Bruce Sterling

bruces@well.sf.ca.us

From THE MAGAZINE OF FANTASY AND SCIENCE FICTION, June 1993.

F&SF, Box 56, Cornwall CT 06753 $26/yr USA $31/yr other

F&SF Science Column #7:

SUPERGLUE

This is the Golden Age of Glue.

For thousands of years, humanity got by with natural glues like pitch, resin, wax, and blood; products of hoof and hide and treesap and tar. But during the past century, and especially during the past thirty years, there has been a silent revolution in adhesion.

This stealthy yet steady technological improvement has been difficult to fully comprehend, for glue is a humble stuff, and the better it works, the harder it is to notice. Nevertheless, much of the basic character of our everyday environment is now due to advanced adhesion chemistry.

Many popular artifacts from the pre-glue epoch look clunky and almost Victorian today. These creations relied on bolts, nuts, rivets, pins, staples, nails, screws, stitches, straps, bevels, knobs, and bent flaps of tin. No more. The popular demand for consumer objects ever lighter, smaller, cheaper, faster and sleeker has led to great changes in the design of everyday things.

Glue determines much of the difference between our grandparent's shoes, with their sturdy leather soles, elaborate stitching, and cobbler's nails, and the eerie-looking modern jogging-shoe with its laminated plastic soles, fabric uppers and sleek foam inlays. Glue also makes much of the difference between the big family radio cabinet of the 1940s and the sleek black hand-sized clamshell of a modern Sony Walkman.

Glue holds this very magazine together. And if you happen to be reading this article off a computer (as you well may), then you are even more indebted to glue; modern microelectronic assembly would be impossible without it.

Glue dominates the modern packaging industry. Glue also has a strong presence in automobiles, aerospace, electronics, dentistry, medicine, and household appliances of all kinds. Glue infiltrates grocery bags, envelopes, books, magazines, labels, paper cups, and cardboard boxes; there are five different kinds of glue in a common filtered cigarette. Glue lurks invisibly in the structure of our shelters, in ceramic tiling, carpets, counter tops, gutters, wall siding, ceiling panels and floor linoleum. It's in furniture, cooking utensils, and cosmetics. This galaxy of applications doesn't even count the vast modern spooling mileage of adhesive tapes: package tape, industrial tape, surgical tape, masking tape, electrical tape, duct tape, plumbing tape, and much, much more.

Glue is a major industrial industry and has been growing at twice the rate of GNP for many years, as adhesives leak and stick into areas formerly dominated by other fasteners. Glues also create new markets all their own, such as Post-it Notes (first premiered in April 1980, and now omnipresent in over 350 varieties).

The global glue industry is estimated to produce about twelve billion pounds of adhesives every year. Adhesion is a $13 billion market in which every major national economy has a stake. The adhesives industry has its own specialty magazines, such as Adhesives Age andSAMPE Journal; its own trade groups, like the Adhesives Manufacturers Association, The Adhesion Society, and the Adhesives and Sealant Council; and its own seminars, workshops and technical conferences. Adhesives corporations like 3M, National Starch, Eastman Kodak, Sumitomo, and Henkel are among the world's most potent technical industries.

Given all this, it's amazing how little is definitively known about how glue actually works -- the actual science of adhesion.

There are quite good industrial rules-of-thumb for creating glues; industrial technicians can now combine all kinds of arcane ingredients to design glues with well-defined specifications: qualities such as shear strength, green strength, tack, electrical conductivity, transparency, and impact resistance. But when it comes to actually describing why glue is sticky, it's a different matter, and a far from simple one.

A good glue has low surface tension; it spreads rapidly and thoroughly, so that it will wet the entire surface of the substrate. Good wetting is a key to strong adhesive bonds; bad wetting leads to problems like "starved joints," and crannies full of trapped air, moisture, or other atmospheric contaminants, which can weaken the bond.

But it is not enough just to wet a surface thoroughly; if that were the case, then water would be a glue. Liquid glue changes form; it cures, creating a solid interface between surfaces that becomes a permanent bond.

The exact nature of that bond is pretty much anybody's guess. There are no less than four major physico-chemical theories about what makes things stick: mechanical theory, adsorption theory, electrostatic theory and diffusion theory. Perhaps molecular strands of glue become physically tangled and hooked around irregularities in the surface, seeping into microscopic pores and cracks. Or, glue molecules may be attracted by covalent bonds, or acid-base interactions, or exotic van der Waals forces and London dispersion forces, which have to do with arcane dipolar resonances between magnetically imbalanced molecules. Diffusion theorists favor the idea that glue actually blends into the top few hundred molecules of the contact surface.

Different glues and different substrates have very different chemical constituents. It's likely that all of these processes may have something to do with the nature of what we call "stickiness" -- that everybody's right, only in different ways and under different circumstances.

In 1989 the National Science Foundation formally established the Center for Polymeric Adhesives and Composites. This Center's charter is to establish "a coherent philosophy and systematic methodology for the creation of new and advanced polymeric adhesives" -- in other words, to bring genuine detailed scientific understanding to a process hitherto dominated by industrial rules of thumb. The Center has been inventing new adhesion test methods involving vacuum ovens, interferometers, and infrared microscopes, and is establishing computer models of the adhesion process. The Center's corporate sponsors -- Amoco, Boeing, DuPont, Exxon, Hoechst Celanese, IBM, Monsanto, Philips, and Shell, to name a few of them -- are wishing them all the best.

We can study the basics of glue through examining one typical candidate. Let's examine one well-known superstar of modern adhesion: that wondrous and well-nigh legendary substance known as "superglue." Superglue, which also travels under the aliases of SuperBonder, Permabond, Pronto, Black Max, Alpha Ace, Krazy Glue and (in Mexico) Kola Loka, is known to chemists as cyanoacrylate (C5H5NO2).

Cyanoacrylate was first discovered in 1942 in a search for materials to make clear plastic gunsights for the second world war. The American researchers quickly rejected cyanoacrylate because the wretched stuff stuck to everything and made a horrible mess. In 1951, cyanoacrylate was rediscovered by Eastman Kodak researchers Harry Coover and Fred Joyner, who ruined a perfectly useful refractometer with it -- and then recognized its true potential. Cyanoacrylate became known as Eastman compound #910. Eastman 910 first captured the popular imagination in 1958, when Dr Coover appeared on the "I've Got a Secret" TV game show and lifted host Gary Moore off the floor with a single drop of the stuff.

This stunt still makes very good television and cyanoacrylate now has a yearly commercial market of $325 million.

Cyanoacrylate is an especially lovely and appealing glue, because it is (relatively) nontoxic, very fast-acting, extremely strong, needs no other mixer or catalyst, sticks with a gentle touch, and does not require any fancy industrial gizmos such as ovens, presses, vices, clamps, or autoclaves. Actually, cyanoacrylate does require a chemical trigger to cause it to set, but with amazing convenience, that trigger is the hydroxyl ions in common water. And under natural atmospheric conditions, a thin layer of water is naturally present on almost any surface one might want to glue.

Cyanoacrylate is a "thermosetting adhesive," which means that (unlike sealing wax, pitch, and other "hot melt" adhesives) it cannot be heated and softened repeatedly. As it cures and sets, cyanoacrylate becomes permanently crosslinked, forming a tough and permanent polymer plastic.

In its natural state in its native Superglue tube from the convenience store, a molecule of cyanoacrylate looks something like this:

```
      CN
     /
CH2=C
     \
      COOR
```

The R is a variable (an "alkyl group") which slightly changes the character of the molecule; cyanoacrylate is commercially available in ethyl, methyl, isopropyl, allyl, butyl, isobutyl, methoxyethyl, and ethoxyethyl cyanoacrylate esters. These chemical variants have slightly different setting properties and degrees of gooiness.

After setting or "ionic polymerization," however, Superglue looks something like this:

```
       CN     CN      CN
       |      |       |
- CH2C -(CH2C)-(CH2C)- (etc. etc. etc)
       |      |       |
       COOR   COOR    COOR
```

The single cyanoacrylate "monomer" joins up like a series of plastic popper-beads, becoming a long chain. Within the thickening liquid glue, these growing chains whip about through Brownian motion, a process technically known as "reptation," named after the crawling of snakes. As the reptating molecules thrash, then wriggle, then finally merely twitch, the once- thin and viscous liquid becomes a tough mass of fossilized, interpenetrating plastic molecular spaghetti.

And it is strong. Even pure cyanoacrylate can lift a ton with a single square-inch bond, and one advanced elastomer-modified '80s mix, "Black Max" from Loctite Corporation, can go up to 3,100 pounds.

This is enough strength to rip the surface right off most substrates. Unless it's made of chrome steel, the object you're gluing will likely give up the ghost well before a properly anchored layer of Superglue will.

Superglue quickly found industrial uses in automotive trim, phonograph needle cartridges, video cassettes, transformer laminations, circuit boards, and sporting goods. But early superglues had definite drawbacks. The stuff dispersed so easily that it sometimes precipitated as vapor, forming a white film on surfaces where it wasn't needed; this is known as "blooming." Though extremely strong under tension, superglue was not very good at sudden lateral shocks or "shear forces," which could cause the glue-bond to snap. Moisture weakened it, especially on metal-to-metal bonds, and prolonged exposure to heat would cook all the strength out of it.

The stuff also coagulated inside the tube with annoying speed, turning into a useless and frustrating plastic lump that no amount of squeezing of pinpoking could budge -- until the tube burst and and the thin slippery gush cemented one's fingers, hair, and desk in a mummified membrane that only acetone could cut.

Today, however, through a quiet process of incremental improvement, superglue has become more potent and more useful than ever. Modern superglues are packaged with stabilizers and thickeners and catalysts and gels, improving heat capacity, reducing brittleness, improving resistance to damp and acids and alkalis. Today the wicked stuff is basically getting into everything.

Including people. In Europe, superglue is routinely used in surgery, actually gluing human flesh and viscera to replace sutures and hemostats. And Superglue is quite an old hand at attaching fake fingernails -- a practice that has sometimes had grisly consequences when the tiny clear superglue bottle is mistaken for a bottle of eyedrops. (I haven't the heart to detail the consequences of this mishap, but if you're not squeamish you might try consulting The Journal of the American Medical Association, May 2, 1990 v263 n17 p2301).

Superglue is potent and almost magical stuff, the champion of popular glues and, in its own quiet way, something of an historical advent. There is something pleasantly marvelous, almost Arabian

Nights-like, about a drop of liquid that can lift a ton; and yet one can buy the stuff anywhere today, and it's cheap. There are many urban legends about terrible things done with superglue; car-doors locked forever, parking meters welded into useless lumps, and various tales of sexual vengeance that are little better than elaborate dirty jokes. There are also persistent rumors of real-life superglue muggings, in which victims are attached spreadeagled to cars or plate-glass windows, while their glue-wielding assailants rifle their pockets at leisure and then stroll off, leaving the victim helplessly immobilized.

While superglue crime is hard to document, there is no question about its real-life use for law enforcement. The detection of fingerprints has been revolutionized with special kits of fuming ethyl-gel cyanoacrylate. The fumes from a ripped-open foil packet of chemically smoking superglue will settle and cure on the skin oils left in human fingerprints, turning the smear into a visible solid object. Thanks to superglue, the lightest touch on a weapon can become a lump of plastic guilt, cementing the perpetrator to his crime in a permanent bond.

And surely it would be simple justice if the world's first convicted superglue mugger were apprehended in just this way.