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## ADHESIVES AND ADHESION

What is a kiss? why this as some approve:  
The sure sweet **cement**, **glue**, **lime** of love.

Robert Herrick 1591-1674

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### GENERAL DISCUSSION:

#### History

Adhesives have been used by people for millennia. Some of the earliest, such as plant resins, starches and sugars, and concentrated proteins are still used for a variety of applications. In English, sticky substances used to join things together have been called by a variety of names. The word '**adhesive**' comes from a Latin root. '**Cement**,' from an Old French root generally describes materials that become very hard after application. '**Glue**,' from Old English, was usually used to describe protein extracted from animal parts but has a more general meaning now. '**Lime**,' a word formerly used to describe any sticky substances (as in 'bird lime' -plant gums used to trap birds by sticking them to the branches) survives now as a word for calcium hydroxide putty used to join stone and bind plaster. Even the word '**mastic**' from the Greek root meaning 'to chew' was more generally used to describe a variety of sticky materials. In the past, all such substances were generally prepared by the user from locally available materials, only becoming commercial commodities in the last few hundred years.

The production of cheap and affective containers may have influenced the availability of proprietary adhesives and fillers just as they did in the case of art materials and drugs. There had already been a steady rise in the quantity of glass bottles produced, with accompanying decline in cost when the introduction of bottle-making machines in the mid-nineteenth century made them truly disposable. Other new and effective packaging systems included the collapsible metal tube, invented by John Rand in 1841, and the introduction of tinned sheet-iron "cans" or "tins" which were steadily improved throughout the nineteenth century. Such packaging improvements gradually eliminated the need for restorers to make their own adhesives. By the early twentieth-century proprietary adhesives and fillers were so common and convenient that some works on restoration from that period rely on them almost exclusively. More recently, conservators have found commercial packaging systems to be useful for the storage of adhesives formulated by the conservator.

#### Terminology and technology

Adhesives are substances capable of holding other materials together by their own agency, or, by acting in concert with mechanical joining methods such as "worked joints" (dovetails, mortise and tenon etc.) used in woodworking, or stitching and wrapping using cordage (as in an arrow-head fastened to a shaft).

**Adhesion** is the bond formed between the **adhesive** and the joined substrate (the "**adherend**"). "**Cohesion**" is the internal attraction of the adhesive to itself.

Adhesives may hold materials together by simply invading tiny pores and undercuts in the adherend surfaces, thereby locking them together mechanically (called "**mechanical adhesion**"), or by molecular attraction of the adhesive and adherend- often the same inter-molecular forces that

generate cohesion. The attraction that molecules of one surface have for those of another is termed "**specific adhesion**" and is greatest between materials that are chemically similar. As everyone knows, oil and water do not mix, and a polar, water-based adhesive is unlikely to adhere well to an oily non-polar substrate.

The forces of attraction depend on very close proximity of molecules. A non-porous solid such as steel will attract itself if the mating surfaces are so perfectly polished that air is excluded and very close contact is made, but such close contact is not possible between most solid surfaces due to roughness, or because they are porous and consist mostly of voids (e.g. wood). This dictates the use of a liquid adhesive which can flow out onto a rough and void-filled surface "**wetting**" it intimately and serving as an intermediate between the solid surfaces. When the adhesive itself becomes solid by cooling (**thermoplastics**) chemical reaction (**thermosets**) or solvent loss (**solution resins/adhesives**), the adherends are firmly stuck together. The "**pressure sensitive**" adhesives are exceptions to this type of adhesion, being soft enough in solid form to conform very closely to surfaces. Pressure sensitive adhesives may also stick by a sort of micro suction cup effect generated by tiny voids on the surface of the adhesive. There is still much that is not known about adhesion. What holds flies and gecko lizards on a ceiling is still subject to debate and competing theories.

In general, the better a substrate is "**wet**" by an adhesive, the better the bond will be because the degree of wetting is itself dictated by the attraction generated between the substrate and adhesive ("specific adhesion"). A way to visualize this wetting is by the "**contact angle**" formed between the surface of a drop of liquid on a solid and the surface of the wet solid. A drop of water on a piece of wax for example "**beads up**" into a spherical shape having a large contact angle. A drop of water that can spread and flatten on an appropriate wettable surface has a small contact angle. Observation of this phenomenon can be a useful guide in judging the appropriateness of an adhesive, or of the condition of the adherend surface which may be too oily to be wet with a water based adhesive.

There are various other practical aspects of adhesive bonding which can be explained by physical phenomena:

### **Surface Preparation**

Dirty surfaces bond poorly. Any sort of loose material deposited on the surface serves as a release agent. Talc and similar fine particulate materials are used intentionally in molding and casting operations to do just that. Surface layers of greasy dirt will repel most adhesives so that they wet poorly. In the case of wood, natural oils and resins will often migrate to the surface after cutting, so freshly cut surfaces should be glued as quickly as possible for best results. Loose and powdery material—either extraneously deposited dirt and dust, or adherend detritus produced by machining and abrading (saw dust for example) will serve as a separation layer preventing good wetting of the substrate. Again with wood, a smooth surface produced by a sharp plane blade will produce a stronger glue joint than a sanded surface because the wood fibers, having been cleanly severed, are undamaged and free of detritus.

### **Glue Line Thickness, Adhesive Failure**

The thickness of the glue layer between the adherend surfaces will affect the strength of a joint in a number of ways. An excessively thick "**glue line**" composed of a thermoplastic adhesive will tend to "**creep**" or gradually change shape and fail under a prolonged loading stress. In some situations the rigid adhered surfaces will restrain movement of the plastic adhesive ("**plastic constraint**") but only where the adhesive line is thin enough that its internal flow characteristics ("**rheological properties**") will not be the dominating factor. Adhesives may be hard and brittle due to their inherent

characteristics (such as low molecular weight or highly cross-linked structures), low temperatures (below the "glass transition" temperature at which they show fragile glass-like characteristics) or due to excessive desiccation (as with hide glues). With such brittle adhesives, a thick glue line may make it possible for flaws and fissures at the edges to serve as "stress raisers" and propagate the cracks throughout the adhesive causing failure. Closely mating surfaces and thin glue lines are generally desirable but even this rule has limits. If excessive clamping pressure is exerted on adherends in order to create a thin glue line, high spots on the surfaces are forced into compression and can then exert a continuous stress on the glue line after the clamps are removed. This stress can cause "strain" or change of shape- and subsequent failure due to either plastic flow or internal fracture.

### **Starved Joints**

Obviously, sufficient adhesive must be present in a glue line to fulfill its intended function. Where insufficient adhesive has been applied to fill the gap between adherend surfaces, or where the porosity of the adherends has drawn adhesive away from the joint by capillary attraction, a "starved joint" will result. Adhesive viscosity plays a large role in this mode of failure. Adhesives with low viscosities are generally unsuitable for use on porous substrates and have no "gap filling" capability where mating surfaces are less than perfect. Also for reasons of reversibility and optical saturation, penetration of inappropriately fluid adhesives is to be avoided.

### **Roughening Surfaces**

An early and possibly naive theoretical model for the interaction of adhesive and adherend stressed the mechanical interlocking of a dried adhesive with voids and undercuts on the substrate surface. Intuition dictated then that a roughened surface would produce a stronger joint and "toothing" planes were traditionally used by cabinet makers to "key up" mating surfaces. Likewise, metal surfaces were often sanded or scratched in order to provide a "key." Modern studies have demonstrated that this may actually decrease adhesion in wood by damaging the fibers and creating loose detritus. The increase in surface area due to roughness should create a stronger joint, but air trapped in voids tends to offset this affect in tests. Modern adhesive science has found very few practical instances where increased roughness aids in adhesion, though admittedly, such studies have not tried to duplicate traditional practices in all respects. Traditional veneering for instance, usually involves working the adhesive into the "toothed" surfaces. This may not only largely eliminate the void effect, but incorporate loose fibers into the adhesive, thereby forming a stronger composite and increasing the mechanical adhesion.

## **FACTORS GOVERNING THE CHOICE OF AN ADHESIVE**

A great number of factors can affect the choice of an adhesive, and while not all of them will apply to a particular situation it is desirable to understand what they might be so that informed choices can be made.

### **Service Conditions**

Look at the big picture first. How strong does a joint need to be? Adhesive scientists will consider a bond to be ideal if mechanical destruction of the joint results in 100% failure in the substrate (e.g. wood) on either side. This behavior is not desirable in most conservation situations where original material should be protected from further damage. The conservation ethos that the adhesive should fail before the substrate does is seldom achievable in practice however, since the variables must be

guessed at. An overly weak adhesive is likely to fail and cause damage to the object as it falls apart. In general, it may often be better to err on the side of strength.

When dealing with antique objects the conditions that will operate on the object after conservation will greatly affect decisions regarding adhesives. Will the object be used and if so, what kinds of loads and stresses will the joins experience? If an object is in a museum collection it may receive regular professional examination at which time previous conservative decisions can be re-evaluated. If the object is going to private collections the work done by a conservator may need to hold up for a very long time. The subsequent care an object will receive must also be evaluated in terms of light levels, humidity, temperature, and vulnerability to mechanical and biological deterioration and all of these factors may affect decisions governing adhesives.

**Reversibility** is a conservation principle that must not be seen in absolute terms, but as a concept that is influenced by service conditions. An adhesive must do its job under the conditions it is exposed to, or it is unsuitable regardless of ideal characteristics of chemical stability and reversibility. As already mentioned, a museum conservator can often make more conservative decisions because re-treatment in the event of failure is feasible, whereas a more intrusive treatment and inherently less reversible adhesive may be advisable if conservation is likely to be a unique event in the life of the object. There are a variety of reasons why the principle of reversibility must be borne in mind by the conservator and they can be very practical as well as more philosophical. Some adhesives and coatings will severely limit the possibility of future treatment or even subsequent operations in the same treatment. For example, consolidation with waxes or stabilization with polyethylene glycols will introduce very effective release agents that make adhesive bonding or coating virtually impossible, and such treatments are practically as well as theoretically irreversible. This concept of 'retreatability' is a suppler guide than the often rigid concept of reversibility.

### **Application characteristics**

Most adhesives have a characteristic "**open time**" during which assembly and clamping can be carried out but after which, assembly is either impossible or the strength of the final bond is affected. Adhesives with very short open times can be chosen where the assembly job is simple or where clamping is not possible owing to shape, fragility or other factors. Conversely, adhesives with long open times are necessary where the assembly job is difficult or where elaborate clamping systems must be deployed.

### **Health Hazards**

Virtually all cured adhesives are of very low toxicity, but this is certainly not true of the un-cured liquid components. The chemicals used to prepare thermosetting adhesives such as epoxies, polyesters and formaldehyde resins are associated with a variety of health hazards as are the solvents used to apply various natural and synthetic resins. Health hazards have become an increasingly important concern as the risks have become more fully understood. Decisions regarding use of toxic materials have been left to the craftsperson or conservator in the past, but are increasingly being made by governmental regulatory agencies. Wherever good alternatives can be found to toxic materials they should be used even if minor disadvantages are evident.

### **Characteristics of Cured Adhesive**

The physical characteristics of the cured or solid adhesive are of obvious importance. Many of these characteristics such as hardness and fragility, softness and potential for cold flow or creep, sensitivity to moisture and heat have already been discussed. Visual characteristics can also be very important.

These considerations include the initial color of the cured adhesive as well as color change as a result of aging. The adhesive can affect the color of the substrate by staining it, or by filling pores and visually darkening it as a result of optical saturation. Some adhesives have useful shelf lives of a few months to a few years. Such problems can be combated by only purchasing in small quantities and only as much as is required for a particular job. The shelf life of most materials can be extended by refrigeration or hermetically sealed storage. Liquid hide glues degrade continuously in the bottle and become less effective with age. Hot hide glues begin to degrade as soon as they are hydrated and heated, and should be made fresh at regular intervals, and not overheated while in use.

Cured adhesives are also more or less vulnerable to processes of chemical degradation which can result in change of color or adhesive and cohesive failure. Adhesives which spontaneously reverse themselves over time have obvious limitations, but from the point of view of a manufacturer in our throw-away society these times can be relatively short and still be acceptable in industry. Claims of permanence by industry must therefore be critically evaluated.

### **Relativity of Choice Factors**

Lastly it is important to note that there are no absolute advantages or disadvantages affecting a choice that will not be governed by service conditions and ethical and aesthetic factors. The characteristic cold-flow or creep of a soft adhesive for instance, while disadvantageous in most situations can accommodate movement in an inherently unstable material such as wood. Epoxy resins are often condemned as being "irreversible" yet on some substrates, and under certain conditions, they may be more reversible in practice than a more freely soluble adhesive. Animal glues for instance, cannot be easily removed from substrates that are bound with animal glues (gesso, bole, water gilding) whereas epoxy resins can. There are no good and bad materials, only poorly considered applications. A conservator is simply eliminating tools from the kit if a prejudice concerning a material is allowed to develop as a result of poor performance under specific conditions. Care must be taken to evaluate each new situation with a clear and open mind.

## **ADHESIVES USED IN CONSERVATION**

### **Introduction**

Given the ingenuity and imagination of human beings it is likely that almost any substance ancient or modern that could be construed as an adhesive has been tried as such. Many were obviously unsuitable, many have had brief vogues and fallen out of favor, and many have continued to be used under various service conditions. The primary literature should of course be consulted--especially for solutions to special problems but the following comments on the major categories of useful adhesives will serve as an introduction. For each category of adhesive brief summaries of the properties already discussed are given where they are notable.

### **ANIMAL GLUES**

#### **Introduction**

Animal glues have great importance in the history of both woodworking and conservation and requires detailed discussion. They are some of the first adhesives used by man, and continued to be virtually the only adhesives employed in furniture construction until the relatively recent adoption of alternative adhesives for many applications in wood bonding. Animal glues have proven extremely durable under ideal circumstances and intact glue joints can be found that are centuries old. Optimum animal glue joints are stronger than the wood itself but even under less ideal circumstances offer

adequate strength. They do not stain wood or impede the application of stains and coatings, are non-toxic and easily cleaned from areas where the adhesive is unwanted. Animal glues have been extensively used for the repair of antiquities and other art objects, both as primary adhesives, and as binders for filling materials and paints. Since they are water-soluble, restorations based on animal glues are relatively easy to reverse. Disadvantages of animal glues include limited working time at room temperatures, poor gap filling abilities, and bio-deterioration under some conditions. As water-soluble adhesives, animal glues are moisture sensitive. This makes them unsuitable for some applications. For furniture conservation, animal glues are recommended by the relative ease of reversibility. Because they are most likely to be the original adhesive in a furniture glue joint, re-gluing an old join with animal glue is generally the best choice in terms of compatibility and strength.

Animal glues can be reversed with water, heat, or wet heat (steam). Glued joins can also be cracked apart by introducing alcohol into the joint. The alcohol desiccates the glue and follows small fractures into the join causing cohesive failure. This technique, sometimes called "dry cracking" can be used where the introduction of water or heat would be problematic.

### Origin and manufacture

Animal glues are derived from **collagen** (*colla*-glue *gen*-creator in Greek) which is the protein present in skins, bones and connective tissue. Until fairly recently, the term "**glue**" meant only one thing, and that was animal glue. Terms such as "Flanders glue" and "Scotch glue," found in period literature refer to places where high quality glue was made. The bulk of animal glue is made from cattle hides and is called **hide glue**. Untanned skin- often tannery waste in the past- is the preferred raw material for glue making. Contrary to popular understanding, hoofs are not used because protein is difficult to extract from this highly organized keratin structure. Other starting stock such as bones (**bone glue**) fish skins (**fish glue**) and small-animal skins (**rabbit-skin glue**) are also used to produce distinctive adhesives. The material commonly called "**gelatin**" is an edible grade, made by filtering glue with activated charcoal in order to extract the color and objectionable smell.

Glue is made by using heat and water to **hydrolyze** the initial collagen, breaking and un-stranding the collagen micro-fibrils into smaller extractable units (**gelatin**). The **glue stock** is first prepared by washing. Fats and oils are removed by saponification (soap formation) in a lime solution, and acid solutions are used to neutralize the lime as well as to remove unwanted mucus-type proteins. The glue stock is then steeped in water at controlled temperatures and a series of broths are drained off as they reach the desired protein concentration. Because the collagen will continue to break down by hydrolysis as the temperature rises and the steeping time increases, a series of extracts of progressively lower molecular weight proteins can be cooked from the glue-stock at progressively higher temperatures until it is exhausted. The highest quality glue comes from the first draining and concentration of the glue-broth. In modern practice, the extracts are dehydrated by low temperature boiling in a vacuum so that they will not be further damaged by high heat. The concentrated broth is cooled until it gels and air-dried to the final product.

### Properties

Animal glues made from mammalian skins possess unique properties that have made them useful in a wide range of applications. A small amount of glue can tie up large quantities of water into a gel structure. The flexible and rubbery gels consist of expanded open networks of protein polymer chains which hold water in the structure by hydrogen bonding and other forces. This gel state is temperature dependent. Animal glue is applied hot and fully fluid in a water solution that can readily

wet a polar substrate such as wood. Setting occurs when the glue gels upon cooling into a rubbery **elastomeric** state. The gel then dehydrates and contracts until it is a hard and tough solid.

Alternately, gel suppressing chemicals such as urea can be added to animal glues so that they remain fluid at room temperature. **Liquid animal glues** of this sort, such as **Franklin's™**, have been used extensively in restoration work due to convenience, though they have been mostly superseded by fish glues.

### Types and Uses

The molecular weight or chain length of a particular glue largely accounts for its properties. High molecular weight glues have greater cohesive strength, take up more water at a given concentration, swell slowly in water, gel at a higher temperature, form more viscous solutions at fluid temperatures and have high **gel strengths** at given concentrations. The reverse applies to low molecular weight animal glues. Commonly used animal glues may be roughly ranked in order of increasing molecular weight as follows: bone glue, lower quality hide glue (often sold in pearl form), higher quality hide glue (often sold in ground or plaque form), "parchment size," and rabbit skin glue.

An understanding of molecular weight and its relation to glue properties can help the user make wise decisions regarding use.

- **Rabbit skin glue** is an excellent binder for gesso and bole in gilding, because it's high strength even at low concentrations forms a tougher gesso than would a low molecular weight glue. It also resists re-dissolving which is advantageous when laying the gold with aqueous "gilder's liquor" particularly when the solution is cool. Rabbit skin glue is a poor choice for most wood joinery however because rapid gelling decreases the time needed to assemble and clamp. Rabbit skin glue has the highest fat content and the lowest surface tension in comparison to other animal glues. Both of these properties make for low foaming, and fewer bubbles ("pin holes") in gesso and bole. Despite the aura of tradition that surrounds rabbit skin glue, it is never mentioned in 19<sup>th</sup> C. texts and is likely to be of recent origin.
- Many gilders have traditionally made fresh "**parchment size**" or dilute glue from parchment clippings. Since the glue stock is very clean, this size may correspond to a high molecular weight first batch in glue manufacture though this varies according to cooking time. It provides a colorless, high-strength binder for gesso and bole.
- **Bone glues** are used for gummed labels and stamps because they re-hydrate very rapidly. Bone glues have been mostly used in bonding of paper and similar materials where high strength is not necessary.
- **Fish glue.** Owing to the particular amino acid mix present in fish collagen, glues made from fish skins gel at temperatures below normal room temperature. This has great advantages in gluing complicated jobs because the open time is so long. Fish glues, such as the **High Tack Fish Glue™** sold by Lee Valley Tools, have seen increasing use in furniture conservation and related specialties. Despite gelling temperatures that in a mammalian glue would indicate short chain length and low strength, fish glues have molecular weights approaching the highest quality hide glues, with correspondingly high strength.

- **Isinglass** is a protein glue with a rich lore. It consists of gelatin boiled from the swim bladders of sturgeons (but other fish are sometimes substituted). Even though it is not generally classed as a fish glue, it behaves as one: High molecular weights are reported, but solutions of isinglass do not gel at room temperature. Gel formation is a highly complex chemical phenomenon in which a number of factors aside from molecular weight operate. Compared to gelatins and rabbit-skin glues, isinglass forms brittle dried films, shows the quickest response to changes in RH, and is prone to elongation and creep at high humidity. Light color and lack of gelling may well be advantageous in such conservation procedures as consolidating flaking paint, particularly where high strength is not required. Low gel temperatures and low viscosity allow for deep penetration into small apertures.

## Polysaccharides. (sugars, starches gums cellulotics)

### Starch

Starches are polymers made up of long chains of simple sugars (polysaccharides). Starches are present in plants in the form of complex granules with no adhesive characteristics. These granules are essentially food storage capsules. If starch granules from any plant source (rice, potato, wheat), are cooked they swell and burst, yielding a water-dispersed colloidal "paste" with good adhesive qualities. Starch adhesives are very polar and wet equally polar cellulosic structures such as paper and wood well. Cellulose itself is a polysaccharide. Starch paste has been used most extensively in paper and ethnographic conservation. In Japan however, where complex worked joints often do the main job of holding wooden structures together starches have been used for woodworking. Starch and plant gum mixtures have also been used for the adhesive backing of textiles. Starch and sugar "pastas" have been used for the traditional lining of easel paintings.

### Seaweed extracts

These polysaccharide type materials also called "**Japanese isinglas**" *funori* and *tengusa*, are extracted from marine seaweed species. Most familiar in the west as the **agar** used to culture microorganisms in the laboratory, they form weak adhesives that have been traditionally used for backing oriental scroll paintings. Since they show very low optical saturation, they have also been used in conservation for consolidating matte paint.

### Dextrin

Dextrins are derived from starches and are also polysaccharides. They are made by hydrolyzing starches to create shorter chain lengths, then re-polymerizing the low molecular weight fragments. Extensively used in bonding paper due to quick tack time, they have seen little use in woodworking or other applications requiring high strength. The viscous, amber colored "**mucilage**" type adhesives sold in office supply stores are dextrin based.

### Gums

Plant gums that are completely or partially soluble in water are also polysaccharides. There are a large number of plant sources. One of the most common is gum Arabic from members of the *Acacia* genus. **Gum Arabic** is the usual binder in water-color paints, and was also used extensively as a binder in restoration fills. Various members of the *Prunus* genus (plums, cherries, peaches) furnished locally available gums to European and American artisans. **Cherry gum**, for example was used in various folk painting traditions such as the *fraktur* of the "Pennsylvania Dutch."



Gums are relatively weak adhesives, but since they are completely non-toxic, they have been used on labels and stamps, as well as in the older "mouth glues" and "wafer"-saliva activated adhesives used for light-duty domestic sticking jobs in the nineteenth century and earlier.

Bond strength	relatively weak and unlikely to cause substrate failure
Open time	long to moderate depending on ambient humidity.
Health hazards	none
Color	white (starches) light amber (plant gums)
Optical saturation	slight but depends on concentration
Machinability	excellent
Chemical stability	excellent (starches) fair to good (plant gums)
water resistance	poor (easily reversible)

### Cellulose derivatives

The hydroxyl groups normally attached to the cyclic cellulose molecule can be substituted by a variety of other functional groups. The **cellulose ethers** have the OH groups partly replaced by ethyl, methyl, hydroxyethyl, carboxymethyl and hydroxypropyl groups. Cellulose ethers have been used primarily in textile, paper, and ethnographic conservation. They are relatively weak adhesives, and so are often used to modify the properties of other adhesives such as starch paste. The cellulose ethers are also used as thickening/gelling agents to limit the penetration of more fluid adhesives. Most are water soluble, but ethyl cellulose and hydroxypropyl cellulose (**Klucel™**) are also soluble in polar organic solvents. They have been used in solvent-release resin adhesive formulations primarily as thickening agents. Ethyl hydroxyethyl cellulose for instance, (EHEC) has been used as a gelling agent in adhesive formulations for backing leather so as to limit penetration. Sodium carboxymethyl cellulose (**CMC**), a stronger adhesive, is sometimes used by itself as a backing adhesive in paper conservation, while ethyl cellulose is often mixed with starch paste.

Bond strength	the weakest of all the carbohydrate adhesives
Health hazards	none
color	white, hydroxypropyl is more inclined to yellow than the others
Optical saturation	very low
Chemical stability	best for methyl cellulose
Water resistance	poor, better for hydroxypropyl

### Waxes

Waxes consist primarily of long-chain hydrocarbons that have a "waxy" feel and appearance. By far the oldest and most common in practice is **beeswax**, which is synthesized by bees to form storage cells. During the nineteenth century, a large number of other waxes besides beeswax came into Commerce. These include waxes from plants (**carnauba**, **candellila**, **esparto**, **ouricuri**), insects (**shellac wax**, **Chinese insect wax**), whales (**spermaceti**), and sheep wool (**lanolin**). Waxes also have geological origins. There are natural deposits of mineral wax called ozokerite in a few parts of the world (Utah and Galicia), and "**montan wax**" began to be extracted on an industrial scale from lignite in Germany around 1910. Waxes extracted from crude oil became available after the beginning of commercial oil drilling in 1859. The low molecular-weight waxes of larger crystalline size are referred to as **paraffin** in the U.S. and the higher molecular-weight waxes with smaller crystalline size are referred to as amorphous or **microcrystalline** waxes.

Waxes are more commonly encountered as coatings and binders than as adhesives (except in the ethnographic context). Wax and wax-resin mixtures have of course been used extensively in painting conservation as lining adhesives, and have been used to consolidate biodeteriorated wood, or to secure flaking polychrome layers to wood substrates. Waxes can be very useful as fill materials in conservation: They are available in a wide range of hardness, are easily colored and easy to apply and level.

Bond strength	generally poor
Health affects	potential fire hazard during melting
Color	white to brown depending on type (high degree of optical saturation when applied hot)
chemical stability	excellent for synthetic waxes and good for organic waxes
water resistance	excellent

## NATURAL RESINS

Natural resins are the naturally occurring, water-insoluble hard organics. They come from a variety of plant and animal sources: Resins from trees derive from angiosperms and gymnosperms, both living and extinct (amber and some varieties of **copal**). They include **damar**, **mastic**, **sandarac**, **rosin** and **copal resins** (the so-called "fossil" resins). Also from trees are the various oleo-resins with volatile components called "**turpentine**" and "**balsams**" (**Strasbourg turpentine**, **Venice turpentine**, **Bordeaux turpentine** and **Canada balsam**). **Shellac** is exuded by scale insects. A component of Mexican lacquer is also extracted from scale insects.

Natural resins generally consist of repeat units of isoprene and are classified as monoterpenes (2 isoprene units- includes oil of turpentine, lavender oil) sesquiterpenes (3 units-includes shellac) diterpenes (4 units- includes rosin, sandarac, copals) triterpenes (6 units- includes mastic, dammar) and long chain polyterpenes (n units-includes natural rubber). As with most natural materials, detailed basic books on occurrence, trade, nomenclature and use date from the end of the last century and the beginning of this one.

Natural resins dissolved in oils were generally called "varnish," and show up in fill recipes fairly frequently. Resins dissolved in solvent are more usual as adhesives. Resins may also be used in fill and adhesive recipes as relatively minor additives meant to modify the properties of the bulk adhesive. When added to animal glue recipes for example, as in gilder's composition and "diamond cement" (see isinglass), natural resins and varnishes increase water resistance and help to mitigate shrinkage. In the thermoplastic "mastics," natural resins are the major constituents. A typical historic example is the filling mastic for flaws in marble consisting of "yellow wax, rosin, burgundy pitch and a little sulfur and plaster" colored to match with suitable pigments (Spon's 1893).

A few of the natural resins, should be described a little more fully due to common and widespread use in a variety of cultures.

- **Rosin (colophony):** Rosin is the solid component of raw pine resin after the volatile "spirits of turpentine" have been distilled off. An alternate name for rosin is colophony (from the Greek words for glue and sound) which refers to its use on bows for stringed instruments. It was a cheap natural resin during the past few hundred years, and was used extensively for low-quality varnishes, for adhesives and for filling materials. Cutler's cement for filling the hollow handles of silver knives and holding the blades in place was commonly made from colophony, sulfur and any convenient bulking agent.

- **Pitch and tar:** These are inexact terms which may refer to a variety of substances including various naturally-occurring minerals (also called **bitumen** and **asphalt**), to the products of the pyrolysis or destructive distillation of both hardwoods and softwoods, or to the less volatile compounds present in fossil coal and crude oil. All of these materials are dark-brown to black in color, sticky, and cheap in comparison to other natural resins, even including rosin. They have all been used since antiquity (with the exception of refined petroleum tar) for caulking seams, hafting weapons, water-proofing textiles and cordage (sailors were called "jack tars"), and generally filling gaps and sticking things together. Bitumen fills have been found as ancient repairs to ceramics. All of these materials can be and have been mixed with a variety of bulking agents to form filling compounds.
- **Shellac:** Shellac is the resin exuded by the scale insects, primarily *Kerria lacca* (Kerr). It has been used as a coating, adhesive and binder in various bulked compositions, including those from which photograph cases and phonograph records were made. Dissolved in alcohol, it has been a popular adhesive for adhering ceramics, stone, and other materials, and sticks of shellac, sometimes softened by the addition of wax or some other softer resin, were used as a thermoplastic fill material. Solid shellac sticks called "**burn in sticks**" have been extensively employed by furniture restorers to fill small damages. Shellac was a popular adhesive for the repair of antiquities in particular. One method of use was to apply shellac in alcohol to the break edges, then ignite the alcohol so as to burn off the solvent and heat the shellac. The parts were then immediately put together. Bonding is virtually instantaneous and so the assembly is rapid. Large-scale export of shellac resin from India increased rapidly after 1870 indicating that shellac as a common and cheap "plastic" (as opposed to an adhesive) may well post-date the 1870s.

## SYNTHETIC RESINS

Man made resins or "plastics" have been and are currently used both as adhesives and as coatings. Virtually all of the tremendous variety now available have had some use, however brief, in adhesives. Synthetic resins are used as adhesives in two distinct forms; un-modified straight-chain resins dissolved in solvents, and extensively modified emulsions which are initially dispersed in water.

## SOLUTION ADHESIVES

Both natural and synthetic resins dissolved in various solvents have seen extensive use as coatings, but have also been used by conservators as consolidants for degraded wood and poorly bound or adhered coatings. The use of resin consolidants is a complex topic better addressed elsewhere. Many solvent-release, solution-type adhesives are used in restoration and conservation.

### Cellulose nitrate and cellulose acetate

Cellulose nitrate resins, developed in the mid-nineteenth century were the first synthetic polymers, and were put into use as adhesives at an early date. Cellulose nitrate dissolved in solvent was termed "**collodion**" and as such was sometimes used as a binder. By itself, collodion was excessively brittle and so was often plasticized with other materials. One "elastic collodion" cement was made with "gun cotton" (cellulose nitrate) dissolved in ether and alcohol with the addition of Venice turpentine and castor oil as plasticizers (Youman 1876). **Celluloid** was plasticized with camphor, and this too was sometimes dissolved in solvent to make adhesives. A series of references beginning in 1899 to cellulose nitrate used in conservation are given in Horie (1987).

**Cellulose acetate**, first synthesized in 1894, has also been used for stiffening textiles used on aircraft and model aircraft ("dope"). Solvent type adhesives based on cellulose-nitrate, cellulose-acetate or both, (**H.M.G., Duco, UHU™** etc.) have seen extensive use by hobbyists as well as in conservation. The long term stability of cellulose-nitrate has been debated in the literature, with some authorities believing that it offers acceptable permanence on some substrates, and others condemning it as chemically unstable.

### **Rubber and gutta-percha**

**Natural rubber** and **gutta-percha** are both derived from hydro-colloid plant latexes. They have identical chemical makeup (poly-isoprene) but are stereo-isomers (right and left handed molecules) of each other, with rubber being cis, and gutta-percha and a related natural latex called **balata** being trans. Natural rubber, also called "India rubber" or "caoutchouc," is elastic and rubbery while gutta-percha is only soft while warm, becoming rigid and flexible at room temperature. Both natural rubber and gutta percha were used alone and in mixtures with other materials as adhesives. A Compound called "Davy's Universal Cement" was composed of equal parts of pitch and gutta-percha (Brannt 1886). In 1922, rubber was synthesized by Hermann Staudiger. The familiar "**rubber cement**" of office supply stores as well as most **contact adhesives** are based on synthetic rubber. Natural and synthetic rubbers as well as gutta-percha are prone to degradation through oxidation and de-polymerization. Rubber first becomes sticky as it deteriorates, then eventually becomes hard and crumbly, while gutta percha degrades by falling into chunks, and eventually powder.

### **Acrylic resin**

Acrylic resins, particularly the Acryloid/Paraloid series produced by Rohm and Haas have seen extensive use as conservation adhesives. **Acryloid B72™** in particular, a copolymer of ethyl acrylate and methyl methacrylate is used in the bonding of almost every category of material, and has been extensively studied in regards to permanence and stability. B72 was first proposed and studied as a varnish resin by Robert Feller in the 1960s. Steven Koob popularized its use as conservation adhesive beginning in the 1970s.

#### **B72 adhesive**

Many conservators use 50% B-72 in acetone for the adhering of low-fired ceramics, ivory and similar organics, and on a variety of other substrates. B72 appears to offer excellent stability, reversibility, hardness and strength.

Some conservators add fumed silica to increase the viscosity, strength, and resistance to creep.

The recipe of Stephen Koob for this adhesive is:

- 100g. acetone
- 1 teaspoon fumed silica
- 50g. B72

-45g. acetone (yielding a final 105g. of adhesive)

The B72 must be dissolved in more solvent than will be retained in the final adhesive. The resin beads are placed in a net bag suspended in the top portion of the solvent and left to dissolve. The excess solvent is evaporated off until the final weight is reached, and the adhesive is packed in aluminum tubes for use.

Cast films of B72 as well as B72 coated onto paper have been used extensively as heat activated (thermoplastic) adhesives, particularly in ethnographic and textile conservation.

Where pots are going to be exhibited and stored in a hot climate, **B48N** is sometimes used. This has a  $T_g$  of  $50^\circ\text{C}$  -somewhat higher than B72. Porcelains, and ceramics with white glazes will often show a dark line in the crack when repaired with a clear adhesive, and this can be mitigated by adding a small amount of titanium dioxide to the adhesive.

### **Polyvinyl acetate resins.**

**PVA** resins (also abbreviated as PVAc), first developed in the 1940s have been used extensively as adhesives and coatings. The resins produced by Union Carbide such as low molecular weight PVA AYAC and higher molecular weight AYAB, AYAA and AYAT (in order of increasing molecular weight), have been particularly popular in conservation treatments. Thermoplastic adhesive "hot melts" used by conservators often employ AYAC due to its low glass-transition temperature. Another popular clear solvent release cement used by many archaeologists is **UHU™**, based on PVA resin. PVA resins are the starting materials for PVA "emulsion" adhesives.

### **Polyvinyl alcohol resins**

Resins sometimes abbreviated as **PVOH**, are made from PVA resins by selectively replacing OH groups with alcohol groups. This makes the resins more-or-less water soluble in addition to being soluble in polar solvents. As replacements for animal glue size they have seen use in gilding conservation. They have also been used for backing and adhering textiles. They may crosslink under acidic conditions (not an issue in calcium based fill materials).

### **Aquasol™ resins**

Poly(2-Ethyl-2-Oxazoline) was first proposed for conservation use in 1994 by Wolbers, McGinn and Duerbeck. Since then it has been taken up by a number of conservators for consolidation and binding of fill materials. Initial studies indicated good chemical stability (with a tendency to de-polymerize rather than cross-linking on ageing). Three molecular weight grades are available- 50, 100 and 500 in increasing molecular weight. The resin is a weak adhesive, and the authors recommended against use in high load applications. A key advantage of the resin is wide solubility in both water and organic solvents. It has been used as a replacement for gelatin in gilding sizes and fills, though it makes a somewhat sticky fill that is difficult to level.

## **RESIN EMULSIONS**

"**Emulsions**" as the term is popularly used in adhesives terminology are solid resin particles of colloidal size (0.001-1 micrometers in diameter) dispersed in water. Technically, they are not emulsions, which are mutually insoluble liquids dispersed one into the other (milk for example). The accurate term is "**dispersion**" which describes a solid of colloidal size dispersed in a liquid. Technically, they may also be described as "**latexes**." Various acrylic and vinyl polymers can be manufactured in emulsion form and the properties are various. Although initially dispersed in water, once emulsions dry, they are no longer water-soluble. Although they have been and still are widely used on porous substrates, they must be considered irreversible, as they have limited solubility in organic solvents also, tending to swell but not dissolve.

### **PVA emulsions**

Polyvinyl acetate (P.V.A.) emulsions were the first of these to be used as wood adhesives, and are familiar to most people as "**white glues**." (**Elmer's Glue™** for instance.) They bond well to wood

and a variety of substrates, are easy to use and clean up, and are readily available. This combination of factors has made them the most commonly used non-industrial woodworking adhesives and the choice of do-it-yourselfers everywhere. While emulsions are initially dispersible in water, they dry to tough films that are only swellable in water. The dried films are softer and less brittle than a solution adhesive prepared from the same resin. Owing to their high molecular weights they are also not completely resolvable in organic solvents as are the parent resins. **PVA emulsions** have been used extensively because they are strong and flexible on leather and textiles. Reversibility is also a problem, and some PVA emulsions are unacceptably acidic and may be prone to generate acetic acid. Some of the PVA emulsions widely reported in the conservation literature include **Jade 403**, **Mowolith DMC-2** and **Elvace™**. Mowolith in particular has been used extensively in the adhesive backing of textiles.

### Acrylic emulsions

The acrylic type resins already described may also be manufactured in emulsion form. Popularly familiar as "acrylic paints," they are also used in conservation as consolidants, adhesives and binders for filling materials. Acrylic resins have better chemical stability than the PVA emulsions, particularly in solution. The **Rhoplex™** series of Rohm and Haas have been commonly reported in the conservation literature. The harder types, such as **AC33** are often used in dried films as thermoplastic adhesives, while the softer types, such as **N580**, see use as contact adhesives.

### "Yellow glues"

Emulsion glues having a yellow color (**Carpenter's Wood Glue™** for example) consist principally of polyvinyl-acetate and ethylene vinylacetate co-polymers. They are sometimes referred to as "aliphatic" glues, but since this term applies to a variety of other adhesives it is so inexact as to be useless. They are generally more viscous than white glues and don't squeeze out as much under clamping pressure. They set very quickly (short open time) are easier to sand than white glues and more creep resistant. They are the most common adhesives used in new furniture construction and a variety of other applications. Yellow glues have relatively short shelf lives of six months to a year.

Bond strength	excellent
Hardness	variable depending on resin and formulation, good machinability
gap filling ability	moderately good. Thicker glue lines will creep more than thin ones.
open time	variable depending on product
health affects	very low toxicity. non-flammable
chemical stability	good to excellent
water resistance	good in regards to high RH, poor in liquid water

### THERMOSETTING ADHESIVES

These adhesives harden by irreversible exothermic chemical reaction. Many natural materials including the "drying oils" (linseed, nut oils) will polymerize to form relatively cross-linked structures by oxidation reactions. A variety of thermosetting resins became available as a result of advances in polymer chemistry. **Phenol-formaldehyde** (phenolic) adhesives were produced in film form for hot pressing soon after 1910, and in liquid form in 1935. **Urea-formaldehyde** adhesives were introduced around 1937, epoxies during the 1940s and **resorcinol-formaldehyde** in 1943. These are the primary adhesives used in industrial wood bonding applications such as plywood and particle-board manufacture, but they have also been available for small shop use where a water proof adhesive is required. All of these adhesives form chemically resistant cross-linked polymers and should be considered irreversible when used on porous substrates (but then most things are).

Modern thermosetting adhesives generally consist of two chemical components which react to form highly crosslinked polymers. The reaction causes relatively little shrinkage, so these catalyzed resins have fair to excellent gap-filling capabilities. The final polymers are generally quite chemically inert making these adhesives water and solvent resistant. Their rigid cross-linked nature gives them high hardness and internal strength, high resistance to creep and excellent machinability.

### **Oriental lacquer**

In use since the Neolithic period (circa 4000 BC) in Japan, China and Southeast Asia, oriental lacquer is one of the oldest adhesive/coating materials. The Japanese term "*urushi*" is now frequently preferred in conservation in order to avoid confusion with Western resin-based lacquers. Urushi is the latex, or colloidal ("hydro-colloid") sap of a small tree or shrub, the most important of which is: Family- *Anacardiaceae*, Genus- *Rhus*, Species- *verniciflua* (sometimes *verniciifera*). *Rhus verniciflua* is the only species used for lacquering in northern China and Japan. A few other *Anacardiaceae* species will yield latex that can be used for lacquering: *Melanorrhoea usitata* yields a lacquer and is used in South-east Asia and Burma. *Rhus succedanea* is used in Taiwan and Viet Nam. Cashew-nut oil (*Anacardium occidentale*) will also crosslink to form a hard film, and is used for lacquering in India. Lacquer cures in a humid environment by internally catalyzed, oxidative crosslinking. It is hard and tough, and extremely resistant to water and organic solvents, though is damaged by light. It will cure in thin layers on a variety of substrates and has been used extensively for restoration mends and fills on material repaired in the East. Uncured *urushi* causes severe allergic dermatitis and other toxic affects in many people, and this, plus availability has always limited its use in the West.

### **White lead putty**

Adhesives based on linseed oil and lead compounds, particularly white lead (lead carbonate) can be found in some of the earliest technical treatises. Lead compounds catalyze the "drying" of linseed and other "drying oils," resulting in final products that are hard but also flexible and tough, with excellent gap-filling capabilities (as one primary use as window-glazing putty attested). The disadvantages were the unsightly mechanical fasteners such as staples and rivets that were necessary to hold ceramic objects together while the putty was drying, and the seeping-out of the linseed oil into adjacent areas of porous objects, causing staining. Most conservators who work on ceramics, stone and other hard materials have encountered repairs made with white-lead putty and staples, a method or repair that is very old.

### **Glycerin/litharge cement**

Similar to white-lead putty, this cement was a mixture of **litharge** (lead monoxide) and glycerin which was used for cementing stone and metal, and for use as a "luting" (sealing cement) that would resist a wide range of chemicals. The mixture hardened within minutes, probably due to polymerization of the glycerin and the formation of metallic soaps. **Glycerin** (also called "sweet oil") was a by-product of the manufacture of soap and was isolated by Scheele in 1779

### **Blood, milk and egg protein adhesives**

These adhesives are also can be regarded as thermosetting because they harden by irreversible chemical reaction. **Blood glues** were extensively used in plywood manufacture during the middle of the last century but are little used today. Egg **albumin** was used in adhesives for gilding, and in applications where colored adhesives were unacceptable. So called "**Chinese cement**" was an item

of commerce in the nineteenth century and consisted of egg white, lime, and powdered glass. **Casein**, from milk was the proteinaceous adhesive that saw the most use (aside from animal glues).

### Casein

Casein glues are one of the oldest thermosetting adhesives. "**Cheese glues**" based on the milk protein casein and calcium hydroxide (lime) are described in many early treatises such as those by Theophilus and Cennini. By the beginning of the 20th Century prepared casein glues that could be mixed with water to form an adhesive or paint binder were available. Prepared casein glues consist of the dry sodium salts of milk protein from skim milk, combined with calcium hydroxide. When water is added the soluble sodium caseinate gradually converts to an insoluble calcium caseinate which hardens more fully as the water evaporates. Casein glues were the most water-resistant glues available until the introduction of other thermosetting adhesives in the 1930s and 40s but they are not waterproof. Casein glues were a popular adhesive before emulsions were available and may be found in small shop construction and do-it-yourself repairs. Casein glues also bond very well to oily and resinous woods like teak, yew and resinous pine due to their high alkalinity.

bond strength	best on soft woods
hardness	hard and creep resistant, good machinability
open time	intermediate between hide glues and other thermosets
health hazards	low toxicity, strongly alkaline
color	light tan, alkalinity can cause staining of some woods (oak, maple)
water resistance	good but not waterproof
reversibility	poor, insoluble in organic solvents only re-soluble in strongly alkaline solutions

### Urea-formaldehyde

This polymer forms from the reaction of urea and formaldehyde. These adhesives are cheaper than phenolics and epoxies but are less water resistant, liberate formaldehyde during and after curing, and cure poorly under about 70° F. These adhesives are of most concern to the conservator because of the danger to some categories of collections posed by formaldehyde in the environment. Urea formaldehyde adhesives have been used extensively for bonding plywood and various forms of fiber and chip-board.

bond strength	excellent, especially on woods with high moisture content
hardness	hard and creep resistant, good machinability
gap filling	poor
open time	highly temperature dependent, may be rapidly cured with heat
health hazards	highly toxic when uncured, long term release of formaldehyde from cured resin
color	light brown
water resistance	intermediate between casein and phenolics

### Phenol-formaldehyde

bond strength	excellent, requires high curing temperatures (170-300° F)
hardness	hard and creep resistant, good machinability
gap filling	good
open time	remains fluid until catalyzed by heat
health hazards	toxic when uncured, relatively low release of formaldehyde after curing
color	brown



water resistance	waterproof, used for exterior and marine grade plywood
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### Resorcinol-formaldehyde

bond strength	excellent, requires a curing temperature over 70 <sup>o</sup> F.
hardness	hard, creep resistant, good machinability
gap filling	good
open time	approximately 1 hour after mixing but highly temperature dependent
health hazards	toxic when uncured, releases formaldehyde while curing but relatively low rate of release after curing
color	dark reddish brown
water resistance	highly waterproof

### Epoxies

Epoxies are a chemically and physically diverse family of thermosetting compounds which have in common the presence of the "epoxide" functional group, a three-membered ring composed of two carbon atoms and one oxygen atom. Adhesives and casting resins normally consist of two components; a resin and a hardener which when mixed together react to form a rigid cross-linked polymer. Epoxy resins are more expensive than the previously discussed thermosetting resins, but they have important advantages. A great number of epoxy resins and adhesives are on the market permitting a great deal of choice in properties and potential applications. Epoxies are solvent-free systems which shrink very little on curing and do not off-gas toxic or reactive compounds once cured. This makes them good gap fillers which can be used without any clamping pressure. They are quite chemically inert after curing, and while they are prone to darken with age they do not lose adhesive or cohesive strength to any significant degree as a result of aging. Epoxies are highly polar adhesives which bond very well to a variety of substrates including wood, metal, glass and stone, but conversely, they do not bond well to non-polar oily and resinous materials. A wide range of resins and hardeners are used in epoxy formulations but a few generalizations can be made: quick-setting epoxies are more viscous, initially darker in color and more prone to darken with age, and build higher temperatures in curing because there is less time for heat-of-reaction to dissipate. The reverse is true of slower setting epoxies which are available in clear ("water white") highly fluid grades. The low-viscosity epoxies **HXTL**, **Fynbond**, and **Epotek 301-2™** are used extensively for bonding and filling clear glass. Epoxy resins bulked with phenolic resin microballoons such as **Araldite 1253™** (Ciba Geigy) are used extensively in furniture conservation because of the similar density and color to wood. Such materials are commonly called "**carvable epoxies**."

bond strength	excellent adhesive and cohesive strength
hardness	hard and brittle to rubbery depending on formulation, creep very low even for soft varieties
open time	highly variable depending on formulation
health hazards	uncured resins and hardeners are toxic, cured films are not
color	white to dark amber. all will darken with age but this affect is very slight for some varieties. Optical saturation of substrates is high
water resistance	epoxies are waterproof
reversibility	irreversible on porous substrates, good on hard and non-porous substrates such as porcelain and glass. (generally requires use of chlorinated solvents)

### Polyesters

Polyester resins, available since 1946 are condensation polymers of variable structure. They may be thermoplastic linear chains (**Melinex**, **Mylar™**), unsaturated (UP) thermosetting polymers (such as are used in glass reinforced resin (GRP) popularly known as "fiberglass," or as the class of coatings known as **alkyds**). As adhesives, polyesters have been used by stone conservators because of good gap-filling when bulked, fairly rapid cure, and good strength in high-load situations. The stone adhesives manufactured by **Tiranti** (UK) and **Akemi** (Germany) are examples. Polyesters were extensively used as filling materials, but since they yellow more than epoxies, shrink more, and are more objectionable to work with, epoxy resins have largely taken over in conservation applications.

bond strength	good on semi-porous substrates such as most stone
hardness	hard and brittle, tougher when bulked
open time	dependent on temperature and catalyst
Health hazards	Generally catalyzed with styrene or methyl-ethyl ketone (MEK) both are toxic. MEK has caused blindness.
color	clear
water resistance	waterproof
chemical stability	prone to photo-oxidation, yellows with time.
reversibility	as a cross-linked polymer, similar to epoxy.

### Polyurethanes

Polyurethane resins are built from units of polyesters or polyethers. First developed in 1943, they are now extremely variable in properties, and may be thermoplastic or thermosetting. In addition to the well-known finishes, they are increasingly important as molding and casting rubbers. Polyurethane adhesives are recently available on the market (**Titebond Polyurethane**, **Gorilla Glue™**) and are being used increasingly by woodworkers and do-it-yourself repairers.

bond strength	excellent, requires moisture to cure (wood must be damp)
hardness	hard and creep-resistant.
open time	long (fifteen to twenty minutes)
health hazards	may provoke allergic reactions, stains and bonds to skin
Water resistance	excellent
chemical stability	degraded primarily photo-oxidation, so not a problem with adhesives
reversibility	as a cross-linked resin, similar to epoxies

### Cyanoacrylates

These adhesives are popularly called "**superglues**" after an early trade name. The first of these adhesives (**Eastman 910™**) was introduced in 1958 and available brands and physical properties have increased since. Unlike the thermosetting resins described so far, no separate hardener is required for curing. The fluid adhesive polymerizes very rapidly in contact with a weak base, or from the hydroxyl groups present in the thin film of water that is present or on most substrates. Cyanoacrylates have the chief advantage of very rapid cure which eliminates the need for any clamping but hand pressure. They will stick to a wide variety of substrates (especially skin) and so are useful in bonding dissimilar materials. Initially, cyanoacrylates had virtually no gap-filling abilities and would not cure in any but very thin glue lines. New varieties are available which have good gap-filling characteristics, and they have found favor with woodworkers for quick repairs of small cracks and losses. Cyanoacrylates may have poor long term chemical stability, but no thorough conservation studies have so far been done. Adhesive joins may become weaker and prone to failure as they age. These fears have limited their use in conservation. They can be extremely

useful in quick assembly and in small quantities can function as clamps in difficult circumstances but should be considered temporary unless backed up by another adhesive or fastener system.

bond strength	excellent but may decrease with time. relatively poor peel strength
hardness	hard, machinable, low creep
open time	measured in seconds, shorter on alkaline substrates, longer on acidic substrates (wood)
health hazards	bonds to skin (used medically for closing wounds)
color	clear
chemical stability	short shelf life, possibly poor long term stability when cured
reversibility	poor on porous substrates, good on non-porous substrates (swellable but not soluble in acetone)

### Silicone rubbers

Organic polymers based primarily on silicon rather than carbon have seen various uses in conservation. Often called **RTVs** (room temperature vulcanizing), These materials may be separately catalyzed, or they may "dry" simply on exposure to air (some types release acetic acid in this process, though some, such as **Dow Corning 737™** do not). As highly-crosslinked elastomeric adhesives, they are very difficult to reverse, particularly on silicate substrates, but in situations where flexibility is required, such as in the repair of architectural glass in situ, they are considered acceptable. Silicone rubbers have been used more extensively by conservators as mold-making materials.

### UV curing resins

These adhesives are generally acrylic, polyester and epoxy resins that cure rapidly by the application of ultra-violet light. Some of them, such as the acrylic resins of **Norland Optical™** have useful properties for the repair of glass, and have been shown to be quite stable in regards to yellowing. They are also useful for the replication of thick glazes in ceramics conservation since they may be cured before the resin layer has a chance to run.

### HOT MELT ADHESIVES

These adhesives are thermoplastics which are capable of wetting and adhering to a surface when melted. They achieve their bond strengths as they cool. A wide variety of hot melts are used in industry but home and small shop use is generally confined to the commercially available sticks that are melted and applied with a **hot glue "gun"**. These sticks are available in a variety of melting ranges which govern open time, and are generally composed of **polyamide** type resins similar to **Nylon™**. Polyamides melt at reasonably low temperatures, are quite polar (compared to polyethylenes for example) and wet substrates well. They are very useful in quick construction of jigs, fixtures and shipping crates. Powdered polyamide adhesives have been used to repair tears in painting conservation. Used as **welding powders**, they are fused by locally applied heat. An example is **Lascaux Polyamide 5060™**.

The sticks made by 3M called **Jet-melt 3792-TC™** are the ones that are used mostly for object housing because they have been found to be inert (regarding off-gassing) and relatively stable.

#### Hot melt adhesives (polyamide glue-gun sticks):

bond strength	poor to fair
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hardness	generally soft and prone to creep, poor machinability
open time	variable according to grade but generally very short
health hazards	irritating fumes given off when too hot
color	white to amber
chemical stability	good (some types pass Oddy test)
water resistance	waterproof

Hot melt adhesives have also been used in sheet or film form for laminating. The adhesive known as **BEVA™** which is based on poly (ethylene/vinyl acetate) and contains other additives has been used extensively in conservation for various applications, both in solvent solutions and as a dried film.

### CONTACT CEMENTS

These adhesives can be characterized as permanently sticky or tacky coatings applied to adherend surfaces, which stick firmly to themselves as soon as they are brought into close contact. A variety of polymers have been used in this way, but the commercial contact cements sold for veneering and laminating usually consist of neoprene, a synthetic rubber, in solvent solution. Most rubbers including neoprene have very poor long-term chemical stability, so while rubber-based contact cements are widely used in new veneering and laminating they should not be used on historic artifacts.

Contact cements may also be made from resin emulsions. These are available commercially as water based contact cements, but may also be made by the conservator from appropriate grades of acrylic emulsion such as those available in the **Lascaux** or **Rhoplex™** lines. These adhesives have much greater chemical stability, are non-toxic and have various applications from gilding to mount-making. **Rhoplex N-580** for example, remains tacky and is easily used as a contact adhesive. Putting felt on the bottom of mounts is one use for N-580. An effective adhesive for gilding (in imitation of oil-gilding) consists of a mixture of N-580 and **AC 33 (50/50)**.

Contact cements of any type have fairly low bond strengths, are soft and prone to creep.

### INORGANIC ADHESIVES

Most of the adhesives described thus far are carbon-based organic materials. Many other inorganic substances have also been used as adhesives, particular in outdoor, and high temperature application where organic materials do not perform well.

#### Plaster

There are two classes of calcium compounds known as "plaster"; "lime plaster" and calcium sulfate or "gypsum plaster." Both have been in use since antiquity. Lime plaster is made by heating calcium carbonate ( $\text{CaCO}_3$ ) to produce calcium oxide (CO "quicklime") and mixing it with water (slaking) to produce calcium hydroxide ( $\text{CaOH}$  "lime putty"). The lime putty is mixed with various aggregates and binders to create mortars and plasters, and hardens by the evaporation of water, and gradual subsequent re-conversion to calcium carbonate over a period of years. Gypsum plaster (also called "**plaster of Paris**") is made by heating calcium sulfate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  "gypsum") to remove part of the chemically bound water, creating a hemihydrate ( $\text{CaSO}_4$

- $\frac{1}{2}\text{H}_2\text{O}$ ). When mixed with water it re-converts to hydrated calcium sulfate, setting in the process.

Unlike lime plaster, gypsum plaster sets without shrinking. In fact, gypsum plaster expands upon setting in most instances, making it virtually unique among materials available to restorers of the past. Gypsum plasters require a substantial quantity of the material in order for re-hydration to take place. Therefore, they were rarely used as adhesives, though extensively for fills. Lime plasters have been preferred for use in building restoration for many centuries, but their alkalinity and shrinkage upon drying would generally have made them undesirable for use on smaller objects meant for indoor use and display.

### Portland Cement

Although the term "Portland Cement" dates to the patent of Aspdin in 1824, it was the natural successor of the so called "hydraulic mortars" or "Pozzolanic mortars" that had been in use since the Roman period. All of these materials set by rapid hydration and crystallization and do not need access to air to harden. Modern Portland cement is made by heating a mixture of calcium carbonate and alumino-silicates (usually clay) to partial vitrification. The resulting "clinker" is ground to a powder. When mixed with water it sets firmly, hardens further by drying, and the lime component re-converts to calcium carbonate over a period of years due to the agency of carbon dioxide. Since they are resistant to water, Portland cement based materials have been used for joining stone and ceramic in the outdoor environment.

### Water Glass

If glass is made with an intentional excess of alkaline fluxes (usually sodium and potassium) it can be dissolved in water (generally by cooking under pressure). The first unequivocal notice of it occurred in about 1640 but it may have been known earlier. Water glass was extensively used as an adhesive ("mineral glue") and as a binder for fills on a wide variety of substrates. It was alkaline enough to denature casein in the same way that lime does. Despite the popularity of water glass it had problems, including the tendency to absorb water and fall apart, as well as causing corrosion on glass. It was difficult to work with owing to the speed of hardening, and was difficult to remove from surfaces when the joining had not been successful. Water glass based paints are still marketed for outdoor mural painting.

### Metal oxides

In 1853, a chemist named Sorel discovered that if zinc chloride was mixed with zinc oxide and water, it set rapidly into a very hard cement. This was described in subsequent technical treatises as **Sorel's Cement**. A more recent compilation of recipes gives Sorel's cement as zinc white and fine sand combined with zinc chloride solution. It seems likely that hardening of such mixtures is the result of the formation of zinc oxychlorides, silicates and borates. It was later discovered that magnesium chloride and magnesium oxide had the same properties, and this material was called **Sorel's Magnesium Cement**. These materials were probably too expensive to have been used on a large scale, but became important as refractory cements ("lutes") and for small scale applications including dental filling.

Adhesives and filling compounds based on iron powder and usually included a chloride-containing rusting-agent such as acid, urine, or sal ammoniac (ammonium chloride) began to be used in the nineteenth century and were commercially available until recently (**Smooth-on Iron Cement™**). One nineteenth century source treats such rust cements or "cast iron cements" as being commonplace, and describes them as consisting of iron powder, sal ammoniac and flowers

of sulfur, which when mixed together and dampened begin to heat and set into a hard mass. Another compound consisted of iron filings, calcium sulfate and calcium phosphate, and it was stated that this would not rust, probably due to the formation of stable iron-phosphates.