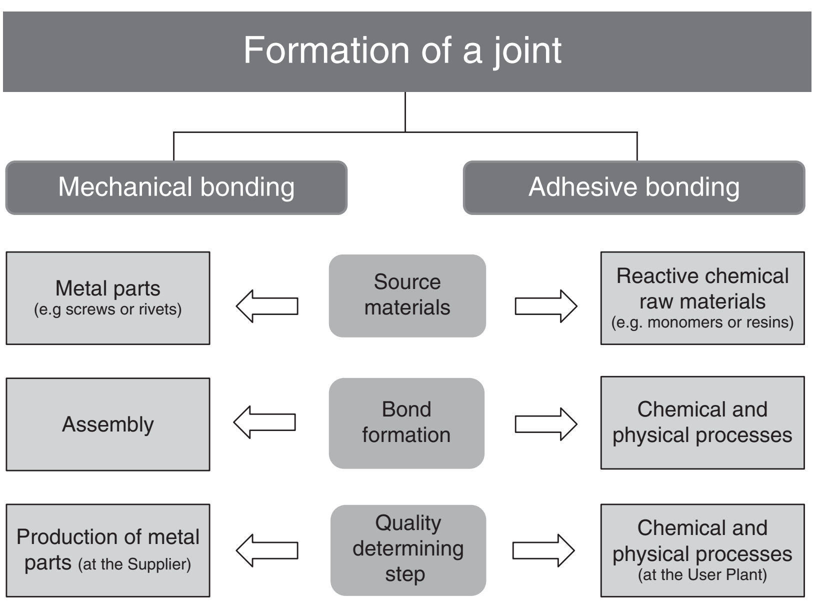

Figure 1.4 Formation of a joint by using the classical methods and adhesive bonding.

1.4 Adhesive Bonding in Industry and Craft

The production of high-quality bonded components in industry and crafts makes high demands, which applies to both the manufacturing process and the environment in which the parts are produced. A key difference from traditional joining techniques such as screwing or riveting, where the joining process has no or little influence on the quality of the joint, is that in adhesive bonding adhesion and cohesion are built up in the manufacturing process. Thus, the process parameters during the manufacture of bonded components are of extreme importance for the quality of the final bond (Figure 1.4).

The mechanism for adhesion formation on material surfaces and the chemical and physical processes that occur when loads are applied to the bond are not fully understood and are still the subject of current and future research. Therefore, the exact calculation of adhesion forces at the beginning and after loading is not possible. This is often seen as a disadvantage of the adhesive-bonding technique. However, it is very well possible to manufacture bonded components with good reliability if appropriate planning is carried out, taking into account existing experience, and extensive proof of the robustness of the bonded joint is provided by investigations on laboratory samples and prototypes.

Figure 1.5 Mussels adhesive bonded to a wooden pile in the North Sea near Domburg, the Netherlands. Source: Dr. Jürgen Klingen, Aboso-Consulting.

1.5 An Example for Adhesive Bonding in Nature

There are also excellent bonded joints in nature that have been optimized by evolution over long periods of time. One example is the bonding of mussels to different surfaces by means of an adhesive made of proteins, whereby this adhesive is produced by the mussels themselves with the help of their specialized glands. This enables the mussels to adhere to materials such as wood, metal, glass, and coral, and to withstand strong impacts from salt water (Figure 1.5). Due to the unique combination of properties, this adhesive is of interest to adhesive researchers and is a candidate for medical adhesive applications, particularly in surgery and regenerative medicine. For example, such biocompatible adhesives could enable the rapid treatment of complicated bone fractures instead of fixing them with screws, nails, or plates. Also, this adhesive developed by nature might be able to quickly close skin wounds and other injuries.

2

History of Adhesive-Bonding Technology

2.1 First Adhesives

> *"From birch tar for shafting weapons to animal glue for holding together the first books."*

A corresponding *Guinness World Record* from 15 July 2019, shows very well how powerful modern adhesive systems are today [1]. An adhesive bond with a diameter of just 7 cm – the diameter of a standard soft drink can – held a 17.5-ton truck on a crane one meter above the ground for one hour. This corresponds to the current performance level of adhesives, which was achieved after numerous research and development efforts over many decades. However, after the first attempts in human history to create an adhesive bond between two material surfaces, the holding power of the bond was still very far from this level of performance. The first adhesive in human history can be considered to be birch tar, which was used in the Stone Age primarily for bonding tools and weapons. The black, tar-like distillate was obtained from birch bark by carbonization in the absence of air. The oldest evidence of this are two 200 000-year-old stone artifacts with traces of birch tar found in Campitello (Italy). Also, the *famous man* from the Tisenjoch – also called *Ötzi* – who died about 5300 years ago and was found not so long ago as a glacier mummy in South Tyrol (Italy), carried arrows made of flint and branches of the wool snowball. The materials were joined with a plant-fiber-reinforced birch tar glue (Figure 2.1).

As early as about 4000 years before Christ, the Sumerians deliberately developed and made an adhesive from animal hides (glutin glue) for building their houses and temples, which they called *segin*. To seal boats and build houses, they also used natural asphalt, which was available in their homeland, southern Mesopotamia, the region around present-day Iraq. Beginning around 1500 before Christ, the Egyptians discovered a concoction of sinew, gristle, and other animal waste as a suitable adhesive for carpentry. This art of *glue cooking* was further developed by the ancient Greeks and Romans, and the profession of glue cook – in Greek *kellopsos* – was introduced early in Greece. The Romans extended the range of glues used at that time to include fish glue produced by boiling fish waste, which did not appear in our latitudes until the sixth century Anno Domini. For special applications, glues were made from the swim bladders of fish. In the early Middle Ages, the development

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Figure 2.1 Birch tar produced in a one-pot process. Source: Jorre, https://en.wikipedia.org/wiki/File:Birkenpech.JPG. Licensed Under CC BY-SA 3.0.

of adhesives in Central Europe stagnated, so that there were hardly any interesting innovations in early adhesive technology until the fifteenth century. It was not until the invention of letterpress printing by Johannes Gutenberg of Mainz in Germany, which took place around 1450, that a new activity began, as special adhesives were needed to finish the books in the bookbindery. In addition, the renaissance of veneering technology in the sixteenth and seventeenth centuries created a great need for suitable adhesives. Thus, the first glue factory was built in Holland in 1690. However, the first patent for a fish glue for joinery was first granted more than 60 years later, in 1754 in England. Although the demand for wood glues increased during this period, there were initially no significant new developments in the field of gluing technology.

2.2 Adhesive-Bonding Technology: 1845–1930

"From the first self-adhesive band-aid to cover wounds to the invention of masking tape that made two-tone painted cars possible."

1845 **–** The first self-adhesive plaster was patented by Horace Day and William Shecut from New York, USA. The related US Patent 3965 describes a new and improved process for making a plaster based on natural rubber and a cotton fabric that had special properties in covering wounds. Its formula was based on rubber, pine gum, Peru balsam, litharge (lead oxide), and turpentine solvent. By perforating the fabric, the new flexible material was able to drain sweat and wound fluid. After the patent was granted, the rights were sold to Thomas Allcock, who marketed the new self-adhesive plasters under the name *Allcock's Porous Plaster*.

At the end of the nineteenth century, the demand for goods of all kinds increased and, with the associated mass production, the packaging problems also grew. New adhesives had to be developed, as the existing products no longer met quality requirements.

1880 **–** Otto Ring, a Berlin merchant, developed the first ready-to-use glutin-based adhesive with the brand name *Syndetikon*. This adhesive quickly became the