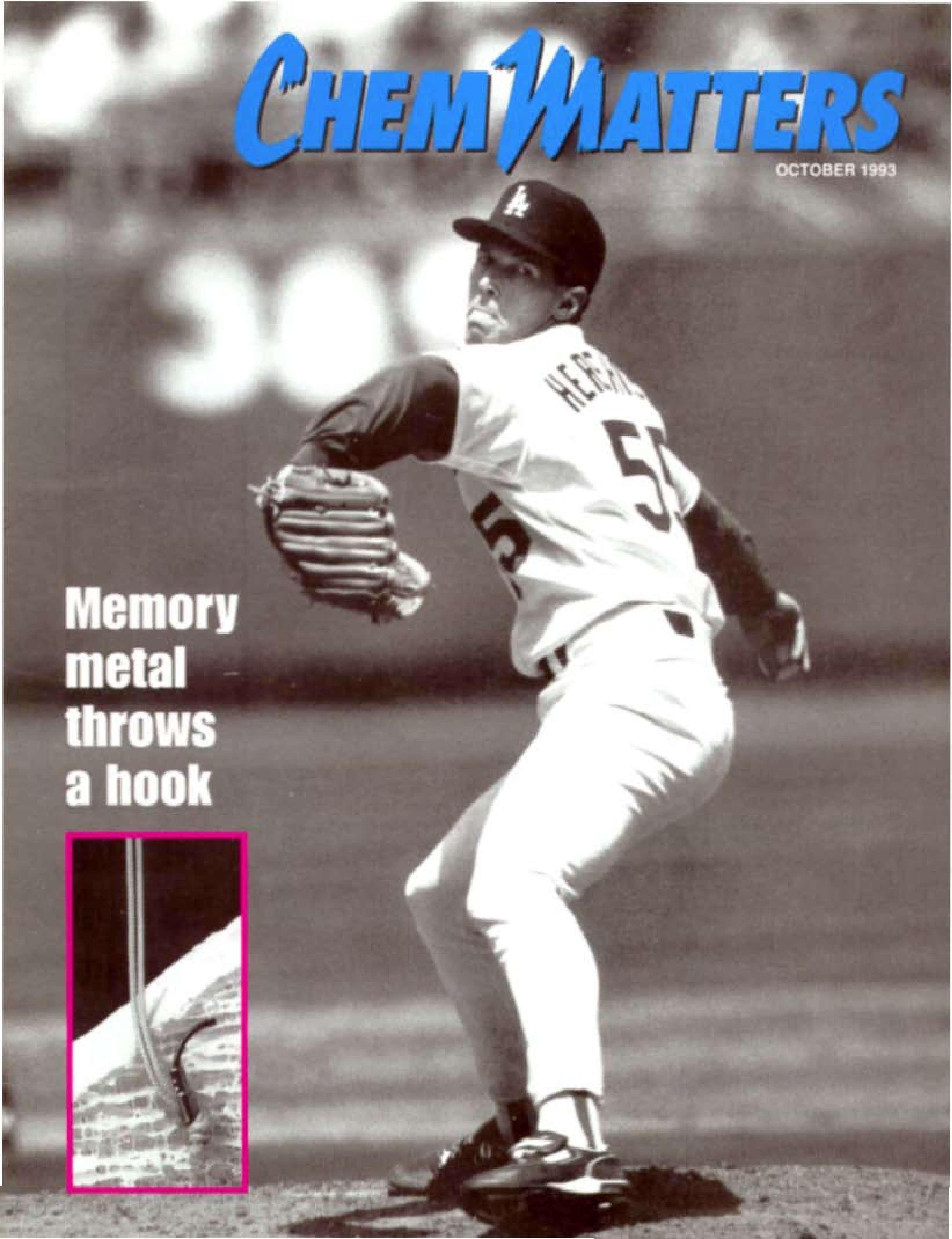
ChemMatters

OCTOBER 1993



Memory metal throws a hook

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October 1993

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Memory

Three years ago, Los Angeles Dodgers pitcher Orel Hershiser suddenly found his brilliant career threatened by severe shoulder problems. After seven years of major league pitching, Hershiser had torn the tissue and tendons in his shoulder so badly that his arm was no longer fixed firmly in the socket. Every time he hurled the ball, he felt more pain and lost more control. The problem had put many a pitcher before him out of business.

But thanks to Nitinol, a strong and flexible nickel–titanium alloy, Hershiser was out only one season and steadily regained most of his original power. Orthopedic surgeons drilled a hole in his shoulder bone and inserted a tiny metal anchor that wedged itself into the hole by the action of a Nitinol hook. Sutures tied to the metal anchor allowed the surgeons to firmly reattach the tendons to bone.

Nitinol can straighten teeth and intercept blood clots. Eyeglass frames constructed of Nitinol can weather severe abuse (you can twist them, sit on them, and otherwise torture them) and they will spring back to their original shape.

Recently, a NASA engineer devised a pair of automatic Nitinol tweezers that are expected to be useful to doctors who must extract minute objects through small incisions.

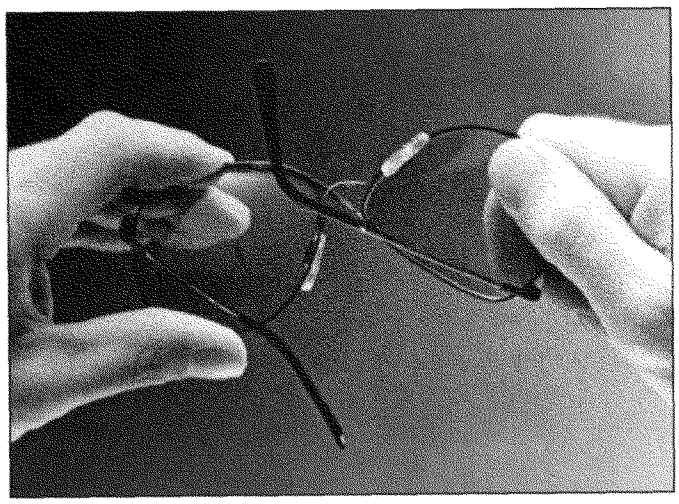
A lot of work and a little luck

Just where did Nitinol come from and, more importantly, how was its ability to remember and return to a predetermined shape discovered? In the late 1950s and early 1960s, William J. Buehler, a researcher at the Naval Ordnance Laboratory in White Oak, Maryland, was looking for a fatigue-, impact-, and heat-resistant alloy (a substance composed of two or more metals) to use in the nose cone of a Navy missile. One of the alloys he investigated was an equiatomic (50%–50%) mixture of nickel and titanium, which exhibited the qualities Buehler desired. He named his discovery Nitinol (*Ni*ckel *Ti*tanium *N*aval *O*rdnance *L*aboratory). Buehler made up long, thin strips of Nitinol to use as "props" in demonstrations for his superiors at the laboratory. He would bend the strip into short folds longitudinally, forming a sort of metal accordion. The strip was then bent and stretched (as an accordion) to show that it wouldn't break. At a routine demonstration at a laboratory management meeting in 1961 an accordion-folded, fatigue-resistant strip of Nitinol was passed around a conference table and flexed repeatedly by all present. One of the Associate Technical Directors, the late Dr. David S. Muzzey, heated the compressed Nitinol strip with his pipe lighter. To the startled amazement of all, it stretched out to its original shape!

The secret of a good memory

What made Nitinol remember its shape? To help get the answer to that Buehler asked Dr. Frederick E. Wang, an expert in crystal physics, to join his research team. It was Wang who discovered the atomic structural changes that endowed the alloy with its unique characteristic.

Phase changes between solids and liquids (melting or solidifying) or liquids and gases (vaporization or condensation) are well known. Less well known, however, is the fact that such changes can occur when both phases are solids. Such phase changes involve the rearrangement of the position of particles (atoms, molecules, or ions) within the crystal structure of the solid. To fix the parent shape (the shape to which you will want Nitinol to return) the Nitinol must be held in the parent position and heated to about 500 °C (932 °F). There is no visible change in the shape of the metal; all the



These expensive glasses were twisted like a pretzel. Who would deliberately do this? Someone who had Nitinol wire frames, which snap back to a proper fit even without being heated. The frames spring back instantly because they are made of a Nitinol alloy whose critical temperature is well below room temperature. This means that the alloy is always in the return-to-memorized-shape mode and, therefore, behaves like a super-elastic spring. Similar alloys are used for the wires in dental braces and surgical anchors, which cannot be heated after insertion.

Metal Metal

by George B. Kauffman
and Isaac Mayo

changes occur at the atomic level. Nitinol metal is a conglomeration of crystals of random size, shape, and orientation. When Nitinol is heated to the high temperature, the thermal energy causes the atoms to arrange themselves into the most compact and regular pattern possible. The Nitinol crystals take on a cubic arrangement called the austenite phase (see Figure 1).

When Nitinol wire cools below a certain

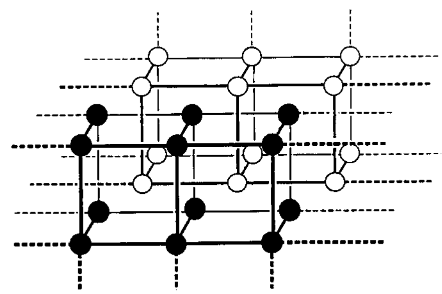


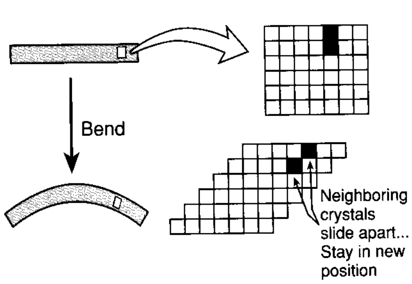
Figure 1. The austenite phase of Nitinol. Nickel atoms (white) are positioned at the corner of a cube that has a titanium atom at its center. The titanium atoms (black) form their own cubes that interlock with the nickel cubes. Each Ni atom is in the center of a Ti cube and vice versa.

DIAGRAM: *MEMORY METAL*, INSTITUTE FOR CHEMICAL EDUCATION

Crystals with good neighbors

A metal object begins as a hot, molten liquid. As the liquid cools, a few atoms attach to each other in a geometric pattern, and this minute solid grows as other atoms cool and join. Because these solid crystals start at many locations, they grow until they eventually bump into other crystals. The boundary, where neighboring crystals meet, is not as strong as the crystal itself. When a metal bends or breaks, it is because the crystal boundaries slide or rupture. Metallurgists are constantly seeking to strengthen these boundaries.

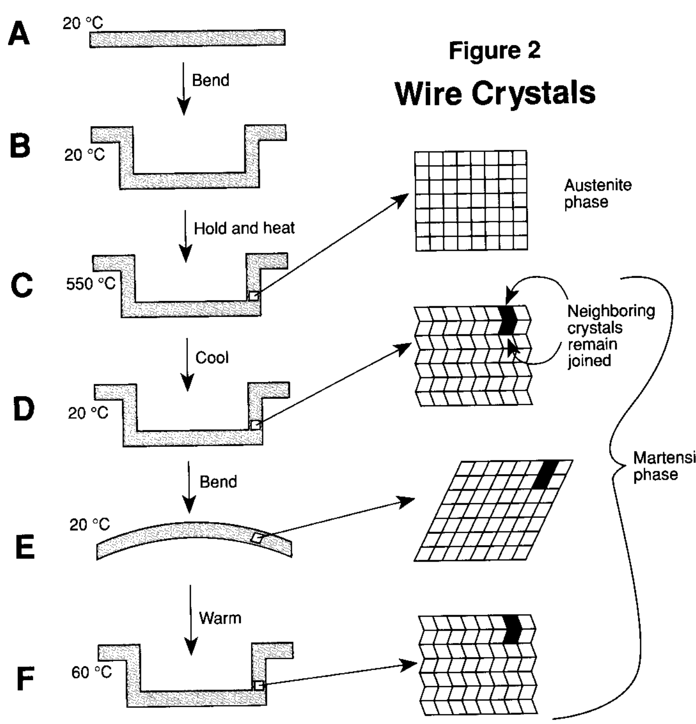
When you bend ordinary metal—such as the iron in a coat hanger—neighboring crystals slide past each other and then stay in their new positions.



Nitinol's unusual behavior is due to the fact that, when it is bent, each martensite crystal can deform to relieve the strain instead of sliding at the crystal boundaries.

In steps A, B, and C, the Nitinol wire is treated at high temperature to set the parent shape. When it is cooled, D, the phase changes from austenite to martensite. Because martensite crystals are slightly flexible, they can deform to accommodate bending of the wire, E, while remaining attached to neighboring crystals. When warmed, F, the martensite crystals revert to their undeformed shape, and the wire magically unbends.

Figure 2
Wire Crystals



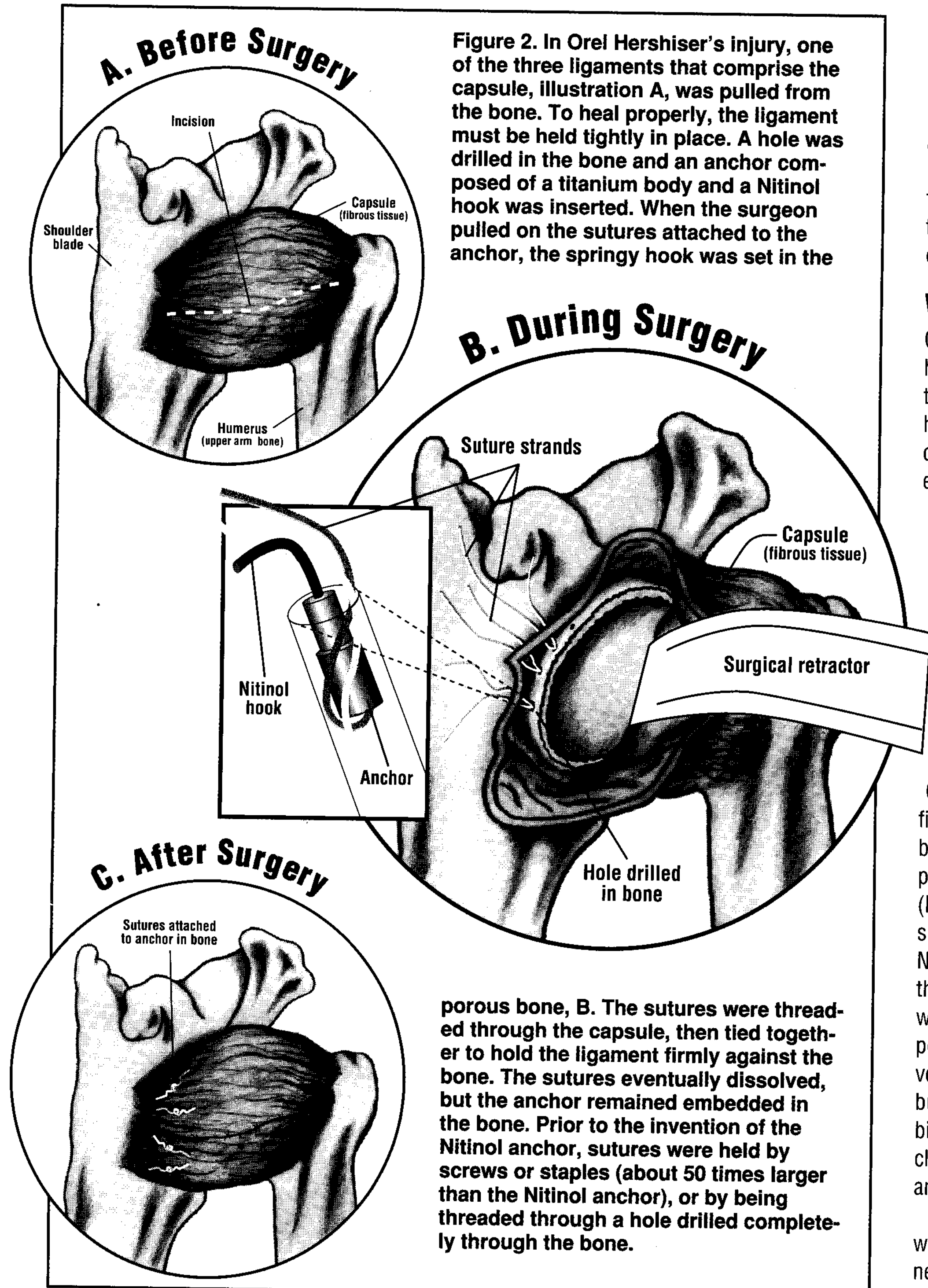


Figure 2. In Orel Hershiser's injury, one of the three ligaments that comprise the capsule, illustration A, was pulled from the bone. To heal properly, the ligament must be held tightly in place. A hole was drilled in the bone and an anchor composed of a titanium body and a Nitinol hook was inserted. When the surgeon pulled on the sutures attached to the anchor, the springy hook was set in the porous bone, B. The sutures were threaded through the capsule, then tied together to hold the ligament firmly against the bone. The sutures eventually dissolved, but the anchor remained embedded in the bone. Prior to the invention of the Nitinol anchor, sutures were held by screws or staples (about 50 times larger than the Nitinol anchor), or by being threaded through a hole drilled completely through the bone.

temperature (the transition temperature), the atoms in the crystals rearrange into the martensite phase. (Remember, there is no change at the visible level. The phase change occurs only at the atomic level.)

As the solid changes from the austenite phase to the martensite phase, the atoms within a crystal rearrange into a slightly different three-dimensional shape, though the crystal retains its original neighbors (see box, Crystals with good neighbors).

To see how this happens, let's examine NASA's Nitinol tweezers, shown in Figure 3. During its manufacture, the alloy's compostion (Ni–Ti ratio) was selected so that the transition temperature is 43 °C (110 °F). Before insertion, the Nitinol is in the martensite phase and the tweezers' tip is closed. At room temperature, the doctor bends the tips open, then inserts the tweezers into the ear canal and guides the tip to the foreign object. At the push of a button, electricity flows and the wire quickly warms up to slightly above body temperature. The thermal motion of the atoms increases and the atoms bump and push away from one another. At 43 °C the crystals are strained and, to relieve this strain, they revert to their austenite configuration, which restores the parent shape of the metal. As the tweezers tips change from the open (deformed) state to the closed (parent) state, they grab the object firmly, making it easy to remove.

What's Nitinol good for?

Once some early manufacturing problems had been solved in the late 1960s, the military began to use Nitinol couplers to join hydraulic lines in F-14 fighter planes. When cooled in liquid nitrogen the couplers expand to a large inner diameter, making them easy to slip over the hydraulic lines to be joined. On warming to room temperature, the coupler shrinks with great force to form a totally sealed joint. These couplers are still being used in the F-14 today.

The health profession is using Nitinol to simplify and remove risk from previously dangerous procedures, as illustrated by the Hershiser surgery. Cardiovascular surgeons often implant wire filters (which resemble birds' nests) in the bodies of patients who are prone to develop potentially fatal pulmonary embolisms (blood clots). At one time this was a major surgical procedure, involving large incisions. Now, by using Nitinol, a surgeon can deform the birdnest-shaped filter into a bundle of wires that can be inserted to the proper position through a catheter in the patient's vein. When released from the catheter, the bundle of wires springs back into its original birds' nest shape, ready to trap any blood clots. The patient, who required only local anesthesia, can go home the same day.

Do you wear braces? If the orthodontic wire in your mouth is Nitinol, you probably need to go to the orthodontist for readjustments far less often than a friend who wears the old-fashioned stainless steel braces. Your braces tend to remember their parent shape and, as your growing teeth deform them, they are always trying to revert to that shape.

An application of Nitinol with perhaps the greatest consumer appeal is in the manufacture of eyeglass frames. Conventional frames are always loosening, falling down your nose, or getting sat upon. Using Nitinol in the frame's bridge, top bar, and temples allows the frames to return to their parent shape upon warming.

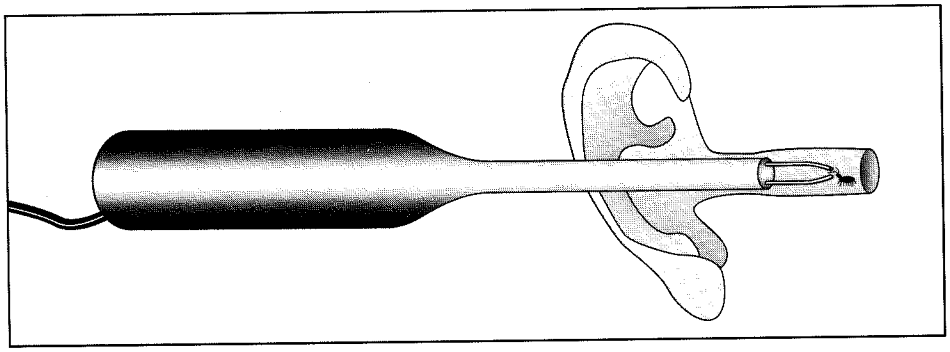


Figure 3: Automatic tweezers recently invented by NASA engineer Earl Angulo. The tips of the tweezers are made of Nitinol wire that is connected to an electrical circuit powered either by a power supply or by a battery in the handle of the instrument. When current flows, the tips are heated slightly and close on the foreign object.

Nitinol is also used in safety devices because of its unique sensitivity to heat. A Nitinol anti-scalding valve on the market can be inserted into water faucets and shower heads. The springlike apparatus is designed so that if the temperature of the water approaches 120 °F (49 °C) the water flow is automatically shut off. With more than 30,000 people (mostly children) receiving scald burns in the bath and shower every year in the U.S. alone, this device will certainly save a lot of pain and suffering.

Nitinol-based fire sprinkler systems are also available. The response time from fire to water release is significantly reduced from that of the older solder systems.

A toy now, an engine later?

In 1980 Dr. Wang left the military and started his own company, Innovative Technology International (ITI), to manufacture Nitinol and do research into possible applications. In 1985 ITI began marketing a toy called the Thermobile™, constructed of two pulleys and a single piece of Nitinol wire wrapped around the pulleys. One end of the Thermobile is inserted in 75 °C (167 °F) water. The single strand of Nitinol wire, passing through the hot water, contracts and tries to straighten out to its parent shape — a straight wire. The resultant torque forces the two pulleys to rotate. Thus the Thermobile converts heat energy to mechanical energy.

PHOTO: AMY MEYER PHIFER

The Thermobile is a simple loop of Nitinol wire mounted on two pulleys. If one pulley is dipped in hot water, one side of the loop tries to straighten, which makes the tension in the two sides of the loop unequal and spins the pulleys. In addition to being a charming toy, the Thermobile may be the world's simplest heat engine. Researcher Frederick Wang has constructed multiloop engines that produce useful power.

Can this type of system be adapted and used as a clean power source? After all, the resulting torque and force could theoretically generate electricity, turn flywheels, propel an airplane, or power a car. Research and experimentation on Nitinol-based engines is under way. ITI and Wang have designed several prototypes of Nitinol-based engines. Wang has demonstrated 40-watt Nitinol engines with internal hot water reservoirs.

Perhaps one day there will no longer be controversy about supposedly "clean" nuclear power plants; maybe our electricity will be generated by Buehler and Wang's incredible alloy. Hey, maybe the fenders of Dad's car will be made of Nitinol. This isn't so far-fetched — research and development on Nitinol car frames is also under way. So you get a little dent in the car? Just apply warm water, and no one, including Dad, will be the wiser.

Nitinol sources

Memory Metal is the latest kit produced by the Institute for Chemical Education. It consists of a booklet containing a brief discussion and description of the chemistry of Nitinol's shape-memory retention and about two feet of Nitinol wire in the form of the letters "ICE." You can experiment by deforming the wire and then heating it to above 80 °C (176 °F) to observe the recovery. Memory Metal (order number 91-011A2) is available for $12 from: Institute for Chemical Education, Department of Chemistry, University of Wisconsin–Madison, 1101 University Avenue, Madison, WI 53706-1396 (Phone: 608/262-3033; Fax: 608/262-0381).

If you would like a Thermobile, send a check for $22.00 to Innovative Technology International, 10747-3 Tucker Street, Beltsville, MD 20705.

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INSECT ARSENALS

by Charles Downey

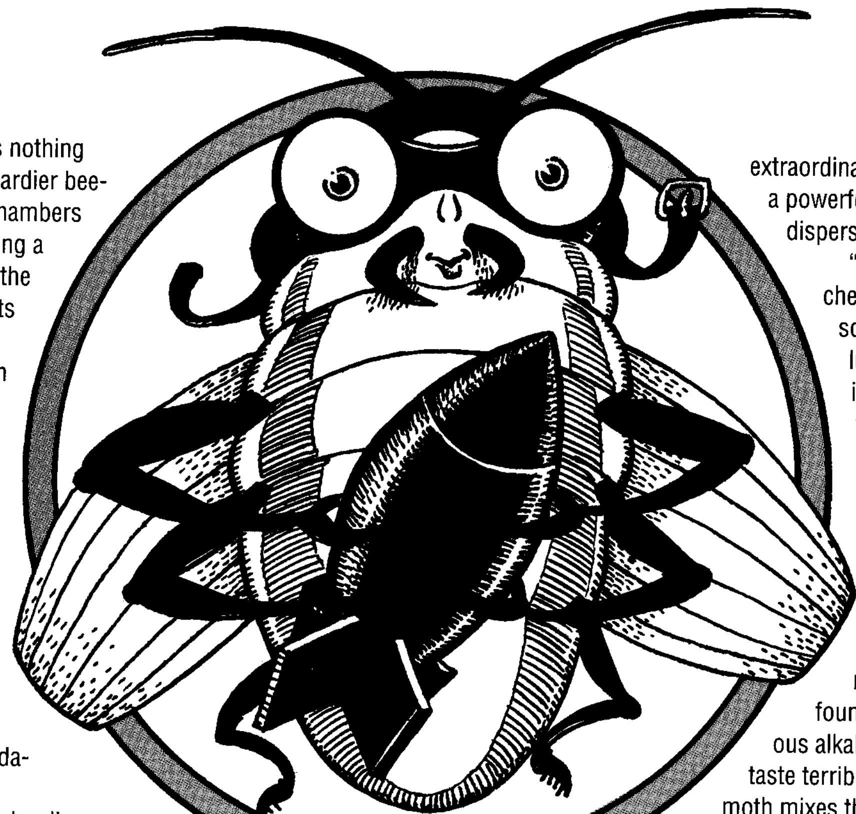


ILLUSTRATION: DAN SHERBO

In all of nature, there is nothing quite like it. The bombardier beetle has two separate chambers on its body, each containing a chemical. When attacked, the beetle releases the contents of those chambers, combines them, and uses them as a ·binary weapon . It shoots out a toxic spray that is also boiling hot at 100 °C. The beetle can fire its weapon like an army rifle — in single shots, or in rapid-fire bursts. Moreover, the beetle has a highly accurate aim with the deadly spray, and can turn and whirl to scorch several predators.

The defenses of the bombardier beetle were intensely studied by professor Thomas Eisner who, along with professor Jerrold Meinwald, are the founding fathers of a new and growing field of science known as chemical ecology. Also known as "the language of nature," chemical ecology studies how animals, plants, and microorganisms interact chemically in nature.

"Insects especially rely on chemicals for defense, to find mates, to find food, to combat disease, and to send danger signals," Dr. Eisner says. "Not only do insects produce the chemicals they need in their own bodies, they also take them from other sources like plants."

Experts say the chemical language of nature is extremely simple, delivering the most straightforward messages like "Come here!" "Go away!" or "Help!"

Drs. Eisner and Meinwald were awarded the 1990 Tyler Prize for their work. Administered by the University of Southern California, the Tyler Prize for Environmental Achievement carries a $150,000 award. Regarded as the world's authority on the chemistry used by insects, Dr. Eisner is the Jacob Gould Schurman Professor of Biology at Cornell University in Ithaca, New York. Dr. Meinwald is the Goldwin Smith Professor of Chemistry. Together, their work is regarded as an "elegant synthesis" of biology and chemistry. There are perhaps two dozen labs worldwide devoted to chemical ecology.

Other unusual creatures

Several other creatures related to insects use unusual chemical defenses. For instance, the whip scorpion shoots at enemies a spray containing 84% acetic acid. Some species of millipedes store deadly hydrogen cyanide in a harmless and protected form. But if there's an attacker, the cyanide is released. Research on another type of millipede isolated the chemical polyzonimine, which has since proven to be an extraordinarily potent insect repellent with a powerful camphor odor. Polyzonimine disperses whole swarms of ants.

"The study of insects and the chemicals they use also confirms some of the theories about evolution," Dr. Eisner says. "For instance, Darwin observed there was such a process in nature known as 'sexual selection.' That means females tend to pick, and mate with, the most genetically fit males available."

When Drs. Eisner and Meinwald studied one type of moth (*Utetheisa ornatrix*), they found the creature takes a poisonous alkaloid from plants to make itself taste terrible to birds and spiders. The moth mixes the alkaloid with its blood and lymph, and ejects it as a yellowish froth with a strange, unpleasant smell. The male moth uses that same chemical to manufacture its courtship compound, which it gives out as an aphrodisiac substance known as a pheromone. The female moth can tell from the pheromone how much of the protective substance her suitor has and how much he will transfer to her and her eggs during mating. That observation was the first chemical confirmation of Darwin's theory of sexual selection.

Courting rituals

Another confirmation was found when Meinwald and Eisner studied the courting rituals of a pyrochroid beetle that displays a cleft in his forehead to females. Mating follows if the female laps up the chemical contained in the cleft. Researchers found the male's cleft contains cantharidin, ($C_{10}H_{12}O_4$), a poisonous compound that protects beetle eggs against ants and other creatures of prey. If the male gets to mate with the female, he bestows on her and her eggs still

BOMBARDIER BEETLE

The bombardier beetle's defensive spray is hot and chemically irritating. The beetle would find it difficult to store the spray in this form, however. Instead, it stores the components and mixes them when needed to discourage a predator.

The beetle keeps its raw materials in two compartments. The first storage compartment contains a solution of hydroquinone, methylhydroquinone, and hydrogen peroxide, with the hydrogen peroxide in larger supply.

Hydrogen peroxide decomposes to form oxygen gas and water, and reacts with hydroquinones to form quinones and water. Normally both of these peroxide reactions are very slow. Enzymes, however, greatly increase the speed of chemical reactions without changing chemically themselves. That is why the beetle's second storage compartment contains a solution of the enzymes catalase and peroxidase.

When the beetle needs its defensive spray, it mixes the enzyme solution with the peroxide/hydroquinone solution in a reaction chamber. Because there is an excess of hydrogen peroxide, a mixture of products from both reactions builds up very quickly, almost explosively.

Many chemical reactions give off heat, but the decomposing hydrogen peroxide gets particularly hot, so much so that some of the water produced boils. This also heats the oxygen gas and, like any gas heated in a rigid container, it exerts pressure as it tries to expand. Eventually the pressure is high enough to force the reacting chemicals out of the chamber. This is accompanied by an audible "pop."

Dr. Eisner's research group has found that the spray is not ejected continuously, but in short pulses. This is because each burst of spray results in a lowering of pressure in the reaction chamber. The valve then closes until the pressure builds up enough to force it open again.

Gail Marsella

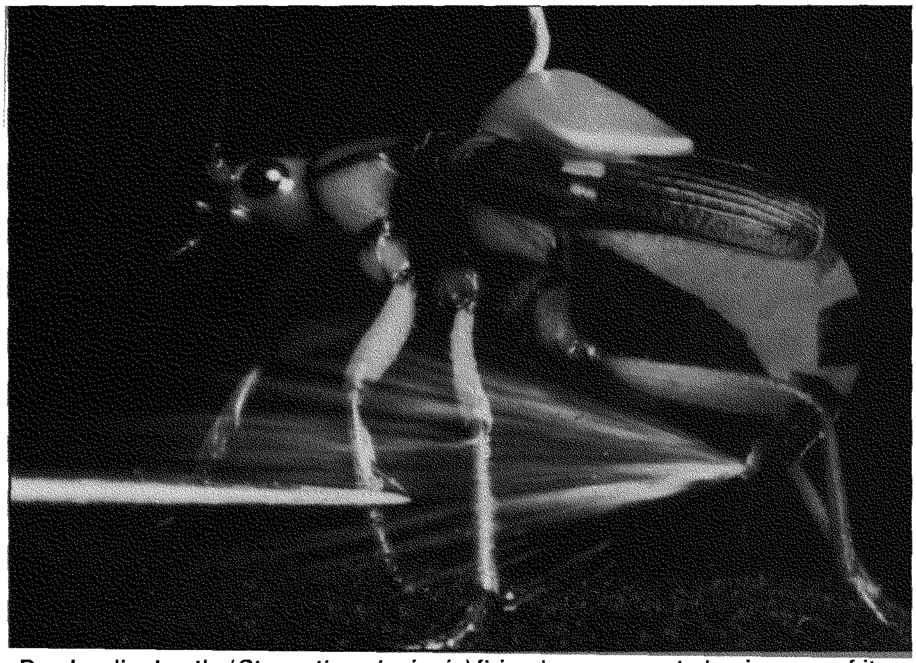
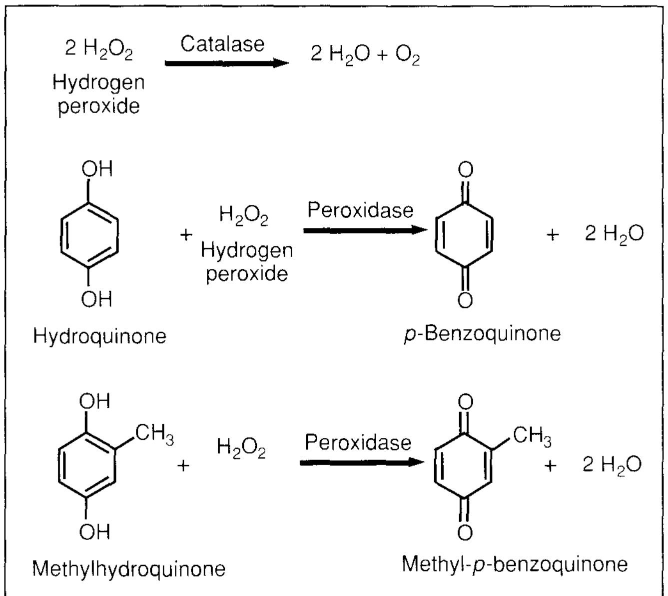
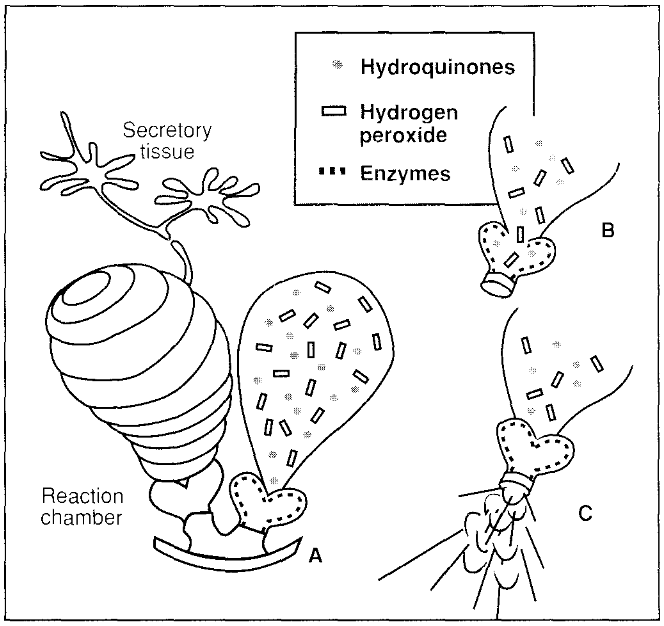


PHOTO: THOMAS EISNER AND DANIEL ANESHANSLEY, CORNELL UNIVERSITY

Bombardier beetle (*Stenaptinus insignis*) firing in response to having one of its legs pinched with forceps. The beetle is immobilized by being fastened to a wire hook with a dab of wax, seen at the top of the photo.





Mode of operation of the bombardier beetle's glandular apparatus. (A) The pair of glands, with compartments of one gland cut open. (B) Intake phase, when chemical precursors from the reservoir are passed into the reaction chamber. (C) Exhaust phase, when the explosion in the reaction chamber causes an ejection of spray. During a discharge the sequence (A)→(B)→(C) is repeated several times, engendering the pulsed emission that characterizes the discharges.

more cantharidin, supplementing what she initially obtained from the cleft.

"It's almost like he's showing her a fat wallet and saying, 'there's more in the bank where that came from," Dr. Eisner says. When the researchers removed all sources of the cantharidin, fewer than 20% of males managed to mate. However, 90% of males with access to cantharidin successfully mated.

"There are perhaps ten to fifteen million insects worldwide," says Dr. Eisner, "and perhaps one million have been described. Perhaps a few hundred have been chemically studied. There are tremendous benefits for humans in medicine, agriculture, the environment, and in evolutionary understanding. But, unfortunately, nature is disappearing before our very eyes."

A wealth of new medicines

To increase research, Dr. Eisner has suggested to the worldwide scientific community an idea he calls "chemical prospecting."

"I've called on the worldwide pharmaceutical industry to link up with Third World nations to prospect for new chemicals in all of nature," Dr. Eisner says. "Although insects are likely to be a rich source of antibiotics, including antifungal agents, I don't know of a single firm now screening insects for compounds that can be used. There's a whole wealth of new medicines waiting for the world, but we must first preserve nature, and biodiversity."

Dr. Eisner's proposal would include prospecting for chemicals among plant life, too. Experts estimate perhaps 5% to 6% of the world's plant life has been explored. About 40% of our current medications come from plants.

The concept calls for putting screening labs in the tropics where Third World nations have been unable to afford conservation programs — yet these very countries are the custodians of untold biotic wealth. Once the compounds are identified, they can be synthesized in labs. (NOTE: this concept is the basis for the recent movie *Medicine Man*, now available for rental on videocassette).

"Chemical exploration would provide a way to turn that untapped wealth into cash and jobs," Dr. Eisner says. "And that would, in turn, provide for the conservation."

Other researchers have turned to the oceans to listen in on the language of nature. Says John Faulkner, professor of Marine Chemistry at the Scripps Institute of Oceanography in La Jolla, California: "Research time is limited and expensive, so scientists look for creatures in the ocean — like sponges and algae — that appear to have no physical defense and can't run away. When we screen those organisms for bioactive substances, we come up with quite a bit."

"Will insects ever become as important a source for new compounds as microorganisms or plants?" Dr. Eisner asks. "Perhaps not. But there's no doubt that bugs have more chemical secrets up their shell-like sleeves than people ever imagined."

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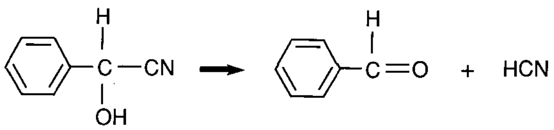
MILLIPEDE

The millipede *Apheloria corrugata* defends itself with hydrogen cyanide gas, an intensely poisonous substance. Cyanide itself would be very difficult for the insect to store safely, partly because it is a gas, and partly because HCN is so toxic. Instead, the millipede produces and stores a relatively harmless liquid compound called mandelonitrile in small, flexible compartments. Mandelonitrile does not dissolve well in water, so tiny droplets of mandelonitrile are mixed with water to form an emulsion.

When the millipede is threatened, muscular contractions squeeze drops of the emulsion out through a smaller compartment. As the drops pass through the smaller compartment, they pick up enzymes that catalyze the breakdown of mandelonitrile to hydrogen cyanide, HCN, and benzaldehyde.



The emulsion and enzyme mixture sticks to the outside of the millipede's body, and as the reaction progresses, benzaldehyde and hydrogen cyanide waft into the air. The benzaldehyde discourages attackers because of its strong, repellant odor, and the cyanide directly poisons them. Each millipede is capable of storing enough reactants to form, on the average, 0.2 mg of hydrogen cyanide, a relatively huge amount (sufficient to kill animals as large as mice), although it is rarely released all at once. Because the poison-producing reaction is rather slow, the millipede is protected for many minutes.

Gail Marsella

PHOTO: THOMAS EISNER, CORNELL UNIVERSITY

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Crazy Candies!

by Joseph Alper

Foaming at the Mouth

Mad Dawg™ is not your typical bubble gum. For one thing, it is noticeably sour when you first start chewing. But the real surprise comes after seven or eight chews, when brightly colored froth begins oozing out of your mouth. Though the effect is dramatic, the cause is a simple acid–base reaction.

The foam is a mixture of sugar and saliva, churned into a bubbly mess by carbon dioxide released when three of Mad Dawg's ingredients — sodium bicarbonate, citric acid, and malic acid — are mashed together in the moist environment of the mouth. In water, all three chemicals ionize. Citric and malic acids produce hydrogen ions, which react with the bicarbonate ion to produce water and carbon dioxide. The acids also stimulate salivation, providing the extra moisture needed to produce great-looking foam. Water-soluble food coloring creates a more colorful mess.

$$NaHCO_3 \longrightarrow Na^+ + HCO_3^-$$

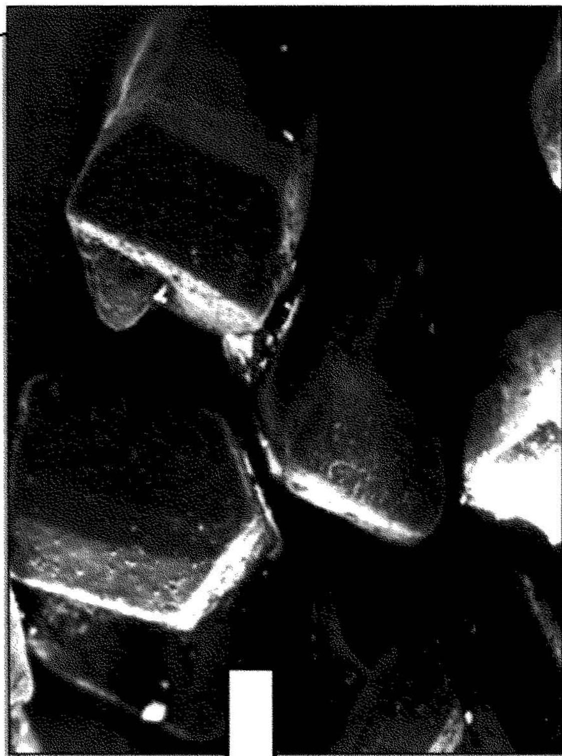
$$H^+ + HCO_3^- \longrightarrow H_2O + CO_2$$

When sodium bicarbonate dissolves in water, it separates into sodium ions and bicarbonate ions (top). When hydrogen ions from an acid mix with bicarbonate, the ions react to give water and carbon dioxide gas (bottom). You can duplicate this reaction by adding some lemon juice to baking soda (sodium bicarbonate).

The chemistry is straightforward, but Mad Dawg's creation was not a simple matter. In fact, early versions exploded as they came out of the candy-making machinery. The problem was keeping the acids and sodium bicarbonate from reacting before chewing begins. As solids, sodium bicarbonate and citric or malic acids do not react, but if the combined ingredients are exposed to even the slightest moisture, they dissolve and reaction begins. Alka Seltzer™, which fizzes because of the same acid–base reaction, is made by compressing dry, solid citric acid, sodium bicarbonate, aspirin, and flavoring ingredients into a tablet. When dropped in water, the ingredients dissolve and react. But Mad Dawg's colors and flavors are applied to the bubble gum core as aqueous solutions. How do they keep the ingredients from reacting before you chomp on the candy? If you closely examine the inside of a Mad Dawg, you may be able to discover the manufacturer's secret.

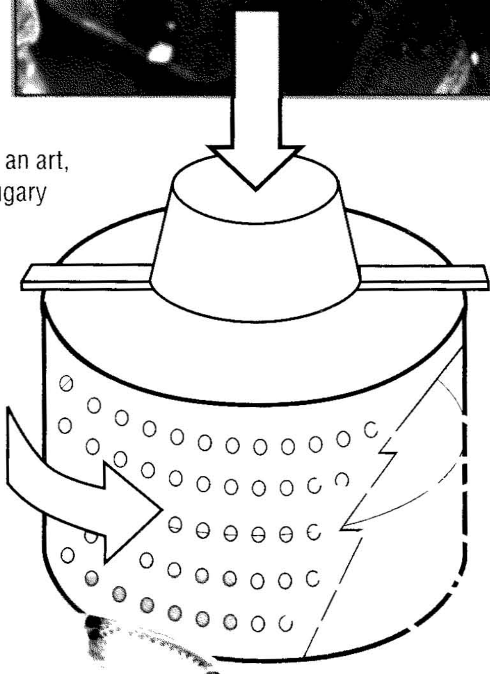
Cotton Candy

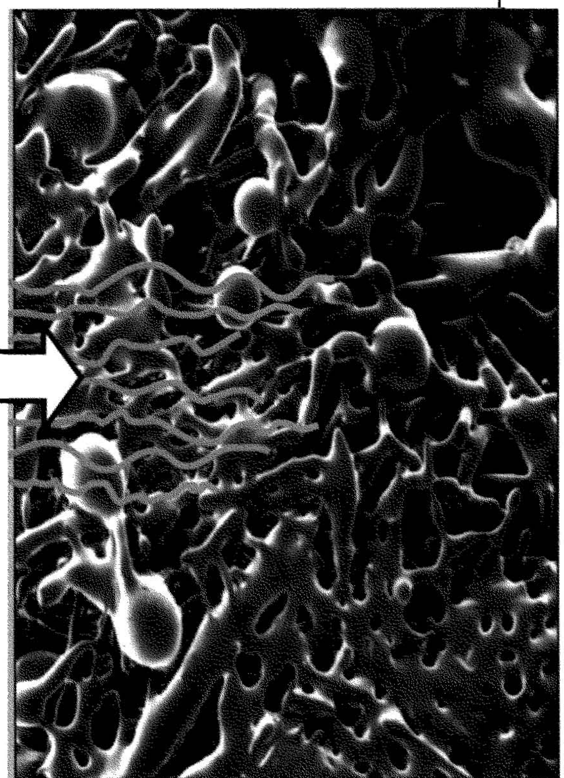
Ninety years ago, in 1903, inventors William J. Morrison and John C. Wharton created cotton candy. Their new confection was unveiled the following year at the World Exposition in St. Louis, which also saw the first ice cream cone, and it was a big hit among fairgoers. Today, cotton candy machines, little changed from Morrison and Wharton's, are spinning out millions of cotton candy cones worldwide in at least a dozen flavors and colors.



MICROGRAPH PHOTOS: ROBERT SHOEMAKER, TOWSON STATE UNIVERSITY ELECTRON MICROSCOPY LABORATORY

Cotton candy begins as crystals of ordinary sugar (top scanning electron micrograph) that are coated with a small amount of coloring and flavoring. The sugar is poured into a heated spinner where it melts at about 150 °C. The rapid rotation forces the liquid out through tiny holes in the wall of the spinner, and the thin streams of molten sugar freeze instantly when they hit the colder air. The results are delicious but unstable. When sucrose is finely divided it becomes hygroscopic—it readily absorbs moisture from the air. The bottom electron micrograph was taken one day after the cotton candy was made, and moisture has melted some of the strands into beads. Both micrographs are magnified 50 times.





Though making a beautiful cotton candy cone is considered an art, the process that produces the sugary cotton is straightforward. Flavored and colored sugar is poured into what's called the spinner head in the center of the machine. An electric heater melts the sugar while the spinner head rotates at several hundred revolutions per minute. The molten sugar shoots from small holes in the spinner head and solidifies into cotton floss as it hits the air. The whirl grip, a plastic netting material that lines the sides of the floss pan, catches the emerging threads. The cotton candy maker makes two passes around the floss pan with a paper cone, gently twisting the cone as 25 to 30 grams (about an ounce) of spun sugar collects on it. The biggest cotton candy machines can make 500 cones an hour.

If the cone of cotton candy is not sold immediately, it must be sealed in a plastic bag to keep it clean and dry. The fine threads of glassy sugar are very hygroscopic (absorb moisture from the air). If you place a piece of cotton candy on a dish, you can watch this happen. After some hours the floss will become moist and shrink as it dissolves in the water it attracts from the air.

PHOTO GOLD MEDAL PRODUCTS CO.

Super Sour

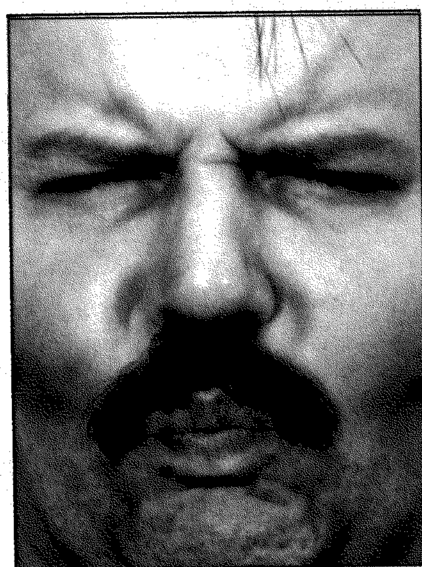
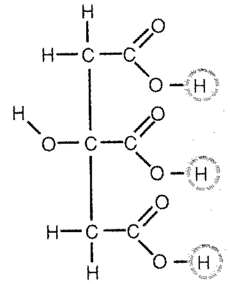


PHOTO: AMY MEYER PHIFER

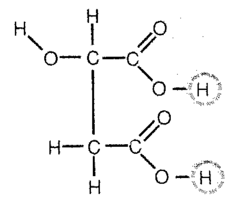
The expression "sourpuss" takes on a whole new meaning when you try a piece of Face Slammers™ bubble gum, the sourest of sour candies.

Your lips pucker, your eyes scrunch up, shivers run through your body, and there is a brief burning sensation on the sides of your tongue. The culprit is a coating of a mixture of malic acid and citric acid. Malic acid is the compound that gives apples their bite, and citric acid is the chief sour chemical in lemons and limes.

The human tongue has four kinds of taste buds — sweet, bitter, salty, and sour — each concentrated in a specific area. Sweet taste buds, for example, are on the tip of the tongue, whereas those that signal "sour" are on the sides. Substances that taste sour are always acids, which is why both citric acid and malic acid are sour. Citric acid is far more sour than malic acid, however, so there must be something, probably relating to a chemical's overall structure, that determines its sour power.



Citric acid



Malic acid

Beneath Face Slammer's sour coating lies a piece of bubble gum, made primarily of sugar, corn syrup, flavoring, softeners derived from vegetable oil, and synthetic rubber. Some bubble gums also contain chicle, the dried latex of the sapodilla tree, which grows in Central and South America and yielded the first material used widely in chewing gum.

Malic acid and citric acid are super sour compounds. They are used in novelty candies because they are natural products (lemon juice is about 6% citric acid) and are solid at room temperature. When dissolved in water, one or more of the hydrogen atoms (shown in color) leave the molecule as hydrogen ions, H^+.

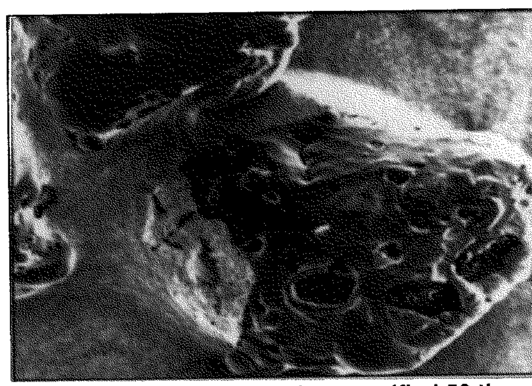
Pop Rocks

Fizzzz. Pop. Your tongue tickles, and your back teeth vibrate. POP. A tiny explosion tingles your front teeth. A highly carbonated cola? No, but close. It's carbonated candy. The fizzing and popping sensations occur when sugar-coated bubbles of carbon dioxide—the same gas that gives soda its pop—escape from the candy as the sugar dissolves in the mouth.

Pop Rocks™, Cosmic Candy™, and other carbonated sweets start out as a mixture of crystalline sucrose and lactose plus corn syrup, containing the sugars glucose, maltose, and dextrin. The candy maker adds a small amount of water to the cooking vessel filled with the sugars, heats the mixture to between 138 °C and 160 °C (280–320 °F) until the sugars dissolve, and then turns on a vacuum pump to evaporate most of the water. When the amount of moisture in the now viscous sugar mixture, called a melt, is between 1% and 5% by weight, the candy maker adds whatever flavors and colors are desired. So far, the process is similar to making ordinary sugar candy (see *Peanut Brittle*, *Chem Matters*, December 1991).

Next comes the critical step, worked out over two decades by researchers at the General Foods Corp. With the temperature no higher than 138 °C, carbon dioxide, CO_2, is pumped into the cooking vessel to a pressure of 34 to 51 atmospheres (500 to 700 psi), and the mixture is stirred for several minutes. This forces bubbles of carbon dioxide into the candy "melt." The proper adjustment of time, temperature, and pressure makes bubbles the right size — the largest are 300–350 microns in diameter — to give the final product a satisfactory pop. If the melt is carbonated at higher temperatures, the bubbles are smaller and the resulting candy fizzes more than it pops.

With the cooking vessel still pressurized, but with the stirrer turned off, the melt is allowed to cool. The candy hardens into a glassy (noncrystalline) solid with carbon dioxide bubbles frozen inside. The pressure is then released rapidly, cracking the carbonated candy into the small pieces that are packaged and sold.



MICROGRAPH PHOTO: ROBERT SHOEMAKER, TOWSON STATE UNIVERSITY ELECTRON MICROSCOPY LABORATORY

Pieces of Pop Rocks candy, magnified 50 times, show cavities that held compressed CO_2 gas.

How much CO_2 can be stored in the candy? You can measure the amount yourself (see Classroom Guide).

Joseph Alper *is a freelance science writer living in Ft. Collins, Colorado. He is the recipient of the American Chemical Society's Grady-Stack Award for excellence in interpreting chemistry for the public.*

REFERENCE

McGee, Harold. *On Food and Cooking: The Science and Lore of the Kitchen.* Charles Scribner's Sons: New York, 1984; 684 pages.

MYSTERY MATTERS

The Canine Cocaine Caper

by Bruce Goldfarb

In September 1992, customs agents at Miami International Airport saw something odd about the cargo coming off a flight from Cali, Colombia. Among the luggage were two dog kennels, the type used by people who travel with their pets.

They were ordinary carriers, made of sturdy fiberglass with a metal grille door. But the customs agents noticed something unusual—there weren't any dogs inside.

Why would somebody ship a dog carrier, at a cost of $138, and not ship the dog? Because the shipment originated in Colombia, an obvious suspicion was that somebody might be trying to smuggle drugs into the U.S. The agents inspected the containers inside and out. There were no false compartments. Drug-sniffing dogs didn't detect any suspicious odors.

Acting on a tip, the agents let the carriers continue to Los Angeles, where two men picked them up at the airport. The Federal Bureau of Investigation (FBI) tailed the men and arrested them for smuggling cocaine.

Where were the drugs concealed?

Laboratory analysis proved that the carriers were made of cocaine—the fiberglass itself was composed of almost 30% cocaine by weight. Each 23-kilogram (50-pound) carrier contained 7 kilograms (15 pounds) of cocaine, with a street value of $500,000.

"Cocaine plastic" is one of the newest methods drug smugglers have developed in the increasingly sophisticated game of cat-and-mouse they play with law enforcement.

Creating cocaine plastic on the shipping end is complicated. "The chemicals to make plastic can be bought, but you need lots of equipment, such as injection molding machines," said Special Agent Roger Martz, chief of the FBI's chemistry lab in Washington, DC. "It's pretty elaborate."

Nearly any plastic can be used, according to Roger Canaff, Deputy Lab Director at the Drug Enforcement Administration's (DEA) field laboratory in Washington, DC. "Just about all plastics, at some point, can easily be in the molten state," he says. "During the time it is in the liquid state, cocaine can be introduced into the mix."

In this case, smugglers first purchased pet carriers made by a legitimate Texas manufacturer. They removed all the metal fittings, made molds of the plastic cases, then fabricated new cases of cocaine-laced fiberglass plastic. With the original hardware installed, the carriers were virtually indistinguishable from the real thing.

Smuggling cocaine by traditional means—fast boats or low-flying planes—is dangerous and expensive. According to the FBI, it costs about $3,000 per kilo of cocaine, or a total of more than $40,000 for the quantity in the two carriers. But shipping the cocaine-laced carriers cost only $276 in air freight.

Usually the drug-sniffing dogs used by customs agents can smell cocaine. But, when encased in plastic, cocaine cannot be detected by the dogs. "Nobody really knows what the dog detects in cocaine," says Martz. "What might be

PHOTO: DOSKOCIL MANUFACTURING CO., INC.

The U.S. Customs Service uses dogs to check incoming freight for drugs , but when smugglers mold cocaine into plastic parts, the dogs cannot detect a scent.

happening is that the chemicals that the dog smells are being suppressed, held in by the plastic, and are not as volatile."

A simple chemical process

Getting the drug out of the plastic sounds complicated but is chemically a simple process (see box, Dissolving cocaine). "Retrieving the cocaine isn't particularly high-tech," says Canaff. "All it takes is a few readily available chemicals and basic knowledge of chemistry."

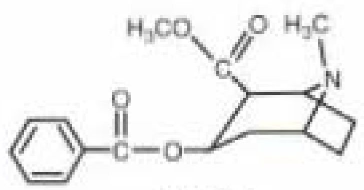
Although cocaine plastic can fool drug-sniffing dogs, U.S. Customs and law enforcement agencies have developed new techniques to detect the drug. A high-power vacuum is swept over the suspect plastic, and the air is forced through a paper filter. The filter is burned at a high temperature in an ion mobility spectrometer, which can classify many types of compounds. "Within a matter of seconds we can tell whether or not cocaine is present," says Martz. The feds have regained the upper hand, for now.

***Bruce Goldfarb** is an independent writer living in Baltimore, Maryland, who specializes in topics dealing with science and medicine.*

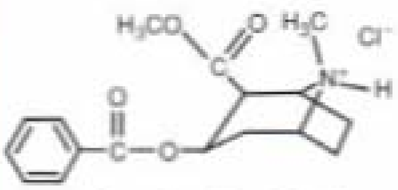
Dissolving cocaine

When the cocaine-containing plastic arrives at its destination, the smugglers retrieve the drug by a chemical process similar in principle to that used to extract the drug from the leaves of the coca plant.

In its natural state, cocaine is an alkaloid that is insoluble in water. "If it were soluble in water, it would wash out of the plant after the first rain," explains Canaff. The smugglers grind up the cocaine-containing plastic, then soak the powder in a dilute solution of hydrochloric acid, HCl. The acid reacts with the cocaine and changes it to cocaine hydrochloride, which is very soluble in water.



Cocaine



Cocaine hydrochloride

The cocaine hydrochloride dissolves, leaving the plastic particles on the bottom. The mixture is decanted (liquid is poured off carefully, leaving solid on the bottom) and filtered to remove the plastic.

"At this point, you can do one of several things with the cocaine hydrochloride solution," says Canaff. "You can let it sit until the water evaporates... the residue is cocaine hydrochloride salt. It's time-consuming, but it's one way to do it." Or it can be converted back to cocaine alkaloid, which drug users call "free base" or "crack."

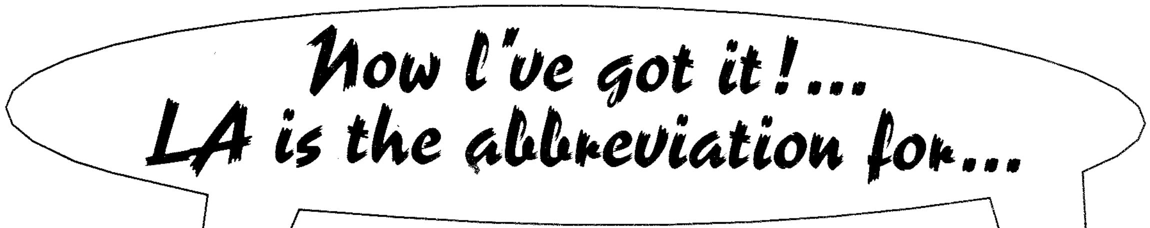
An alkali, such as sodium hydroxide, NaOH, or sodium carbonate, Na_2CO_3, is added, and this reverses the acid reaction and reforms cocaine. The solution is then shaken with an organic solvent, such as ether, which forms a separate liquid layer, on top of the water. The cocaine dissolves in the ether layer, which is then decanted to separate it from the water. When the ether evaporates, cocaine alkaloid crystals remain.

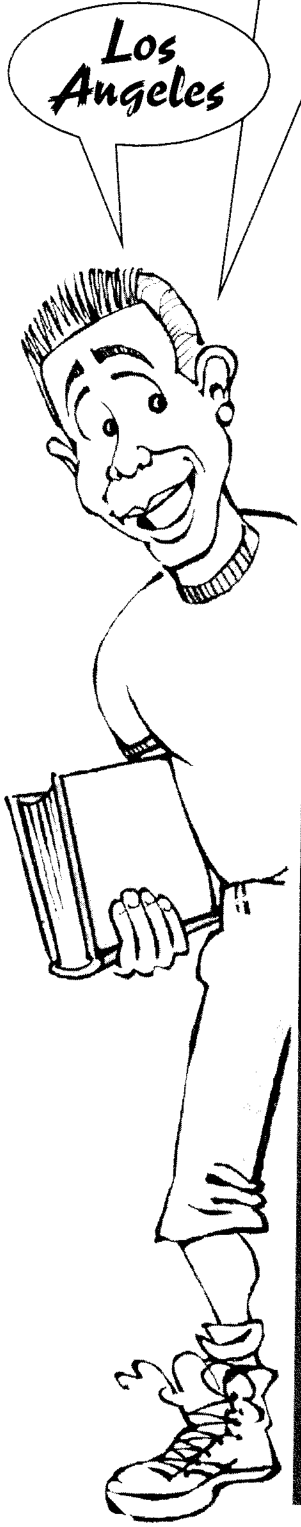
REFERENCE

Stinson, Stephen. "Cocaine Smuggled as Ingredient in Plastic." *Chemical and Engineering News*, Vol. 69, No. 27, July 8, 1991; p. 6.

Double Meaning

by Dorothy Mann Lamb, Chicago State University





Nonchemical meaning	Symbol	Chemical meaning (element)
Largest city in California	LA	lanthanum
1. The opposite of yes		
2. A prefix meaning "again"		
3. A serious lung disease		
4. Home state of Bill Clinton		
5. One of Santa Claus's favorite words		
6. Short for YMCA or YWCA		
7. Seventh note in the musical scale that begins "Do, Re, Mi..."		
8. West on a map		
9. Rogers & Hammerstein wrote a musical about this state		*(two elements)*

Now, rearrange the letters of the symbols to fill in the blanks below and spell what chemistry students like to do. You should use every letter at least once (including the letters in the example at the top of the table), and one letter more than once. Capital letters may be changed to lower case, and the two letters in a chemical symbol may be separated.

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Answers