ADHESIVES '90

CONFERENCE PAPERS

October 1-4, 1990
Schaumburg, Illinois

Sponsored by the Society of Manufacturing Engineers
One SME Drive, P.O. Box 930, Dearborn, MI 48121

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PREFACE

As we enter this new decade, the adhesive and sealant industry can look back on a period of phenomenal growth. Much of this success can be attributed to our attention to new market potentials and our constant focus on research and development.

Thanks to substantial investments in R & D, few industries in the manufacturing arena are as poised for future success as is our own. Also, thanks to continuous technological advancement, it has never been more important, even *imperative* for the manufacturing engineer to keep abreast of the ever increasing number of current uses and potential applications for our products, processes and equipment. From aerospace to baby diapers, from plywood to mini vans, the industry faces unique challenges and incredible opportunities in a multitude of markets.

SME's "ADHESIVES '90" again presents a vitally important forum for the exchange of ideas and information regarding adhesives and sealants. This year's conference, the seventh annual, brings together the top professionals in the field. We are grateful for their participation and willingness to share their knowledge and experience, and sincerely congratulate them on their contributions to the industry's success.

Through "ADHESIVES '90," all attendees have the opportunity to review all aspects of adhesive technology, from formulation and selection to dispensing alternatives from initial products design to final quality inspection. Whether you are a newcomer to the field or a seasoned professional, the knowledge that you gain will help you understand the adhesive process, improve bond quality, cut operating costs and improve overall productivity.

As you review this publication, it is our hope that you will find it a valuable resource and an exciting record of just some of the progress we have achieved. Again, thanks to the contributors for their fine presentations.

Nick Schultz
Sealant Equipment & Engineering, Incorporated
ADHESIVES '90 Conference Chair

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TECHNICAL PAPER

AD90-450

Criteria for Proper Adhesive Selection: From Application to Viscosity

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abstract

For a novice, the number of topics that need to be addressed prior to the adoption of an adhesive for fastening a particular part can be overwhelming. This paper simplifies the procedure through the use of a methodical multi-step sequence. Each step is discussed briefly thereby bringing to mind the important aspects that need to be considered. Certainly, each manufacturing site has its own unique strengths and limitations; however, by following through the sequence presented here, the full advantage of adhesive bonding will be brought to fruition.

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Introduction

The criteria for the proper selection of an adhesive for a particular application can be a bit overwhelming unless it is approached by a very methodical procedure. What is described in this paper is a multi-step process of considerations that must be examined in order to make the appropriate choice of adhesive for the application in hand. An attempt will be made to highlight these considerations, but each must be tempered with the circumstances of manufacturing found at each industrial site.

Criterion I: Properties of the Substrate

In order for the strongest adhesive bond to form, the uncured adhesive must wet the substrate's surface. That is, the adhesive must spread out in a uniform coating over the entire surface without "beading-up" and leaving gaps where there is no adhesive. The critical property in this case is the surface energy of the substrate/adhesive combination. Every liquid in contact with a surface has two principle forces acting upon it. First, there is the attraction of the liquid molecules for each other. (This internal cohesive force is what forces water into drops as it falls as rain.) The second force is the attraction of the liquid molecules to the atoms or molecules that make up the substrate's surface. If the attraction of the liquid molecules to themselves (cohesive forces) is less than that force that exists between the liquid molecules and those of the substrate (adhesive force), then the liquid will tend to spread out on the substrate's surface and it is said to "wet" the surface. The opposite effect is observed when water is placed on a newly-waxed car. The formation of water beads indicates non-wetting.

Surfaces are classified as either low- or high-energy surfaces. This classification is surface/liquid dependent. That is, a surface may be classified as a low-energy surface with respect to one liquid and be classified as a high-energy surface with respect to a second liquid. A given liquid will wet a surface that is classified as a high-energy surface with respect to that particular liquid. Solubility parameters may be used to predict the compatibility of a liquid with a surface (1).

Most adhesive formulations have functional groups in the polymer molecule that are available to interact with sites on the substrate's surface. The more similar the functional groups of the adhesive are to those of the substrate's surface, the more likely wetting will occur. Polar groups (regions where there is a surplus or deficiency of electrons) on the adhesive molecule will secondarily bond to similar sites of the surface. However, often there are surface coatings, residual oil, etc. that prevent this secondary bonding from occurring. This, then, gives rise to the need of some type of surface preparation.

The amount of surface preparation depends to a great degree upon the extent of contamination on the surface. The surface may require little preparation (simple dusting with a clean cloth) to extensive preparation such as plasma treatment or chemical etching. (See references 2 and 3 for details of various surface preparation techniques.) It should be understood that contamination may not be the only problem with a given substrate. For example, the bond of polyethylene or polyproplyene is difficult because the polymer molecules do not contain polar groups that allow for the interaction with polar groups on the adhesive molecule. It is these types of surfaces that require more aggressive surface preparation techniques.

If an attempt is made to bond dissimilar substrates, then a consideration must be made concerning the coefficient of thermal expansion. For example, the bonding of polyethylene to a fused quartz surface would be very difficult because the value of the linear coefficient of thermal expansion for polyethylene is some 180 times larger than that of the fused quartz (4). This example is certainly an extreme; however, significant amounts of stress can develop within a bond line if the two substrates being bonded have a mismatch in their coefficient of thermal expansion.

The current industry philosophy is to consider adhesive failure (failure at the interface between the cured adhesive and substrate) as unacceptable. But rather, the acceptable mode of failure is the cohesive failure of the substrate (delamination failure of a composite for example). There is evidence that this philosophy is too restrictive and may be overly conservative (5).

Finally, the previously-prepared surface must be considered. Has the surface been painted or coated, for example. The painting or coating of a surface not only changes the available active sites for the active sites on the adhesive molecule to react with, but also the porosity and surface roughness is changed. Certain types of adhesives, especially water-based, depend upon the porosity of the substrate's surface to draw away the solvent leaving the adhesive behind to form the bond. If this porosity does not exist, then curing will occur at a much reduced rate if at all. On the other hand, certain adhesives are very low viscosity liquids and may not be used on a porous surface because to do so would result in the liquid migrating into the pores of the solid leaving behind little adhesive to form the bond. This is known as a "starved bond-line". The surface roughness must also be considered. If the surface is too rough, then the possibility exists for air gaps and voids to exist when the adhesive cures, thereby producing a weakened bond. An extremely smooth surface can also result in a weakened bond since there would be fewer active sites available on such a surface to interact with the active species on the adhesive molecule. Certainly, painting or coating the surface changes the chemical species on the surface and also changes the surface's porosity and roughness (6).

Criterion II: Joint Design

There are several types of loading that may occur on a given bond-line. They include:

1) Shear
2) Peel
3) Tension/Compression
4) Cleavage
5) Creep
6) Vibrational fatigue
7) Mechanical shock
8) Thermal shock

Adhesives are notoriously weak in peel and cleavage with much greater strength in shear and tension/compression. These points should be considered when actually designing the workpiece. If it is known that a specific design is going to result in a bond experiencing vibrational fatigue or mechanical or thermal shock, then an adhesive that has a built-in flexibility (through the incorporation of rubber, etc.) may want to be investigated.

Criterion III: Service Environment

Typically, the service environment of a part is less vigorous if that part is to be used in an inside environment; however, certain considerations still need to be met: For example, the temperature that the part will be exposed is of importance. Certain adhesives are designed to withstand high temperatures while others are formulated to withstand low temperatures without becoming brittle. It is unusual to find an adhesive that can experience wide variations in temperature without loss of strength. One must be concerned about the types of solvent to which the bond line will be exposed. Water and high relative humidity can degrade certain types of adhesives quickly. Since the rule of thumb of "Like Dissolves Like" tends to hold, one must also be aware that certain organic solvents may attack adhesive bonds. Finally, certain adhesives can be formulated to prevent fungus growth which may be a problem in warm, moist environments.

Some of the same factors must be considered for outside service environment as for indoor service, such as temperature extremes, fungus growth, solvents, water and humidity. However, outside service may result in even more severe conditions. For example, the exposure to ultraviolet light (UV) can be extremely damaging. UV light has enough energy to break chemical bonds thereby changing the characteristics of the polymer molecules making up the adhesive. Photoabsorbers can be formulated into adhesives so that the effect of UV light can be minimized. Ozone, O_3, a very reactive species found in photochemical smog, may attack adhesive bonds. UV light, ozone, acid rain, and salt fog are all considerations for adhesives used on the exterior of a vehicle. In addition, certain parts may be exposed to acids or bases, de-icing solvents (alcohol-based solvents), glycols (antifreeze), and fuels. One must be cognizant of the service environment that the adhesive bond will be exposed to so that appropriate measures may be formulated into the prospective adhesive to lessen these effects on the bond as it ages.

Criterion IV: Properties of the Adhesive

One of the fundamental properties of any adhesive formulation is the solvent in which the pre-polymer is carried. Because of environmental concerns due to volatile organic compounds (VOC's), many states and the federal government have issued restrictions to the amount of solvent that may be released to the environment. These regulations have increased the interest in water-based adhesives, 100% resin adhesives, hot melts, and pressure-sensitive adhesives. There are certain properties that are difficult to achieve with non-organic based solvent adhesives; however, great strides are being made in improving the properties of these adhesives.

Certain solvents, curing agents, etc. used in adhesives may be toxic or cause dermatitis if exposed skin comes in contact with said material. If the adhesive of choice has one of these short-comings, then appropriate safety measures (gloves, glasses, masks, etc.) need to be supplied to the workers exposed to the adhesive. Many of the organic-based solvent adhesives are flammable; therefore, appropriate procedures need to be in place to prevent flames or sparks (do not forget the possibility of a build up of static electricity which can result in sparks) from coming into contact with the uncured adhesive. Also, proper ventilation must be provided to remove undesirable fumes. A special consideration must be given to the usage of cyanoacrylate adhesives since these products will bond skin on contact. If cyanoacrylates ("super-glue" type adhesives) are to be used, then workers must be trained in its proper use.

In the Criterion I section, a discussion on wettability of a surface was presented. An adhesive must be selected that will wet the surface either as the substrate is received or after substrate surface preparation has been done. Another important consideration is the interactions that are possible between the adhesive and adherents. Some additives found in adhesive formulations may corrode the adherend's surface resulting in a weakening bond with age. There is the possibility of the phenomenon of blooming occurring. Blooming is the process where vapors released by the adhesive as it cures precipitate as a haze on the surfaces adjacent to the bondline. Under certain circumstances this may be an undesirable effect and steps must be taken to have the adhesive formulated to lower its vapor pressure.

The adhesive bond may be used as a buffer to counteract changes in thermal expansion of dissimilar substrates. If such a demand is needed for the adhesive bond, then appropriate adhesive formulation must be chosen. In the same vein, some applications require that a seal be made between the two adherents to prevent migration of liquids, gases, or noise. This type of application is in the realm of a sealant rather than an adhesive if excess strength is not demanded by the joint design. The choice of an adhesive with little solvent (nearly 100% resin if not 100% resin) would be in order for this application where little shrinkage is allowable.

Some adhesives form such strong bonds with certain substrates that they will telegraph through the adherend. This results in dimpling of the adherend which may be undesirable for cosmetic reasons. To avoid this problem, a less aggressively bonding adhesive would need to be selected or using a thicker substrate would result in the desired quality surface.

For some applications it is important that the adhesive be optically clear (lens bonding, for example) colored, or colorable. Colored adhesives have an advantage in that it is easier to visually inspect parts prior to bonding to determine if the adhesive was appropriately applied. Some adhesives have formulations which will fluoresce when exposed to ultraviolet light. This may also be useful in determining if adhesives were properly applied. Placing parts which have been disassembled in UV light to determine if the failure was adhesive or cohesive, can be aided using fluorescence also. It is possible for a very thin film of adhesive to adhere to the adherent giving rise to what appears to be adhesive failure, but when exposed to ultraviolet light, evidence of a thin layer of adhesive on each adherent (thus cohesive failure within the adhesive itself) becomes evident. Once again, for cosmetic reasons it may be important for an adhesive to be colorable to match the adherends.

The viscosity of the adhesive affects what type of dispensing method will be used (See Criterion V for dispensing topics.) Poiseuille's Law states for laminar flow of liquid at a given temperature

$$V/t = [\ \pi r^4\ (P_1-P_2)]/[8\eta(y_2-y_1)]$$

(See reference 7.) where V is the volume of liquid that passes a cross section of a tube in time t and $(P_2 - P_1)/(y_2 - y_1)$ is the pressure gradient along the tube. In this derivation it should be noted that $P_2 < P_1$. The radius of the tube is r and the viscosity is η. Viscosity is measured by a variety of methods. These include the use of the Brookfield Viscosimeter, falling ball method , Ostwald Method, Ford Cup, and Zahn Cup. The Brookfield method measures the tension applied to a calibrated spiral spring that results from the resistance of flow of a liquid as a spindle is rotated at a specific speed through the liquid. The falling ball method utilizes the technique of measuring the time it takes for a ball of known dimensions and mass to fall a given distance in a liquid. Using Archimedes principle, it can be shown that

$$v = [2(\rho - \rho_{fl})\ gr^2]/9\eta$$

where ρ and ρ_{fl} are the densities of the ball and the fluid, respectively, g is gravity, r the radius of the ball and η is the viscosity. By measuring the terminal speed, v, of the ball in the liquid, the viscosity can be calculated.

The Ostwald method measures the time for a liquid to fall from one level to another level through a capillary tube. Generally the time is compared to that of a liquid whose viscosity is known using the equation

$$[\eta_b/\eta_a] = (\rho_b\ t_b)/(\rho_a\ t_a)$$

where η_b and η_a are the viscosities of liquids b and a, respectively, ρ_a and ρ_b are the densities of b and a, and t_b and t_a are the times for b and a.

The Ford cup and Zahn Cup methods are similar in that they both use the concept of the time it takes to allow a liquid to flow out of a container through a hole in the container's base. Both Ford and Zahn Cups are available in several sizes which correspond to different sized orifices in the cup's bottom. Both the Zahn and Ford Cup methods are usually standardized against known viscosity standards.

Fluids are classified as either Newtonian or Non-Newtonian. Newtonian liquids are those in which viscosity remains constant as the shear rate is varied. This means that the viscosity will be independent of the rate in which the spindle of a Brookfield is rotated. There are, however, many fluids which are classified as Non-Newtonian. This group of Non-Newtonian fluids includes many adhesive formulations.

There are several subgroups under the general classification of Non-Newtonian fluids. See reference 8. These subgroups include:

(1) Pseudoplastic materials whose viscosity decrease with increasing shear rate (paints and emulsions)
(2) Dilatant materials whose viscosity increases with increasing shear rate (corn starch in water)
(3) Plastic materials are those that remain solid until a criterical yield value is reached at which time the material will flow (tomato catsup). Plastic materials may show Newtonian, pseudoplastic or dilatant behavior once it starts to flow.

Thixotropic materials will undergo a decrease in viscosity with time when subject to constant shearing. Rheopexy is the name given to materials that demonstrate the opposite behavior of thixotropic materials. Many adhesives are thixotropic. Non-Newtonian materials can give rise to serious pumping and dispensing problems; therefore, Newtonian versus Non-Newtonian behavior must be determined before the method of application of any fluid is attempted.

Depending upon the material, temperature can have a great deal of affect on the viscosity. For example, the viscosity of water changes from 1.787 cp at 0°C to 0.7975 cp at 30°C while glycerin changes from12110 cp at 0°C to 629 at 30°C (See reference 9). It is evident from this that temperature control of liquids may be a crucial element in the application of the desired amount of material. Many adhesives need to be temperature controlled, especially in robotic applications, so that the quantity of adhesive that is supplied and the quality of the bead applied stay within the acceptable range.

The most common unit used to describe viscosity is Centipoise (cp). One centipoise is one one hundredth of a poise. A poise, is defined as (one gram)/ (second x centimeter) . Kinematic viscosity, is measured in stokes or centistokes. One centipoise is equal to one centistoke times the density of the liquid at the temperature that the viscosity is being measured.

Because of their inherent reactivities, some adhesives are supplied as multi-component systems which require mixing prior to application. This requirement has, in the past, been a major deterrent for some users. The attitude of some users was that a multi-component adhesive was not reliable; therefore, these users refused to use them. However, with new techniques outlined in Criterion V, these fears are subsiding. One does need to be aware if multi-component adhesives are to be used and to plan for their method of application in advance.

Pot-life, shelf-life, open-time, and curing-time all need to be considered when selecting an adhesive. If a long shelf-life is required, then perhaps a two-part or multi-component adhesive would be appropriate. In a two-part adhesive, the curing mechanism does not start until the two components are mixed. This often gives rise to a curing-time that is relatively short at room temperature. However, single-component systems may have a shorter shelf-life, require a primer, and require elevated temperatures for curing.

Finally, the cost of the adhesive must be considered. Cost is, however, more than just the dollars per pound of adhesive. Some adhesives require a very thin bond-line; therefore, a small amount goes a long way. Others may be formulated with a substantial amount of fillers included. These fillers lower the cost per pound and also change the characteristics of the adhesive in both the cured and uncured states. The presence of fillers can also add additional wear to pumping systems, lines, and nozzles, thereby increasing the cost of each part produced. Certainly two other areas of expense are the costs of clean up and waste disposal. The costs for solid waste disposal are increasing dramatically; therefore, any process which generates solid wastes (the automatic purging of robotic applications, for example) adds additional expense that needs to be considered.

<u>Criterion V</u>: <u>Dispensing Methods</u>

Two questions that need to be considered when deciding upon the correct dispensing methods are:

1) At what rate must the parts be bonded?
2) Will a multi-component adhesive be used?

Application methods (manual or robotic) may include the use of rollers, dippers, sprayers, brushes, bottles, or silk screens. Pumping systems may be required. Pumps usually are either geared or piston driven. If a two-part adhesive is being used, then a decision on the type of mixing and metering system to be employed must be made. Static mixers, specially designed tips that are attached to the end of the two-part delivery system, are relatively inexpensive and eliminate the mess that is often associated with dynamic mixing systems.

The quantity of adhesive that will be required for a particular application will determine the size of container that the vendor will supply the adhesive in. For small applications, one ounce bottles may be appropriate while in other applications fifty-five gallon drums or larger containers may be best. How much of the adhesive that will be stored, in what size containers, and in what type of facility (fire proof, air conditioned, etc.) must be considered.

Criterion VI: Assembly Needs

Many adhesives do not bond instantly; therefore, some type of clamping system might be required to hold the two adherends together until the curing mechanism has furnished enough strength for handling or until the part passes through some type of curing system (See Criterion VII for curing systems.) where the adhesive is totally cured. In some applications, bonding of wood products, for example, heated presses are used to speed the cure and force the water that was used as the solvent in the adhesive into the pores of the adherend. Even for pressure-sensitive adhesives (tapes, films, labels, etc.) pressure must be applied for a specific time to guarantee bonding; therefore, clamping is necessary if only for a very brief interval. Heaters may be an assembly need also. The requirement for temperature conditioning has already been addressed in the topic on viscosity (Criterion IV); however, for hot-melt adhesives, some type of heating system must be supplied to convert the solid adhesive into a molten liquid appropriate for application. The heating systems can be a heated hopper where solid adhesive is heated to molten temperature and is delivered to the workpiece through heated hoses or it may be a hot tip of a hot melt gun. In either case, as the name implies, hot-melt adhesives require heat.

Criterion VII: Curing Methods

The curing of all adhesives involves the process in which small molecules combine with other molecules to form high molecular weight polymers. For this process to occur some type of curing mechanism is required. (One could argue that the above statements are not strictly true for hot melt adhesives since the process for this type of adhesive is the cooling of the low viscosity molten liquid into a solid.) In order to facilitate this curing mechanism, several types of curing methods are possible. Perhaps the most common curing method is the conventional oven. Parts may be run through such ovens on a conveyor belt or in batches depending on assembly methods. Often parts are painted after assembly. Paint-curing ovens perform a two-fold function-the curing of the paint and the curing of the adhesive. If such a system is to be used, the adhesive will need to generate enough strength for handling prior to painting or be clamped so that it can be handled. Caution must be observed in the case where the paint-curing oven is of such temperature as to cause softening of hot-melt adhesives or the thermal decomposition of the adhesive thereby weakening the bond.

A group of adhesives known as anaerobic adhesives cure by a chain reaction driven by the formation of radicals. The presence of oxygen inhibits this reaction. For anaerobic adhesives to cure, oxygen must be removed from the adhesive or a metal catalyst be made present. For these types of adhesive the elimination of oxygen is the curing method (placing in a confined space - the threads of a fastener, for example) and no curing oven is required; however, curing ovens can be used to speed up the curing process if desired.

Ultraviolet (UV) light is often used to initiate curing in acrylic and acrylate adhesives(10). Contained in these formulations are photoinitiators that absorb UV light and in turn form radicals. These radicals react through a chain reaction mechanism to cause the formation of the large polymer molecules required for bonding. A major consideration that must be given to UV curing is that one of the substrates must be transparent to the wave length of light being used to initiate the chain reaction. UV light curing methods result in curing times as short as a few seconds or less.

Two other curing methods that are used and are sometimes confused are dielectric and induction curing. In dielectric curing, rapidly changing electric fields are directed through the adhesive to be cured. If the adhesive resin is polar, then the adhesive molecules tend to align themselves in the electric field. Since the electric field is changing very rapidly, the adhesive molecules change orientation very rapidly. This results in internal heating which accelerates the curing process. This method is used in wood bonding where wood adhesives are often polar molecules.

Induction curing involves a rapidly-changing magnetic field being placed in the region of the adhesive. Induction curing uses the heat generated by eddy currents formed in a conductive substrate or the heat generated by the re-orientation of magnetic domains in ferromagnetic substrates to accelerate the curing process.

Some type of curing mechanism must be used even if it is as simple as waiting for the adhesive to cure at room temperature. Some of the methods outlined above are very fast, some very expensive, and some with unique safety problems. Whatever method that is chosen, floor space in the assembly plant and appropriate equipment must be planned for.

<u>Criterion VIII</u>: <u>Vendor Selection</u>

Unless the application is quite exotic, it is likely that several vendors are available to supply the needed adhesive. Each vendor's product will likely have slightly different characteristics and different costs, but would likely perform adequately. Unless the new application is of extreme importance, it is probably unlikely that many vendors would be willing to develop an entirely new product. There are three points that need to be considered when deciding upon an adhesive vendor. They are:

1) Is the vendor reliable? (Check out references and other users that the vendor supplies adhesives to.)

2) Can the vendor produce the volume of adhesive to fill your project demand?

3) Will the vendor assist in the proper selection of adhesive and supply the user with appropriate information on quality control?