Understanding the use of Polyvinyl Acetate (PVA) Adhesives in Bookbinding

By Jack Bendror

For more than 40 years MEKATRONICS has designed innovative, reliable equipment to help the labor-intensive library bindery industry streamline their operations, reduce costs -- and still maintain quality.

Library binding is a separate and distinct industry in the bookbinding segment of the graphic arts. In contrast with edition binding where multiple copies of the same size book blocks are being processed, library binders bind book blocks in single copies of randomly intermixed sizes. The principal mission of the library binding industry since its emergence early in this century has been to extend the useful life of library books and periodicals by maintaining rigorous technical standards that emphasize careful performance of all procedures and the use of high quality materials.

Our introduction of the Ehlermann equipment to the library binding industry made it important that we acquire as much information as possible on the PVA emulsion adhesives that play a major role in that process.

Most people find modern adhesive technology difficult to understand. This is understandable because the average binder:

a. Is not a chemist or is too small to afford the services of one.

b. Is not familiar with the terms used in modern adhesive technology so that he or she:

c. Must rely on the adhesive supplier to provide her or him with a product suitable for the particular bindery operation.

This presentation is an attempt to provide some guidelines concerning properties and characteristics desired in a particular adhesive for a demanding binding operation.

Efforts were made to make this presentation as non-technical as possible. Since the use of certain adhesive terminology could not be avoided, a Definition of Terms list compiled from information from the American Society for Testing Materials (ASTM) and from the Handbook of Adhesives by Irving Skeist has been provided.

In the late 60’s, along with the Ehlermann machines, we also introduced the LB-Super and LB Rapid 300N recommended for the various Ehlermann machines. Not only did we rely on our supplier’s data regarding the performance characteristics of the adhesive, but we also made independent investigations. In particular, we questioned the need to import an adhesive when the technology for producing it existed in the United States. The following facts will shed some light on this complex subject.
Historical Background

- The vinyl acetate monomer was first invented in Germany in 1912.
- Real commercial development began in Germany in 1925.
- Commercial polymerization was in progress by 1929.
- In the 1930’s Emil Lumbeck pioneered the “Double-Fan” principle of leaf attachment known throughout Europe as the “Lumbeck System”. What made the process unique was the combination of double fanning with the use of specially formulated polyvinyl acetate emulsions that demonstrated exceptionally good stability.
- Hans Ehlermann, Lumbeck’s son-in-law, advanced the development of the Double-Fan binding machines and the European binders adopted the process as the primary method of leaf attachment.
- Although available in the United States and Canada since the 1930’s, polyvinyl acetate emulsions were not introduced commercially until the 1940’s during World War II as a synthetic resin substitute for animal-hide glue, then in short supply.

For these reasons, it made sense that we should take advantage of the vast knowledge and experience of the German suppliers of PVA emulsions.

Following the sale of the Ehlermann company in 1987 and the ensuing uncertainty of maintaining an uninterrupted source of supply, we began a search of the European market for a quality adhesive that would equal or exceed the performance characteristics of the Ehlermann adhesives which we had been supplying for over 25 years. After visiting many European library binders, we found Eukalin to be a highly respected supplier of adhesive products. Eukalin, established in 1904, had a reputation for producing a quality product consistently from batch to batch over many years.

While performance is very important in the selection of an adhesive, secondary considerations such as manner and type of application are often very important in the selection process. The experience acquired as distributors of the Ehlermann machines was reflected in the formulation of the line of ULTRAFLEX™ adhesives. Independent laboratory tests on the ULTRAFLEX™ 4056 for example, revealed to our greatest satisfaction that ULTRAFLEX™ 4056 was 86% stronger than its predecessor LB-Super.

After its being in use by library binders in North America for over 25 years, it was the opinion of experts in the library community that copolymers were the safest, most conservative choice for bindings that need to perform for extended service lives (as much as 300 years, the life of alkaline paper) than homopolymers.

To answer the question whether an externally plasticized homopolymer or an internally plasticized copolymer PVAc emulsion should be used for adhesive binding, the following facts must be considered:
• PVA adhesives like the ULTRAFLEX™ 4056, LB-Super, Rapid 300N, Planatol, Henkel and other similar European PVAc emulsions have been in use in Europe for over 60 years and for about 30 years in North America. Unbeknownst to library binders in North America, all of the above were externally plasticized homopolymers that are best suited for leaf attachment.

• A pure PVAc emulsion without any plasticizer will, upon aging, become hard and brittle. However, the addition of the proper amount of plasticizer will soften it and eliminate embrittlement with age. By way of information, the German word for “plasticizer” is “weichmacher” which is equivalent to the English “weak maker” or “weaker.” It becomes apparent, therefore, that the amount of plasticizer added to the PVAc formulation must be kept within the proper limits to ensure the integrity of the product.

• Little plasticizer migration will take place if:
  a. Amount of plasticizer is kept below 15% (see table)

<table>
<thead>
<tr>
<th>Adhesive</th>
<th>Plasticizer Approx. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>ULTRAFLEX™ 4056</td>
<td>7.5</td>
</tr>
<tr>
<td>Ehlermann LB-Super</td>
<td>9.0</td>
</tr>
<tr>
<td>Planatol BB</td>
<td>10.0</td>
</tr>
</tbody>
</table>

  b. If books are stored at room temperature.

• **Strength**

Externally plasticized homopolymers are considerably stronger than internally plasticized copolymers because in aging, following a small loss of plasticizer for a brief period of time, the externally plasticized emulsions will experience hardening of the PVAc resulting in increased pull-test values (in the order of magnitude of almost 100%), following which the adhesive becomes stabilized.

• **Creep Resistance**

Creep is the dimensional change with time of the material under load, following the initial instantaneous elastic or rapid deformation. Creep at room temperature is sometimes called Cold Flow.

Externally plasticized homopolymers have superior Creep Resistance to that of copolymers.
• Setting Speed

Setting Speed is the speed at which an adhesive is allowed to convert into a fixed or hardened state. Externally plasticized homopolymers set faster than internally plasticized copolymers, thus increasing productivity by allowing the work to be moved more rapidly through the bindery.

• Water Resistance

It should be noted that water resistance and ease-of-clean up are inversely related. Homopolymers exhibit a fair degree of water sensitivity. This allows them to be easily cleaned from equipment and permits their use in remoistenable adhesives. Copolymers, on the other hand, have excellent water resistance with the consequence of making it difficult for equipment to be cleaned.

• Range of Adhesion

Copolymers of polyvinyl acetates are used primarily for adhesion to synthetic foils or films or nitro- varnished surfaces where plasticizer migration is of concern, such as in case-making and casing-in applications. The non-migratory properties of copolymers make them ideal for a wide spectrum of adhesion other than leaf attachment where homopolymers perform best.

The above touches briefly on some of the fundamental differences between two polymers. However, in addition to plasticizers an adhesive may contain components such as viscosity modifiers, tackifiers/extenders, solvents, fillers, humectants, wetting and foam control agents and biocides which may be compounded in order to tailor the product for the particular application. Such compounding facilitates application on equipment and bonding on specific substrates.
DEFINITION OF TERMS

Adherend:

A body that is held to another body by an adhesive (see also substrate).

Adhesive:

A substance capable of adhering or sticking to a surface, primarily to promote a bond between that surface and another material. Before the wide-scale utilization of synthetic resins, the terms “adhesive” and “glue” were considered synonymous because the earliest commercial adhesives were glues and were generally of animal or marine origin.

Binder:

A component of an adhesive composition that is primarily responsible for the adhesive forces that hold two bodies together. (See also Extender and Filler.)

Biocide:

Biocides are required when animal or vegetable substances or their derivatives (starches, casein and other proteins, nutshell flours, sugar and cellulose resins) are incorporated into polyvinyl acetate homo- or copolymer emulsion adhesives. Growing microorganisms digest these substances and can generate foul odors, discolor the adhesive, lower its viscosity, and weaken the bond.

Blocking:

An undesired adhesion between touching layers of material, such as occurs under moderate pressure during storage or use.

Bond:

The union of materials by adhesives.

Cold flow:

See Creep.

Copolymer:

See Polymer.
Copolymerization:

See Polymerization.

Creep:

The dimensional change with time of a material under load, following the initial instantaneous elastic or rapid deformation. Creep at room temperature is also called Cold Flow.

Dry Film:

Solid residue after solvents have evaporated.

Extenders:

These are resins that increase the tackiness and setting speed of adhesives. They increase tackiness by softening the polyvinyl acetate polymer, both in the wet and the dry adhesive film. They are added to an adhesive to reduce the amount of the primary binder required per unit area. By virtue of adding to the adhesive properties of the polyvinyl acetate emulsion, extenders are also tackifiers. They accelerate setting speed by raising the total solids content of the emulsion. (See also Binder, Diluent, Filler, and Thinner).

Filler:

A relatively non-adhesive substance added to emulsion adhesives to reduce cost by replacing resin solids without decreasing total solids, to reduce penetration into porous substrate, and to change the viscosity of the compound.

Foam Control Agents:

Foam causes problems in the manufacturing and application of adhesives. Form control agents include antifoam and defoamer compounds.

Glue:

Originally, a hard gelatin obtained from hides, tendons, cartilage, bones, etc., of animals. Also, an adhesive prepared from this substance by heating with water. Through general use the term is non synonymous with the term “adhesive.” (See Adhesives and Paste.)
Humectants:

A humectant is a hygroscopic substance, one that absorbs and retains moisture from the atmosphere. In emulsion adhesives, humectants prevent the surface of the compound from skinning by keeping it wet. When polyvinyl alcohol or starch is present, the humectant holds water, which plasticizes these materials and keeps them flexible after drying. By retarding drying, humectants also slow setting speed and extend the open-time of the adhesives.

Modifier:

Any chemically inert ingredient added to an adhesive formulation that changes its properties. (See also Filler, Plasticizer, and Extenders.)

Monomer:

A relatively simple compound that can react to form a polymer. (See also Polymer.)

Open-Time:

The time interval between the spreading of the adhesive on the adherend and application of pressure or heat, or both, to the assembly.

Paste:

An adhesive composition having a characteristic plastic-type consistency, that is, a high order of yield value, such as that of a paste prepared by heating a mixture of starch and water and subsequently cooling the hydrolyzed product. (See also Adhesive and glue).

Plasticizer:

A material incorporated in an adhesive to increase its flexibility, workability, or distensibility. The addition of the plasticizer may cause a reduction in melt viscosity, lower the temperature of the second-order transition, or lower the elastic modulus of the solidified adhesive.

Polymer:

A compound formed by the reaction of simple molecules having functional groups which permit their combination to proceed to high molecular weights under suitable conditions. Polymers may be formed by polymerization (addition polymer) or polycondensation (condensation polymer). When two or more monomers are involved, the product is called a copolymer.
Polymerization:

A chemical reaction in which the molecules of a monomer are linked together to form large molecules whose molecular weight is a multiple of that of the original substance. When two or more monomers are involved, the process is called copolymerization or heteropolymerization.

Solids Content:

The percentage by weight of the non-volatile matter in an adhesive.

Solvents:

Because of their volatility, solvents perform like plasticizers on a temporary basis. Solvents increase the viscosity over that of emulsions; they also dissolve wax resin coatings, accelerate setting speed, reduce film-forming temperature, reduce adhesive (wet) cost, increase wet tack, dissolve tackifiers and lower the freezing point.

Substrate:

A material upon the surface of which an adhesive-containing substance is spread for any purpose, such as bonding or coating. A broader term than adherent. (See also Adherend.)

Tack:

The property of an adhesive that enables it to form a bond of measurable strength immediately after adhesive and adherend are brought into contact under low pressure.

Tackifiers:

See Extenders.

Viscosity:

The internal frictional resistance of an adhesive to flow when that resistance is directly proportional to the applied force. Thickeners added to an adhesive will raise viscosity and permit dilution with water. This reduces the total solids of the adhesive and thus lowers its (wet) cost.

Wetting Agents:

Wetting agents aid the adhesive to wet the surface of the adherend, thereby improving adhesion.