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Adhesive Bonding

Materials, Applications and Technology

Translated by Bettina Mikhail

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Further Reading

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Applied Adhesive Bonding

A Practical Guide for Flawless Results

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Preface

Today, there is a large body of international literature on the basics and manifold applications of adhesive bonding. The interdisciplinary nature of the subject, however, contributes towards publications being entered into this body from a wide variety of sources, making information extremely difficult and time-consuming to find. Moreover, the interactions between adhesives and adherents, as well as the long-term durability of adhesive bonded joints when exposed to hostile environments, have yet to be fully explored, leaving considerable gaps in our knowledge. Both, a solid knowledge of the basics and an empirical-based, expert knowledge gathered from many years of practical experience, are needed to create solid and reliable, longlasting adhesive bonds. The current literature, however, is rather uninformative in this regard.

The second, revised edition of this Handbook provides such comprehensive knowledge in a compact and well-structured form for the English reader. Specialists in a variety of disciplines, from both academia and industry, have compiled a store of knowledge about the performance and potential of adhesive bonding over a wide range of applications.

The reader will first become acquainted with the basics of adhesive bonding, followed by some practice-relevant issues such as the correct selection of adhesive, and the design and manufacture – as well as quality assurance of – adhesive bonds. A variety of applications of adhesive bonding is extensively presented, from structural high-performance bonding in aircraft and automobile manufacture and in the construction and building industry, to nonstructural bonding applications, for example in the packaging and lamination industry. The details of some amazing bonding methods found in Nature are also described, as are adhesive bonded joints between steel and rubber, which form an integral part of our everyday life, without being noticed as such. Subsequently, the reader will learn about 'bonding on demand', bonding in the medical and electronics sectors, and many other areas of application. This Handbook is the very first to provide such comprehensive knowledge about a joining technique that stands out for its versatility. It is both instructive and fascinating to learn about this wealth of experience gained with adhesive bonding since the very beginning of mankind.

Unfortunately, despite bonding having an enormous achievement potential when the bond is properly designed and implemented, people are often skeptical towards adhesive bonding. This Handbook provides valuable guidance for the successful implementation of adhesive bonded joints.

Our thanks go to Bettina Mikhail for translating, and to the publisher for releasing this Handbook for the English reader. May it contribute greatly to the advancement of adhesive bonding technology.

Kaiserslautern, September 2008 *The Authors*

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1
Adhesive Bonding as a Joining Technique

Bonding is the surface-to-surface joining of similar or dissimilar materials using a substance which usually is of a different type, and which adheres to the surfaces of the two adherents to be joined, transferring the forces from one adherent to the other. According to DIN EN 923, an adhesive is a nonmetallic substance capable of joining materials by surface bonding (adhesion), and the bond possessing adequate internal strength (cohesion). Bonding is a material joining technique that, in the traditional sense, cannot be broken without destruction of the bond. Recently, specific bonding-on-demand techniques have been developed (see Section 8.16.5), for example as an assembly tool without further function, or for recycling based on a separation of materials, a method that today is becoming increasingly important.

Bonding is by far the most universal joining technique. Virtually all technically useful materials can be joined with each other, and one with another, by means of this surface-to-surface and material-joining technique.

Adhesive bonding technology offers great design flexibility as it can be easily integrated into almost all available industrial sequences of single-piece work or mass production. Historically, bonding has long been recognized as a high-performance joining technique. The large majority of original natural binding materials have now been replaced by synthetically prepared adhesives. For example, phenolic resins were first introduced in the late 1920s, while during the 1940s epoxide resins and polyurethane were developed which have since made possible the production of synthetic adhesives (see Chapter 2).

As polymer chemistry has advanced in terms of knowledge, specific adhesives have been developed that bind very strongly to organic or inorganic materials. With regard to adhesive strength and deformation, these adhesives meet very specific requirements that result from the configuration of the adhesive joint. Meanwhile, high-strength adhesive assemblies have been created with quite short curing periods. In fact, the longstanding problem of extensive curing times necessary to obtain high-strength joints has been almost completely resolved with the introduction of new chemical developments in the creation of adhesives. Moreover, skepticism is no longer justified as to the long-term durability of adhesive joints exposed to adverse environments, provided that the bonding is properly conceived.

Table 1.1 Characteristic features of adhesive joints.

Advantages	Disadvantages
• The adherents are not affected by heat	• Limited stability to heat
• Uniform stress distribution	• Long-term use may alter the properties of the bond-line
• Possibility to join large surfaces	
• Possibility to join different materials	• Cleaning and surface preparation of the adherents is necessary in many cases
• Possibility to join very thin adherents	• Specific production requirements to be met
• Gas-proof and liquid-tight	• Specific clamping devices are often required to fix the joint
• No crevice corrosion	• Nondestructive quality testing is only possible to a certain extent
• No contact corrosion	
• No precise fits of the adherent surfaces are necessary	
• Good damping properties	
• High dynamic strength	

Bonding rarely competes with other joining techniques used in industry. For example, one would not consider bonding a steel bridge or a gantry, but for the lightweight construction of car bodies using steel, aluminum, glass and plastics, adhesive joining offers extremely interesting applications. Adhesive joining is particularly well suited to the joining of large-sized surfaces of different materials, such as in the construction of sandwich assemblies.

The possibilities, advantages and disadvantages of adhesive bonding compared to other joining techniques are summarized in Table 1.1

One of the many advantages of bonding is that little or no heat is needed to create the joint. As a result, the material structure of the adherents to be joined is not macroscopically affected, and deformations or internal stress – which generally are related to the application of heat – rarely occur. Even those materials with finished surfaces or coated materials can easily be bonded without any heat supply. From this point of view, there are no limits with regard to the combinations of materials that can be joined.

One important disadvantage of adhesive bonding, however, is the relatively poor heat resistance of the bond-line as compared to inorganic materials such as metal or glass. Hence, in order to obtain high-performance assemblies the production parameters must meet the specific requirements of the material used. This applies not only to the manufacturing sequences but also to the ambient conditions in which the joints are produced, because adhesion generally develops only during the production process, and the production parameters can have a decisive effect on the quality of the bond. The same more often than not applies to the cohesion of the adhesive layer. The technical properties of cohesion only develop during the course of the production process (with the exception of pressure-sensitive adhesives) after different setting processes. In this case, too, the production parameters mostly have a considerable effect on the quality of the final joint. By way of contrast, the joining process itself has only a minimally significant effect on the quality of traditional joining techniques, such as screw joints.

As the mechanisms of adhesion and the long-term behavior of adhesives are not yet completely known, it has not been possible to develop strict mathematical models for adhesive joints. Although this may be considered to be a disadvantage of bonding, the empirical values obtained with adhesive joints have meanwhile made it possible to conceive safe and sufficiently reliable bonded structures.

2
The Historical Development of Adhesive Bonding

To our best knowledge, bonding has been used as joining technique since the most ancient of times. As long ago as 4000 BC, the Mesopotamians are known to have used asphalt for construction purposes, while in 3000 BC the Sumerians produced glue from animal skins and called the product ‘Se-gin’. The discovery of a wooden, gold-plated Ram statue that contained adhesive made from asphalt indicates that, in Ur, about 1000 years later, glue was used for the manufacture of statuettes. Gluing was also known to have been used in Egypt in 1475 BC, since in the tomb of Rekhmara in Thebes the process is depicted on a mural painting dating from that time. The ancient Egyptians presumably used animal glues. In the tomb of Nebanon and Ipuki, which dates back to the same period, another painting shows the gluing of a shrine.

A glue tablet was found in a cave at the upper level of the mortuary temple of Queen Hatshepsut at Deir-el-bahari, i.e. in the tomb of Tutankhamun. The glue’s properties were investigated in the 1920s and shown to be identical to those of the skin glue still in use at the time of the archeological investigations, despite the tablet being 3500 years old. These findings give rise to the assumption that, over millenniums – and with few exceptions – adhesives have been subject to only insignificant further developments.

In the Talmud – a collection of Jewish after-Bible laws and religious traditions – reference is made to casein that had been used many years previously by the Israelites as a binder for pigments, although the large-scale use of casein glue was not introduced until much later.

Glue was also clearly well known in Greece, as the famous legend of Daedalus and Ikarus – which falls into the period between 2000 and 1600 BC – is based on the failure of adhesive bonds produced using wax (Figure 2.1). In *A History of Plants*, Theophrastus (371–287 BC) wrote that, for the carpenter’s purposes, fir could best be glued together and that it was said not even to crack when glued.

In 79 AD, Pliny the Elder (Gaius Plinius Secundus), in his book *Naturalis Historia* (*Natural History*), wrote that the entrance-doors of the Temple of Artemis (or Diana) at Ephesus, 400 years after having been reconstructed in 324 BC after the burning of the temple which had taken place in 356 BC, still appeared to be new. He noted that it was remarkable that the wings of the door were left in the glue clamp for four years. In

Figure 2.1 The fall of Ikarus. A copper plate in Ovid's *Metamorphosis* from the 18th century (Bildarchiv Preußischer Kulturbesitz, Berlin).

other chapters, too, he made remarkable notes on glues [1]. In Volume 3, Book XVI, for example, when describing different kinds of wood, he wrote: "Magna autem et glutinatio propter ea, quae sectilibus laminis aut alio genere operiuntur." ("Gluing is also important because of those things covered with cut boards or by other means.") Shortly after that, he made a remarkable note (still worthy of consideration nowadays): "Quaedam et inter se cum aliis insociabilia glutino, sicut robur, nec fere cohaerent nisi similia natura, ut si quis lapidem lignumque coniungat." ("Some (woods), e.g. robur, cannot be glued with other woods of the same kind or any other, and they almost never adhere to each other, unless they have a similar nature. The same applies to stone which would never adhere to wood.")

In Ancient Greece, woodworking glue was called Xylokolla (ξυλοκολλα), ox glue Taurokolla (ταυροκολλα) and fish glue Ichthykolla (ιχθυκολλα), while the glue maker was called the Kollepsos (κολλεπσοζ). As early as 530 BC, Theodorus of Samos mentioned the 'gluing of metals', which probably was figurative for a firm joint. It can be concluded, however, that the experience gained with adhesives was quite positive.

In 1122–1123 AD, Theophilus, in his books *De diversis artibus*, described different adhesives and mentioned casein glue which, apparently, was known of by the ancient Israelites. Somewhat amazingly, this glue was still in use when the first bonded technical structures of modern times were created, such as the construction of rigid airships by Schütte-Lanz between 1908 and 1919. The girders of these airships were made from wood glued with casein (see Figures 2.2 and 2.3).

Figure 2.2 The girder of a rigid airship made from glued asp wood (Schütte-Lanz, ca. 1915).

The rough and damp environment, in which naval airships were operated, often resulted in a failure of the glued joints. Their resistance was only slightly improved even when the glued assemblies were exposed to formalin vapors as postcure treatment (see Section 5.9.3.2), or when they were coated with lacquer.

Theophilus also described ground hartshorn that was added to animal glue as a filler, and Isinglass glue, the beluga quality of which was particularly praised in later time. Last, but not least, it is interesting to quote from the Merseburg charms originating from the early Middle Ages: "Bein ze beine, bluot ze bluote sollen sie gelimida sin." (Bone to bone, blood to blood should be glued."), which referred to general joints created by means of bonding for reparative purposes in medicine.

The bonding industry began to develop rapidly during the seventeenth and eighteenth centuries (Figure 2.4). In particular, an interesting treatise, *L'Art de Faire Différentes Sortes de Colle*, was written by Henry Duhamel du Monceau in Paris in 1771. This was published one year later in Germany, with the title *Die Kunst verschiedene Arten von Leim zu machen* (*The art of making different kinds of glue*) by the Prussian Academy of Sciences. In his treatise, Duhamel du Monceau provides a variety of recipes for the manufacture of different types of glue, and notes that garlic can be used as adhesion promoter when rubbed on wood before applying the glue.

Figure 2.3 A junction between three-dimensional airship girders made from glued wood (Schütte-Lanz, ca. 1915).

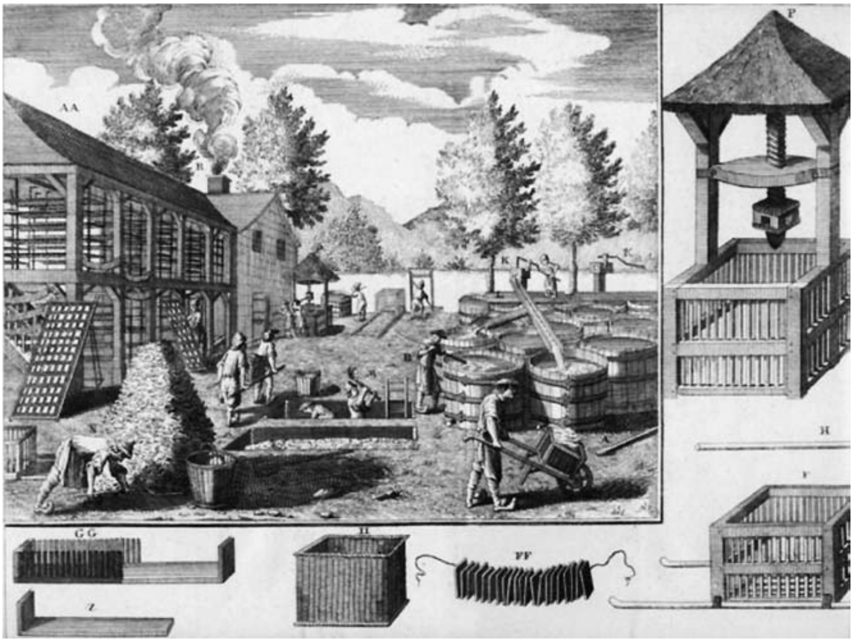

Figure 2.4 A glue factory from the mid-18th century (according to Duhamel du Monceau).

These details indicate that the existence of adhesion promoters was already recognized in very early times (the chemical structure of garlic extracts gives rise to the assumption that it is very efficient, in that they contain molecular configurations capable of building up chelate complex bonds; see Section 5.10.2).

It must be said that the development of adhesives took a long time, despite their widespread use. However, more important progress was made in the nineteenth century, when self-adhesive substances and tapes for use in medicine were developed and employed from the middle of the century onwards [2]. Horace H. Day was the inventor of pressure-sensitive adhesives based on natural rubber, while in 1845 William H. Shecut and Horace H. Day were granted a US patent for the improvement of adhesive tapes [3]. In Germany, a patent for a tape coated with a pressure-sensitive adhesive based on natural rubber was granted to the druggist Paul C. Beiersdorf in 1882.

For a long time, early pressure-sensitive adhesives were unable to meet the requirements of industrial applications, although their properties could be improved by these inventions and by various other developmental activities. The breakthrough was achieved by Richard G. Drew of the American Minnesota Mining and Manufacturing Company (3M) in the early 1920s, when he developed the first adhesive masking tapes based on crepe paper for lacquering processes in the automobile industry [4]. In 1926, Drew opened the first 3M adhesive tape laboratory, but later developed a cellophane adhesive tape to be used for packaging. This was the first transparent tape on the market, and it became an all round-solution for the office and the home [5]. Whereas, until the

1950s, pressure-sensitive adhesives did not attract much attention, today they have one of the most important growth rates of all groups of adhesives (see Section 5.1).

Meanwhile, in 1889 at Hannover, Germany, Ferdinand Sichel invented the first ready-made plant glue. However, the age of synthetically produced polymers truly began when Leo Hendrik Baekeland was awarded a patent for phenolic resins in 1909. In 1914, Victor Rollett and Fritz Klatte were granted a patent for the production of polyvinyl acetate (PVA), a synthetic raw material that is widely used to the present today, despite not gaining commercial importance until the 1920s. Although, urea resin had been known since 1919, it was not until 1929 – when a curing technique was developed – that it was used in the production of adhesives. Carboxymethyl cellulose and methyl cellulose have been used in painter's size and wallpaper pastes since the 1930s, while in 1931 Wallace Hume Carothers reported details of the production of polychlorobutadiene, through this material did not become important until the 1950s and 1960s.

Alexander Matting described various old recipes [6], notably the so-called 'marine glue' which was particularly famous and was produced from rubber solutions to which shellac or asphalt had been added. Another interesting recipe was used for the production of putties made from 60% lead oxide (PbO), 30% liquid phenol–formaldehyde resin and 10% magnesium carbonate. According to present knowledge, it was possible to achieve bond lines of high durability.

In the history of adhesives, another famous example was the so-called 'Atlas-Ago bonding technique', which used adhesives based on celluloid, was patented in 1912, and used in the shoe industry. From the late 1920s onwards, the former IG Farben produced a hot-curing and cold-curing urea condensation product which is still known by the name of 'Kaurit glue' (BASF). In 1928, Goldschmidt introduced an adhesive based on phenolic resin called 'Tegofilm'; with this fully synthetic, hot-curing adhesive it was possible to create absolutely water-resistant plywood joints. The same effect was achieved later with similar cold-curing systems, many of which are still in use today, having largely displaced the former casein and blood albumin glues (see Section 5.9).

In the early 1940s, the invention of phenolic resins modified with polyvinylformal by Norman Adrian de Bruyne marked a breakthrough in structural bonding not only of wood, but also of metals [7]. These resins contributed greatly to the improvement of aircraft structures, and are still appreciated today for their extraordinary durability, especially in case of aluminum bonding (see Section 8.2.1). They are referred to as 'REDUX', the term being derived from their place of origin (<u>Re</u>search at <u>Dux</u>ford). Remarkable among de Bruyne's concepts was that he used a combination of different polymer systems that previously had been used systematically only in pressure-sensitive adhesives.

Another name of historical value in the field of epoxy resins is that of 'Araldit' (CIBA). This was the merit of Eduard Preiswerk who, in 1944, discovered that epoxy resins cured with phthalic anhydride, produced synthetically by Pierre Castan in 1937, offered a wide variety of possibilities to create bonded joints, even between metals [8]. Castan intended to use these epoxy resins for dental purposes but, according to reports, he abandoned his experiments because the adhesion between those resins and other materials did not have sufficient water resistance. Both, hot-curing and cold-curing epoxy resins have been considered as standard products of structural adhesive bonding technology (see Section 5.5.1).

The patent for polyurethanes, awarded to Otto Bayer as early as in 1937, marked a milestone in the history of adhesives. Although, for adhesives production polyurethanes were taken into consideration only during the 1950s, they are at present one of the most important raw materials used in the adhesives industries, due mainly to the wide variety of ways in which they can be modified (see Section 5.6).

An interesting note with regard to the early bonding technologies can be found in a book published in 1933 [9]: “The owners of really good recipes for the production of specialty adhesives will be beware of disclosing them urbi et orbi (to the city and to the world).” Indeed, the adhesives industry has been adhering to this concept to the present day.

It is self-evident that this short historical review cannot be complete. Hence, further detailed information with regard to the development and properties of the different groups of adhesives is provided in the following chapters.