Gerhard Gierenz, Werner Karmann (Editors)

Adhesives and Adhesive Tapes
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**Adhesives and Adhesive Tapes**
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Preface

The impressive developments in numerous fields of technology – anything we can imagine from bookbinding, food packaging, electronic devices, automobile manufacture to building and aircraft constructions – all engineering progress in these and other areas is enabled and accelerated by innovations in adhesive technology.

Although adhesive applications mostly are not readily evident in daily life – except for some do-it-yourself areas, e. g. paper gluing, and repairs – experts in the development and engineering departments value adhesive technology as an important tool to find solutions to a wide range of technical problems. Strong points are the great variability in the kind and the properties of the adhesives, e. g. drying or reacting liquids, melting solids, adhesive tapes and die cuts.

This book, a special edition of the chapters “Adhesives” and “Adhesive Tapes” of Ullmann’s Encyclopedia of Industrial Chemistry, is intended as a guidance for everybody interested in getting an overview on the various adhesives, their different properties, and the wide field of applications.

Gerhard Gierenz                      Werner Karmann
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1. Adhesives

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1.1. Introduction

Adhesives are defined as nonmetallic substances capable of joining materials by surface bonding (adhesion), the bond itself possessing adequate internal strength (cohesion). Adhesive is a generic term and covers other common terms, such as glue, paste, gums, adhesive cement, and bonding agent.
History. Adhesion is among the oldest technologies of mankind [129]. As early as the Stone Age, our ancestors made stone axes and other tools using mineral pitch or wood rosin. Asphalt was used in building the Tower of Babel. In ancient Egypt, it was already customary to veneer furniture with the aid of animal glues. Flour- and casein-based adhesives were applied in ancient Rome. Adhesives of plant origin such as wood rosin were as well-known in China, as was the gum arabic and the caoutchouc ("weeping wood") from the tropical regions of South America and Asia.

In the Middle Ages, the first glue-boiling plants came into being and produced protein glues from animal raw materials (glutin from hides and bones, blood albumin, casein from milk) or starch paste from plants.

With the developments in chemistry in the early 1900s, the technology of adhesives began to boom. Phenolic resins (ca. 1900), melamine resins, and urea resins (ca. 1930), polymer dispersions, epoxy resins (1938), and cyanoacrylates (1957) largely superseded the classic natural adhesives and, with a multitude of bindings agents, form the basis for modern adhesive technology, which is one of the most advanced joining processes.

Composition. An adhesive is composed of basic raw materials, which are called binders [1] and which determine its adhesiveness (adhesion) and its internal strength (cohesion), and of frequently necessary auxiliaries, which establish particular end-use and processing characteristics. The adhesiveness of an adhesive, its internal strength after setting, and its processing characteristics are the fundamental properties that determine its suitability for use in forming adhesive joints. Adhesive joints are the joints formed between substrates and adherents using adhesives.

The binders used for adhesives are primarily high polymers having optimal strength properties. High internal strength (cohesion) is essential if the adhesive in an adhesive joint is to be able to transmit forces from one adherent to the other. Most adhesives contain high molecular mass organic substances as their basic raw materials or reactive organic compounds that are preliminary stages of polymers and that react during the bonding process to form polymers. Inorganic polymers, such as the various types of waterglass, are used only to a very limited extent.

Virtually any standard polycondensate, homopolymer, and copolymer and also polyadducts may be used, provided they can be applied as solutions, dispersions, emulsions, or melts. In addition to these raw materials, auxiliaries such as resins, plasticizers, fillers, thickeners, solvents, antiagers, preservatives, hardeners, or setting retarders, are required, depending on the end use. Their function is inter alia to adjust tack, to improve adhesion, to make flexible, to regulate viscosity, to stabilize, and to influence setting or hardening.

Adhesive Joints. In many cases, adhesion is as effective as other joining techniques, such as riveting, welding, soldering, and screwing; in some cases it complements those techniques; and frequently it affords numerous advantages. On the other hand, certain processing requirements and material properties related to chemical structure can restrict the use of adhesives.
Bonding has the advantage that the joining of adherents can be carried out very rationally, often extremely quickly, and particularly economically [2]. One important feature common to all adhesive joints is the highly uniform distribution of forces over the entire joint area by comparison with rivet and screw joints. The uniform stress levels frequently provide for more optimal utilization of material strength. Accordingly, thinner and hence lighter sections of material may be used. This has resulted in the saving of material and, for example, in the automotive, aircraft, manufacturing, and furniture industries, in totally new structural elements (sandwich elements).

The use of adhesives enables numerous materials, even those differing widely in type, to be joined to one another. This applies above all to materials that cannot be joined to one another by other techniques. Because some adhesives set even in relatively thick layers, any unevenness in the constituent material of the adherents may be smoothed out during bonding, or significant dimensional tolerances may even be bridged by the gap-filling principle. The adhesive layer of an adhesive joint even may have a vibration-dampening effect and, by virtue of its insulating properties, can prevent contact corrosion in adhesive joints involving metals of different normal potential. Another advantage is the fact that many adhesives can be applied at room temperature or, when heat must be used for application, it is sufficient to apply temperatures at which the constituent materials of the adherents are not affected, as can happen in the welding of metals and plastics.

The usability of adhesives can be restricted when stringent requirements are imposed on the thermal stability of an adhesive joint [2]. Like all plastics, adhesives based on organic polymers also show a marked dependence on temperature in their strength properties. The strength properties of an adhesive joint can be kept constant and sufficiently high in only a relatively narrow temperature range. Adhesives cured by thermal cross-linking which are still relatively temperature resistant are generally capable of withstanding temperatures of up to about 150 °C. Using new, but more difficult to apply adhesives based on polyimides [3], it is possible to form adhesive joints which are capable of withstanding temperatures of the order of 250 °C for long periods. On the other hand, some adhesives, when subjected to heavy static stress for long periods, show a tendency even at room temperature to creep, a plastic deformation that can result in separation of the adhesive joint.

1.2. Adhesion Theories

The atoms or molecules in any solid are held together by so-called cohesion forces. These interatomic and intermolecular forces are conservative in character, i.e., not dependent upon the pretreatment of the material [4, p. 1]. After a break in the solid, the two fragments cannot be put back together in such a way as to restore the solid to its original state. Reactivation of the cohesion forces would be possible only if the original intervals between atoms or molecules could be reestablished. The same may be
said also of the joining of two different materials; a mutual convergence over the entire joint area on the radius of interaction of the molecules would result in adhesion of the same order of magnitude as the cohesion forces [5]. In practice such convergence is not possible. There are three reasons for this: first, the surface roughness of the adherents; second, a reduction in the effective surface for boundary layer reactions due to the surface tension of the adhesive; and third, the formation of the so-called weak boundary layer [130], [131]. This is a region within the adhesive film close to the boundary layer where the reactive groups of the molecules are directed to the adherent and consequently do not contribute to the curing process, that is, no cross-linking occurs. Therefore, the weak boundary layer is always a weak link in the adhesive joint. The function of the adhesive in the boundary zone is to compensate for the effects of surface roughness by providing optimal wetting of the adherents.

Over the years, several different theories have been developed as to the mode of action of adhesives, i.e., the mechanism of adhesion. They extend from the simple mechanical theory via the electrostatic and adsorption theory to the diffusion theory, these being the most important [6]. One feature common to all these theories is that, for some adhesion phenomena, these theories allow qualitatively satisfactory assertions to be made, but in other respects they fail totally and, in some cases, even lead to conflicting results. The adhesion of adhesive to an adherent, on which any joint is based, is clearly not a consistent and isolatable process [7] but a complex addition of various adhesion effects. Because the number of individual processes involved, apart from exceptions, is extremely difficult to estimate, definitive confirmation or rejection of individual theories is hardly possible.

**Mechanical Theory of Adhesion.** The oldest theory of adhesion is definitely the mechanical theory. It is based on mechanical anchorage of the adhesive in pores and irregularities in the adherent and is discussed primarily in reference to wood and similar porous materials [8].

**Electrostatic Theory of Adhesion.** According to the electrostatic theory [9], the adhesion forces between adherent and adhesive layer are applied by contact or transfer potentials. These transfer potentials cause the buildup of an electric double layer at the adhesive–adherent boundary and corresponding Coulomb attraction forces between the two components. In principle, the occurrence of transfer potentials is unquestionable, as shown by the electrostatic discharges that can be detected in the destruction of adhesive joints. However, the practical significance of the attraction forces associated with these discharges is still being debated [4, pp. 150–153], [10].

**Adsorption Theory.** As its name indicates, this theory of adhesion draws upon surface forces for explaining the observed phenomena [11]. It regards adhesion as essentially a special property of phase interfaces. The forces that are responsible for adhesion in this process are the so-called secondary valence or van der Waal's forces. These forces have three components, namely Keesom's dipole orienting effect, Debye's
induced dipole effect, and London's dispersion effect [12]–[14]. For these forces to become active, the distances between the molecules of adhesive and adherent must converge toward molecular intervals. This requires complete spreading of the adhesive over the surface of the adherent. Good adhesion can be expected if the adhesive (in liquid form or in a liquid medium) wets the adherent [8]. Accordingly, the adsorption theory may be placed on an entirely thermodynamic basis. Adhesion is thus determined by the ratio between the surface energies of the adhesive and the constituent material of the adherent in the sense that the specific surface energy of the adhesive must be lower than that of the adherent. Accordingly, materials having high surface energy levels, such as metals, and those having medium surface energy levels, such as wood and paper, may be bonded relatively easily. In the case of polymers, bonding becomes increasingly more difficult [15], and finally almost impossible as surface energy decreases (polyolefins and polytetrafluoroethylene). The remedial surface treatment of materials such as these may be interpreted as increasing their surface energy [16].

The adsorption theory also shows that the adhesion forces of two materials are not reciprocal. For example, if a liquid epoxy resin adhesive is allowed to set on the surface of polytetrafluoroethylene or polyethylene, a very weak adhesive joint is formed. If, by contrast, liquid polytetrafluoroethylene or polyethylene is applied to the surface of hardened epoxy resin, strong adhesive joints are obtained [17]. In practice, this theory is not free from contradictions either; above all, it does not answer the question whether the difference in the surface energies between two materials is indicative of the intensity of the adhesion force [18].

**Diffusion Theory.** The diffusion theory of adhesion is essentially applicable to the bonding of high polymers. According to this principle, adhesion is obtained by the mutual penetration of adhesive and substrate [19], [20]. This mobility is based on the fundamental properties of high polymers: their chainlike structure and resulting mobility, allowing the possibility that the chains possess Brownian molecular movements in a submolecular range. By virtue of their greater mobility, the adhesive molecules normally play a greater part in the diffusion process. However, if the adhesive is in solution, which is generally the case, and if the substrate is slightly soluble in the solvent, substrate molecules or parts thereof also diffuse into the spread adhesive. A diffusion bond is characterized by the disappearance of a clear boundary between the two phases and by the development of a gradual transition from one phase to the other. The mechanism of adhesion has developed into a three-dimensional process and is no longer confined to one interface.

The interdiffusion of the polymer molecules of adhesive and substrate is dependent upon various parameters, such as pressure, time, temperature, molecule size, and, of course, the reciprocal solubility, as shown by the correlation between the compatibility of the polymers and the quality of the bond [21]. Examples of bonds to which the diffusion theory is applicable include the bonding of PVC-U adherents to PVC in solvents containing tetrahydrofuran and so-called contact bonding, where the diffusion