TMI PRODUCTS
248 Claridge Curve, Peachtree City, GA 30269
770-631-7897 fax: 770-755-5200 MainOffice@TMIProducts.net

CYANOACRYLATE ADHESIVES

Cyanoacrylate – another step up the ladder of adhesive technology

By Joseph Matwick

For ages there has been a need to bond surfaces together. Technology has catapulted basic glues into a wide variety of adhesives to meet general to very specific bonding requirements. Glues in one form or another have been used for the past 6000 years; however, the technological development of adhesives has rapidly evolved over the past 100 years. One of the most unique adhesives to emerge from this new technology is cyanoacrylate, usually referred to as CA or superglue.

Historical Developments:

The first evidence of the use of a liquid substance as a method of bonding dates to 4000 BC. This first known "glue" was tree sap. By 2000 BC animal glue was used, making it an early step up the developmental ladder. Paintings dating from 1500-2000 BC depict the assembly and gluing of various items. Researchers have even found evidence that King Tutt's casket used glue in its fabrication. Egyptians used glue to make laminates, furnishings, and other objects. Bonding veneers with glue are dated from 100 to 500 AD. Glues of this time period were made from egg whites, blood, bones, hides, milk, vegetables and grains. Romans were the first to use tar and bees wax as a bonder/sealer/caulking to fabricate boats. In 1000 AD Genghis Kahn was believed to use glue to make weapons but it is hard to determine what weapons were. In one case lemon wood was laminated to bull horns. Beginning about 1500 AD, glue began to be used to make fine artistic furniture. Two of the better known families to do this are Chippendale and Duncan-Phyfe. In 1700, the first known commercial glue, an animal hide glue, was manufactured and sold in Holland. The first glue patent, a fish-based glue, was issued in Britain in 1750. Between 1750 to 1800 additional patents were issued on glues that were based on natural rubber, animal bones, fish, starch, and milk protein. By 1900, many companies world-wide were producing and selling glue in one form or another.

Synthetic Adhesives:

The Industrial Revolution changed the world, and certainly it changed the world of glue as technology moved organic-based glues to synthetically created adhesives. The ability to synthesize materials by chemical reaction provided the leap from old world glues. One of the first materials to be synthesized was from cellulose wood and its first known commercial use was the manufacturing of billiard balls originally made from Ivory. In 1910 phenolics, used extensively in adhesives, was synthesized from formaldehyde. The 1920s to 1940s saw the development of many synthetic plastics and adhesives, usually created to meet the needs of the times. For example synthetic rubber was used for tires and nylon for women's stockings during World War II. The evolution of "glues to adhesives" has been driven by a never ending demand for better products that are more physically capable, structurally stronger, more stable, faster and easier to use, and will last longer as a fastening agent in a myriad of applications.

Development Shelved and Rediscovered:

Cyanoacrylate was first discovered in 1941 by Dr. Harry Coover at the Kodak Research Laboratories. He was searching for a material to replace spider web based glue used to bond clear plastic lens for gun sights. The results of the initial experiments were disappointing. The chemists defined the substance (not yet classified or known as cyanoacrylate) as unstable, not refinable, not producible, and "just too sticky". The project was shelved.

In 1951, cyanoacrylate was revisited by Dr. Coover and Dr. Fred Joiner. The formulation was used as a distortion free adhesive to bond prisms together. They still had little idea of the significance of what they had and it took about seven more years to develop production techniques that would make CA a commercially viable product.

In 1958, Dr. Coover appeared as a guest on the TV show "I've Got a Secret". He demonstrated the instant bonding capability of CA by "gluing" a handle on a large heavy item and within seconds, lifting it up. One wonders if the term "super glue" didn't originate at that point.

Early Marketing Efforts:

This early product was labeled "cyanoacrylate" and marketed by the Eastman Company as "EASTMAN 910". It was sold in 1 oz bottles for approximately $40 per bottle, a value of at least $250 per ounce today.

One of the first volume uses for CA was medically related, beginning in the latter part of the Korean War. It became more extensively used in the M.A.S.H. units in Vietnam in the 1960s. It was primarily used to bond human skin tissue together.

Eastman's patents expired in the late 60s and the Loctite Corporation began producing and marketing an industrial level CA in 1972/73. Another major producer that evolved was the German chemical company, Henkel. Eventually, Henkel acquired Loctite and are currently producing CA in Ireland and Puerto Rico. Today much of the consumer level CA is produced overseas.

Manufacturing Processes:

The basis of a good quality CA starts with the formulation and advanced manufacturing techniques. A chemical synthesis process produces CA by changing acetate to acrylate. This is the first step in making CA. It is then further purified through distillation until the crude acrylate becomes a cyanoacrylate monomer. A high level of purity (99.5%) is the benchmark of a CA that has superior bond strength, fast curing characteristics, good storage stability and long bond life.

Many consumer level CAs are formulated to primarily "stay liquid" in their container, but not to necessarily provide a good bond for an extended period of time. Keep in mind that all CAs are not the same and quality levels vary greatly.

Consumer Market:

Over the past 30 years, the applications for CA has expanded from the early medical field to all levels of industrial manufacturing, electronics, aerospace, automotive, wood fabrication, hobby and crafts and finally down to the retail consumer markets. Each area of use has its own mechanical, chemical, and quality requirements. As the markets developed more uses – especially at the consumer level, more suppliers emerged from various parts of the world, each trying to make their CA more competitive. This created what is sometimes referred to as the "junk glue market".

Although intending to be cost competitive, the average package sold in hardware, hobby, building supply, drug stores, etc. contains 2 to 3 grams is priced at 65 cents per gram. The average 1 oz and 2 oz bottles sold industrially and through craft catalogs (normally a higher quality product) are currently priced in the 15 to16 cents per gram range.

Curing Process:

One of the least understood facts about CA is the curing process and we often hear that it cures in the absence of oxygen. – This is not true – Anaerobics, a common material used as a thread and gasket sealant and bonder, cures in the absence of air, which may be the cause of all the confusion.

CA is formulated with stabilizers that keep the adhesive from curing in the bottle. When the CA is applied to the surface of the part to be bonded, it reacts to the Ph level on the surface primarily created by water vapor from the relative humidity in the air. The moisture neutralizes the stabilizer and the curing process begins by forming a polymer chain once the parts are mated together. This polymerization or curing process is very rapid and substantial structural strength is achieved in a matter of seconds.

The set curing time of CA varies depending on the amount dispensed, viscosity, type of surface and the condition of the surface. Different viscosities have progressive rates of cure. Based on wood applications the following are averages:

VISCOSITY	**APPROX SET TIME**
Thin - 2 to 8 cps	3 to 8 seconds
Medium – 500 to 700 cps	8 to 15 seconds
Thick – 2000 to 2400 cps	10 to 25 seconds

Wood has one of the more variable surfaces with which to contend because different woods are more or less acidic, and/or more or less dry. Bonding a dry, acidic wood requires a longer set time and a curing activator may be required for highly acidic surfaces. When an activator is applied to speed up or create a cure, additives in the spray initiate a chemical reaction rather than a moisture reaction. Because this is a chemical reaction, activators should be used sparingly. Too much will cause the CA to bubble (foam) due to excessive heat created by a rapid exothermic reaction as a by-product of curing process. Activators are available in sprayable form; however, the most efficient, easiest to use, and most economical are the aerosol types.

Health Considerations:

Like other curing adhesives, CA has cautionary health considerations. The cured product is considered safe when used as a finish coat on items that contact with food. Fumes released during application can be an eye and respiratory irritant. However, CAs are not flammable or toxic.

CA Will bond a wide variety of materials: metal, glass, ceramics, rubber, plastics, fabrics, wood, and especially your fingers. Highly effective DeBonders are available that will dissolve even cured CA on skin and bonded surfaces. Acetone can also be used but works at a much slower rate. If neither of these is available, continued washing of the bonded skin area with warm water and soap will eventually work. Do not use excessive force to separate the bonded area apart. Should CA come in contact with your eyes or other mucus membranes, **do not** even consider using the noted solvents to treat the problem. Instead, flush eyes or area with water and **do not** try to force the bonded area apart. If corneal surfaces and the eyelid are bonded, treat with a suitable anti-irritant ointment and allow eye to remain closed. Bond separation will occur naturally with time. But in any case, you should see a physician. The best preventive action is to always wear adequate eye protection.

It is recommended that adequate ventilation be available where CA is being used. Even a fan blowing away from the application area will help. Ideally, a respiratory mask with proper filters should be worn and provides one of the best protections for people with fume sensitivity.

Most common complaint:

One of the most asked question about CAs from users is "how do I keep the stuff from curing in the bottle, especially the tips?"

Historically, most suppliers have recommended storing unopened bottles in the refrigerator – but not in the freezer. The refrigerator works well before the bottle is opened, providing you allow the CA to return to room temperature before using. However, after the bottle has been opened the change in temperature from refrigerator to ambient can create moisture condensation in the bottle. This condensation accelerates the reduction in shelf life and the CA will start to thicken. Putting CA into the freezer after opening will definitely cause moisture to crystallize as can be seen on frozen food and will become water droplets when they thaw significantly reducing shelf life

Keep the tip clear of dried CA. After dispensing, tap the bottom of the bottle on a hard surface forcing the CA in the tip back down in the bottle. If any CA remains in the tip, slightly squeeze the bottle to "burp" the tip clear being cautious where you are aiming the tip. A clogged tip can be cleaned with DeBonder or by soaking in acetone for a day or two. Just be sure all contaminants are removed before reusing.

Storage:

The most effective way to keep opened CA usable for a longer time is to store it in a dry, cool (40-75F) place – not in the sunlight on a window sill. Next to moisture, heat is the leading cause of premature thickening/curing of CA in the bottle.

My tested technique for the best storage is to keep opened bottles in a moisture barrier container (glass or PET - peanut butter jar) with a desiccant drying agent. A color change desiccant drying agent is available from Stick Fast that changes colors as moisture is absorbed. When color changes from blue to pink it is time to replace or "recharge" by putting the bag into a microwave to dry it out and ready to use again. Create your own "Dry Box" to greatly extend the shelf life of your CA.

As an extra note, Stick Fast purges each bottle with a special stabilizing gas that inhibits the cure inside the bottle and to eliminate contaminants that may be in the bottle. This greatly increases the unopened shelf life while it is on your favorite store's shelves. Once the bottle is opened the gas escapes but has done its job to provide you with a better product.

The types of applications and use techniques for CAs are a story unto itself. Fabricating, bonding, sealing, coating, finishing, repairing, and more are found in almost all fields of work; from manufacturing to lapidary, aerospace to dentistry, crime investigation to wood turning.

Author: Joseph Matwick

Joe has been a pioneer in the dispensing and application of adhesives for over 45 years. Originally from Southern California he founded an engineering and manufacturing company in 1961 that specialized in fluid dispensing systems and custom packaging of high-tech aerospace adhesives, sealants and coatings. After selling the business and retiring in 1988, his knowledge of the technical aspects of adhesives became the basis of developing another business with his son in 1995. TMI Products Inc – Stick Fast Adhesives (www.StickFast.net) specializes in marketing unique CA adhesive systems, epoxy, and dispensing accessories to the woodworking world.

Joe learned to turn wood from Nick Cook and enjoys the diversity. He is also on the Board of Directors at the John C. Campbell Folk School and currently resides in Hiawassee, Georgia.

Joe welcomes your questions and comments and can be reached by mail at 248 Claridge Curve, Peachtree City, GA 30269 or via email at info@StickFast.net.