

History of Adhesives

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The dictionary defines an adhesive as “a substance capable of holding materials together by surface attachment.” This is a simple definition for a material that is the basis of a multi-billion dollar industry with more than 750 companies competing for a share of the market. It is estimated that 50 of those companies are responsible for 50 percent of the sales dollars in the adhesive industry.

The first evidence of a substance being used as an adhesive dates back to 4000 B.C. Archaeologists studying burial sites of prehistoric tribes found foodstuffs buried with the deceased in broken pottery vessels that had been repaired with sticky resins from tree sap. Archaeologists have also uncovered statues from Babylonian temples that have ivory eyeballs glued into eyesockets. This tar-like glue has held for almost 6,000 years.

The period of time between 1500-1000 B.C. gave further proof that glue had become a method of assembly. Paintings and murals showed details of wood gluing operations. A casket removed from the tomb of King Tut shows the use of glue in its construction. Our museums today contain many art objects and furnishings from the tombs of Egyptian pharaohs that are bonded or laminated with some type of animal glue.

The first references in literature concerning glue and the art of glue appear about the year 200 B.C. Simple procedures for making and using animal glue were written.

The next period of activity is from 1-500 A.D. when the Romans and Greeks developed the art of veneering and marquetry, which is the bonding of thin sections or layers of wood.

From this art, the making of animal and fish glues were refined and other types of adhesives were developed, such as an adhesive from egg whites to bond golf leaf. In addition to egg whites, other natural ingredients were used to prepare glue, such as blood, bones, hide, milk, cheese, vegetables, and grains. The Romans were one of the first to use

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tar and beeswax to caulk the planking in boats and ships.

A study of history shows the use of glue fell into disuse until about 1500-1700 A.D., when adhesives were used in the building of furniture. Some of the greatest furniture and cabinet makers of all time used adhesives in their products — names you will still recognize today, like Chippendale and Duncan Phyfe.

Other notable names in history who may owe their notoriety, at least in part, to adhesives; about the year 1000 A.D., Genghis Khan overcame all attackers because of the exceptional power and range of the weaponry his men carried. Bows were made from laminated lemonwood and bullhorn bonded with an adhesive whose formula has been lost in antiquity.

The secret of violins made by Antonio Stradivarius was the adhesive process used to laminate his specially treated woods. His methods have also been lost in antiquity and have not been rediscovered, even with today's sophisticated analytical methods.

About 1700 A.D., the widespread use of glue brought about some rapid changes in the history of adhesives. The first commercial glue factory was started in Holland to manufacture animal glue from hides.

About 1750, the first glue patent was issued in Britain for a fish glue. Patents were then rapidly issued for adhesives using natural rubber, animal bones, fish, starch, and milk protein (casein). By 1900, the United States had a number of factories producing glue from these bases.

The industrial revolution caused an explosion in technical breakthroughs that resulted in new materials becoming available for use in formulating adhesives. The first plastic polymer to be synthesized was cellulose nitrate, a thermoplastic material derived from the cellulose of wood. Its first use was in the manufacture of

billiard balls, which had been made from ivory. The era of plastics began with the production of bakelite phenolic, a thermoset plastic, in 1910. Within a year, adhesives using phenolic resin were put on the market. The 1920s, '30s, and '40s saw many new plastics and rubbers synthetically produced, many out of an urgent necessity developed during World War II. Although adhesives have been known for about 6,000 years, most of the technology of adhesives has been developed during the last 100 years.

The development of plastics and elastomers has rapidly advanced the development of adhesives and has given formulators a wide variety of products that can change and improve various properties of adhesives, such as flexibility, toughness, curing or setting time, temperature and chemical resistance.

Adhesives touch our lives every day. They are never more than an arm's length away, even though we may not be aware of their presence. A description of some of the more common types of adhesives and their uses should make you more aware of how adhesives touch your life.

Animal Glues — are made from the protein extracted from the bones, hide, hoofs, and horns of animals by boiling. The extract is cooked to form a gelatin material. The gelatin can be re-liquified with heat, which gives it quick setting properties. Its major use has been in the wood and furniture industry. If you have seen a heated glue pot with a brush in it, it was probably an animal glue. Animal byproducts from meat processing have been the source of supply for this type of glue as well as the sources of jokes about old Dobbin being past his prime and only good for the "glue pot."

Fish Glue — is a similar protein-based glue made from the skins and bones of fish. An exceptionally clear adhesive can be

made from fish and was the first adhesive used for photographic emulsions for photo film and photo resist coatings for photoengraving processes.

Casein Glue — is made from a protein isolated from milk. The extraction process creates an adhesive that is waterproof. Its first use was in bonding the seam of cigarette paper. It provides a fast-setting bond that requires very little adhesive; one gram of adhesive can bond 2,000 cigarettes.

Starch — is a carbohydrate extracted from vegetable plants such as corn, rice, wheat, potatoes, and is probably better known as paste. Major use area is in bonding paper and paper products such as bookbinding, corrugated boxes, paper bags, and wallpaper paste (nonremovable); it is also used as a sizing in textiles. The laundry uses starch on your shirt collars to stiffen and give shape to your shirt.

Cellulose Adhesive — is made from a natural polymer found in trees and woody plants. It is the adhesive used on the cellophane wrapper on cigarette packs; it is the adhesive on decals we put on windows; and, interestingly enough, the adhesive used on the strippable wallpaper we have in our homes that allows us to remove the paper easily.

Rubber-Based Solvent Cements — are adhesives made by combining one or more rubbers or elastomers in a solvent. These solutions are further modified with additives to improve the tack or stickiness, the degree of peel strength, flexibility, viscosity, or body. Rubber-based adhesives are used in a wide variety of applications, such as contact adhesive for plastic laminates like counter tops, cabinets, desks, and tables. It is the adhesive on pressure-sensitive tapes used as floor tile adhesive and carpeting adhesive. Self-

sealing envelopes and shipping containers use rubber cements. Solvent-based rubber adhesives have been the mainstay of the shoe and leather industry.

Epoxies — are adhesive systems made by a complex chemical reaction. Various resins are made synthetically by reacting two or more chemicals. The resultant resin can then be reacted or cured by the addition of another chemical called a hardener, or catalyst. The basic epoxy resin systems are further modified to change their physical properties by the addition of such things as: flexibilizers for impact resistance and flexibility; dilutents or solvents to reduce the viscosity fillers; and reinforcements like glass fiber, alumina, silica sand, clay, metal powders and flakes to change properties such as heat and electrical resistance, fire retardance, strength and adhesion to certain substrates or materials.

Epoxy adhesives can bond a wide variety of substrates (particularly metals) with high strength. They have been used to replace some traditional metalworking methods of joining like nuts and bolts, rivets, welding, crimping, brazing, and soldering. High-strength epoxies are used to construct rotor blades for helicopters and to attach aluminum skins to the struts of aircraft wings and tail sections. Those of you who ski may know that your skis are laminates of plastics, wood, and metal joined with an epoxy. If you are a golfer, the heads of your clubs are bonded with an epoxy.

Hot Melt Adhesives — are thermoplastic polymers that are tough and solid at room temperature but are very liquid at elevated temperatures. The origin of hot melts probably started with the use of sealing wax used to seal documents and letters with a signature ring or stamp, but the art of hot melts was not pursued until the 1960s.

The major use of hot melt adhesive is in case and carton sealing. Probably if you purchased products such as frozen food, breakfast cereal, laundry detergent, a case of beer, or anything shipped in a corrugated box, the flaps were bonded with a hot melt adhesive. Hot melts are also used in home workshops for fast repairs around the home.

Other adhesives that you may have heard of that represent higher technology and/or complicated chemical processes include:

RTV Silicone Adhesives — are a rubber-like polymer called polydimethylsiloxanes. RTV stands for “room temperature vulcanizing,” or simply a rubber that cures at room temperature.

Silicone rubber adhesives are made from a complicated process that turns elemental silicon metal made from sand (silica) into a rubbery polymer when cured. Silicone rubber adhesives/sealants have excellent resistance to heat (500-600F) and moisture, which makes them exceptionally suited for outdoor weathering applications as sealants and caulking compounds in the construction industry.

Because of their exceptional properties, silicone adhesives have been used in some exotic applications, such as the soles of boots worn by the first astronauts to walk on the moon. Silicone adhesive/sealants are used to seal windows, doors, and portholes on the space shuttle and many satellite missiles. A special silicone adhesive is used to bond the heat shield tiles on the space shuttle.

Anaerobic Adhesives — are derived from methacrylates, a monomer related to acrylics or more commonly known as plexiglass. The term anaerobic is used to describe this family of adhesives because this type of adhesive “comes to life” or hardens in the absence of air. There are many different types of anaerobics used for

specific applications such as threadlocking, threadsealing, flangesealing, or retaining.

Cyanoacrylates — are extremely rapid curing adhesives commonly called “superglue.”

These adhesives were actually discovered by accident at Eastman Chemical Company. In trying to characterize certain polymers, they ended up gluing their microscope slides together. Cyanoacrylates are typically used in applications where there is a need for a rapid-curing, single-component adhesive that provides high adhesion, high tensile strength, and easy dispensing.

The following list demonstrates a few common, everyday items that use adhesives in some form and that would most likely not be around today if not for the existence of adhesives:

- Cardboard cartons hot melt adhesives
- Golf club heads epoxy adhesives
- Cigarette packs casein glue
- Furniture joints animal glue
- Wallpaper wetting glues and pressure sensitive adhesives
- Envelopes wetting glues and pressure sensitive adhesives
- Band-Aids pressure sensitive adhesives
- Baby diapers pressure sensitive adhesives
- Floor tiles pressure sensitive adhesives
- Bookbinding starch paste
- Skis epoxy adhesives