

# CHEM **MATTERS**

FEBRUARY 2006

DEMYSTIFYING  
EVERYDAY CHEMISTRY



**Digital Photography  
and Printing**

**Also Inside:**

**Your vintage car could  
rust away!**

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# Question From the Classroom

By Bob Becker

**Q:** My parents just bought new tires for their car, and the salesman told them they should inflate them with nitrogen gas instead of regular air. Is paying extra for nitrogen gas in car tires worth it?

**A:** This is a very intriguing question. My initial reaction is to assume that salespeople are just looking for one more way to squeeze a buck out of gullible customers. After all, air is 78% nitrogen. Why would inflating your car tires with pure nitrogen make that big of a difference? But this question is particularly tricky for me because it pertains to chemistry, which I have taught for the past 22 years. And cars, though I have driven for the past 29 years, I know next to nothing about. I do, however, know where to go for advice about cars: the famous Magliozzi Brothers, Tom and Ray, a.k.a. "Click and Clack, the Tappet Brothers" (Their NPR radio show "Car Talk" is a weekend favorite.)

Their Car Talk website (<http://www.cartalk.com>) reveals that they have addressed the nitrogen question quite a few times, most recently in April 2005. Their advice: For the average driver, filling tires with nitrogen gas is not worth the added cost. Still, for a chemist, the "nitrogen in tires" question has an intriguing mix of silly and plausible claims swirling about it.

Race car drivers do it. Why? Air contains about 78% nitrogen, 20% oxygen and small quantities of other gases, including, most importantly, water vapor. On humid days, air contains considerably more water

vapor than it does on dry days. What's more, because of the extensive hydrogen bonding, water vapor deviates quite dramatically from ideal gas behavior. Thus, as it heats up, an air-filled tire tends to show much more inconsistency in pressure changes than does a tire filled with pure nitrogen gas. In car racing, contact between the tire and the track is everything, and a fraction of a psi (pounds per square inch) in the tire can make the difference between winning, losing, or spinning out of control. NASCAR mechanics figured out years ago that the pressure in a nitrogen-filled tire was far more consistent and reliable than the pressure in air-filled tires. Does that necessarily mean that the average Joe or Jane on the street should swap out the air in their tires for nitrogen gas? Is it worth spending the extra money? Again, probably not.

A large number of web sites disagree. But, consider this: These sites tend to be the ones selling nitrogen. As such, the information they offer should be scrutinized and not merely accepted as factual.

One argument is that nitrogen is far less reactive than oxygen and thus does less damage to the inside of the tire. This all may be true, but it has been my experience that tire treads wear off long before any kind of

deterioration from the inside could make a difference. Maybe nitrogen causes less oxidation of the wheel rims? But again, is this really even an issue?

They also contend that nitrogen-filled tires dissipate heat more quickly and thus run at a lower temperature. Unless this effect can be attributed to the water vapor, it makes very little sense, since nitrogen and oxygen have very similar thermal conductivities (0.02583 and 0.02658 W/mK respectively) and specific heat capacities (29.1 and 29.4 J/molK, respectively).



COREL

All the same, one of their more convincing arguments pertains to nitrogen's ability to maintain tire pressure. Nitrogen reportedly leaks out of tires more slowly than air. If you have discussed Graham's law in chemistry class this year, then you would probably expect the opposite to be true. Because nitrogen has a somewhat lower molecular weight than oxygen, its average molecular velocity should be greater and it should therefore escape or effuse through a small hole more readily. But effusion has to do with the passing of a gas through a small opening into a relative vacuum.

For the leaking out of a gas through a thick permeable layer of rubber, there is something else to consider. Molecular size and polarity play important roles too.

Gas permeability of rubber is believed to involve dissolution of the gas in the polymer, diffusion through the thickness of the rubber, and loss on the other side. The N-N bond is much shorter than the O-O bond, and the highest-energy electrons of O<sub>2</sub> are more polarizable than for N<sub>2</sub> (O<sub>2</sub> has a higher boiling point than N<sub>2</sub> for much the same reason). The greater polarizability of oxygen should make it slightly more soluble than nitrogen in rubbers. (For example, oxygen is more soluble in organic solvents than is nitrogen.)

This would mean that a nitrogen-filled tire should hold its pressure longer than one filled with air. How much longer? Here the websites disagreed, and it is important to note that not one of the commercial websites actually cited any scientific studies in their arguments.

An issue that far outweighs the nitrogen issue is this: An estimated 80% of the tires on the road today are not properly inflated; they're either underinflated or overinflated. Both conditions can shorten the lifetime of a tire.



MIKE CIESIELSKI

Underinflation lowers gas mileage and over inflation can dangerously lower the amount of traction your car has on the road. Drivers

should check their tire pressure every month or so, and add or remove air as needed. ▲



MIKE CIESIELSKI

## Question From the Classroom

2

Is paying extra for nitrogen gas in car tires worth it?

## ChemSumer

### The Chemistry of Digital Photography and Printing

4

Once upon a time, people put stuff called film in their cameras. First, they paid for it. Then they took photos, but couldn't view them on a screen. No deleting, no computer editing—they paid for strangers to develop every miserable photo, hoping that a few were OK! So primitive! So last-century!



## ChemMystery

### Real or Fake? The James Ossuary Case

8

Is it a priceless artifact? A bone box with a controversial inscription, is put to the test—a test that includes <sup>18</sup>O isotopic analysis.

## Super Fibers

11

Carbon nanotubes could be the key to spinning the future's hottest threads.



## Salting Roads: The Solution for Winter Driving

14

In northern parts of the United States, salt is the winter miracle that keeps life moving. But after the ice is cleared, you'll find crystals of it on the ground or coating the undersides of cars. What's the chemistry

involved?



MIKE CIESIELSKI

## Flaking Away

17

From Ferraris to Ford Pintos, nearly every car fights a losing battle with rust.

## Chem.matters.links

20

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FIND YOUR COMPLETE  
TEACHER'S GUIDE FOR THIS ISSUE AT  
[www.chemistry.org/education/chemmatters.html](http://www.chemistry.org/education/chemmatters.html)



# The Chemistry of Digital Photography and Printing

***Once upon a time, people put stuff called film in their cameras. First, they paid for it. Then they took photos, but couldn't preview them on a screen. No deleting, no computer editing—they paid strangers to develop every miserable photo, hoping that a few were OK! So primitive! So last-century!***



**By Brian Rohrig**

Imagine needing eight hours to take a single photograph! That's how long it took French scientist and inventor Joseph Niepce to take the world's first photograph in 1826. And the end result didn't win any prizes—it was a grainy image of some buildings viewed from a third-floor window. We have come a long way since then! Today, any amateur photographer can produce a glossy full-color photo in a matter of minutes using a digital camera and computer. In just the past 10 years, digital photography has taken the world by storm, threatening to do to film what the DVD has done to video.



The world's first photograph!

Most of your family photos were probably taken the old-fashioned way, with film that had to be taken to a photo shop to be developed. There is a fascinating bunch of chemistry involved in this process. All photographic film is coated with a thin layer of a silver halide compound, such as silver bromide ( $\text{AgBr}$ ). When light strikes this layer, an image is recorded on film, which is made visible during the developing process. If you have ever been inside a darkroom, you have probably seen all sorts of mysterious chemicals such as developers, fixers, and baths. Even if you don't

quite know how it all works, you can still appreciate the fact that a lot of chemistry goes into developing pictures.

Does digital processing mark the end of chemistry in photography? There is actually plenty of fascinating chemistry going on—it's just on a much smaller scale.

## Sensing light

All cameras work by focusing light through lenses to create an image. A conventional camera records this image on film. A digital camera records this image on a permanent part of the camera known as a sensor. A typical sensor in a digital camera measures only 4.4 mm × 6.6 mm. This is about the size of a fingernail.

Sensor technology has enabled manufacturers to make digital cameras so small they can even be incorporated into cell phones. Similar sensor devices are used in fax machines, scanners, copy machines, and bar code readers at the grocery checkout.

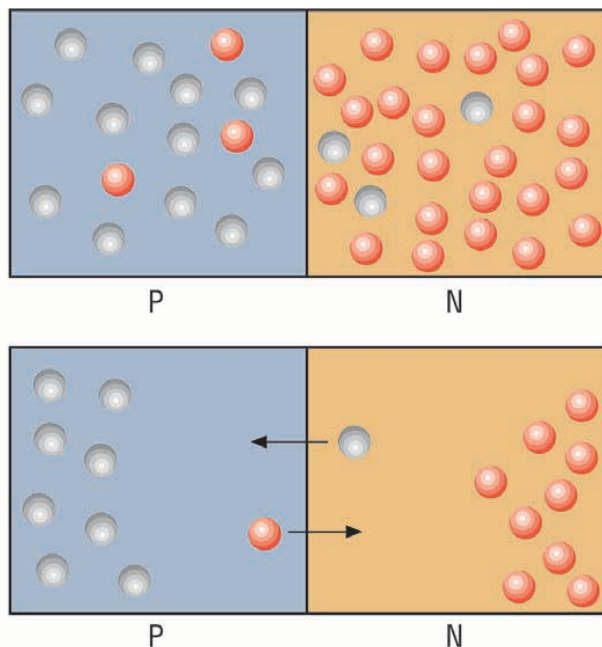
The sensor is a semiconductor. Silicon is the material of choice for most semiconductors. This is ironic because silicon barely conducts electricity at all in its pure form. But

if a small amount of impurity is added, through a process known as doping, then silicon becomes a fair conductor of electricity.

The sensor in a digital camera comprises many tiny semiconductors known as diodes. Diodes allow current to flow in one direction, but not another. Diodes are composed of two different types of doped silicon layers sandwiched together. One type of silicon is doped with phosphorus or arsenic. Both of these elements contain five valence electrons. Because silicon atoms only have four valence electrons, the doping agents provide the extra electrons that move throughout the material. With its excess of electrons, this type of silicon is known as *n*-type, with the “*n*” referring to the negative charge resulting from the free electrons.

Another type of silicon is doped with either boron or gallium, which only have three valence electrons. These doping agents create a deficiency of electrons in the structure, since silicon atoms have four valence electrons. This electron deficiency creates electron “holes” in the structure. Silicon doped with these deficient atoms is referred to as *p*-type silicon, with the “*p*” standing for the positive charge resulting from the deficiency of electrons.

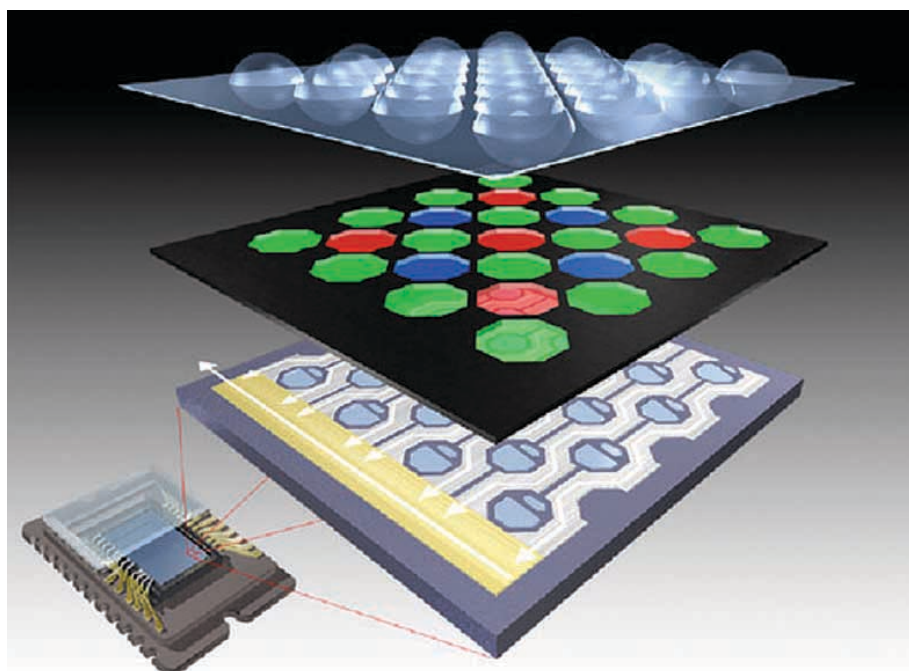
When placed together, these two types of silicon form a diode, the one-directional conductor described above. Think of a diode as a one-way street for electrons. At the *p*-*n* junction, a positive charge builds on the *n* side, and a negative charge on the *p* side until the internal electric field counteracts the tendency of the electrons to fill the holes. The internal electric field then permits current to pass in one direction.



As more and more holes are filled with electrons, a region, neither *P* nor *N*, forms, called the depletion zone. Holes are shown as . Electrons are shown as .

## Photosites

Each diode in a sensor is a *photosite*. Each photosite represents one picture element—better known as a pixel. The greater



SuperCCD SR structure diagram, one microlens, one color filter, two photodiodes per photosite.



erally, each image sensor can record 256 different shades of gray, ranging from pure white to pure black.

either a red, blue, or green filter is placed over each photosite on the sensor of a camera. The most common pattern is known as the Bayer pattern, which alternates a row of red and green filters with a row of blue and green fil-

the number of pixels, the greater the resolution and overall quality of the pictures you take. For example, a typical digital camera may have a resolution of  $640 \times 480$  pixels, for a total resolution of 307,200 pixels. The best digital cameras on the market today have a resolution of more than 10 million pixels (10 megapixels). For comparison, you should take pride in your personal sensor. The human eye contains 120 million pixels!

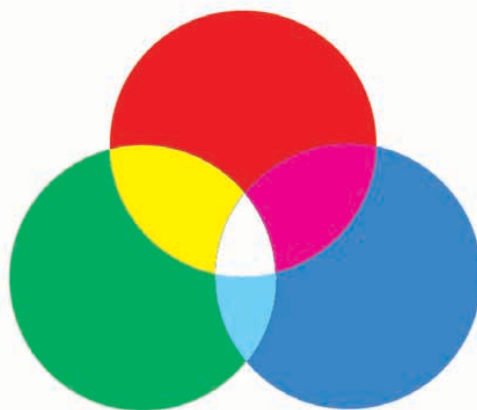
The pixels of any photo can be clearly seen through the low power of a microscope. The larger the pixel size in a photo, the poorer the quality, as larger pixels mean fewer pixels within a certain area. If you compare a normal color photo with a newspaper photo, you can see a huge difference in pixel size. Newspaper photos will have larger pixels, representing poorer quality.

When you take a picture with a digital camera, each tiny photosite on the sensor is exposed to light. When a photon is absorbed by the semiconductor, it promotes an electron to a higher energy level. What this means is that the high-energy electron acts like an electron that was added by doping: It is free to move about the semiconductor. Normally, the electron would just relax back to its lower-energy state. However, if it is near the *p-n* junction, it is attracted to the positive side, and migrates there, where it is collected.

As more photons strike a photosite, more electrons are knocked free. The greater the intensity of the light that strikes a photosite, the more electrons accumulate. A useful analogy is to think of the photosite as a tree, the photons as balls that you throw into the tree, and the electrons as leaves on the tree. Suppose that every time you throw a ball into a tree, a leaf is knocked loose. The more balls that you throw into the tree, the more leaves will accumulate on the ground below. A photosite that has been exposed to very bright light will contain far more electrons than one that has been exposed to dimmer light. Gen-



Information from photosites is converted to digital form and stored on memory cards for later retrieval.



## Seeing in color

So then, how do digital cameras take color photos, if the sensors can only record shades of gray? The trick is to use filters, that combine to produce any color imaginable. Most cameras use the 3-color system to produce color. The three primary light colors are red, green, and blue. Together, these three colors make white. Any other color can be produced by mixing together various shades of these three colors. To accomplish this feat,

ters. This configuration gives you twice as many green filters as blue or red. Because the human eye is not sensitive to all three colors equally, extra green filters must be used to produce the best color for our eyes.

Next, the information at each of these photosites is converted to digital form. By themselves, electrons that accumulate at each photosite do not represent digital information that can be read by your computer. So every digital camera carries its own built-in computer that converts information to digital form and stores it on your memory card.

## Printing

Once an image is recorded digitally by a camera and downloaded onto a computer, it can be printed. Or, it can be manipulated using software on a computer and then printed. The ability to choose, alter, and crop photos on screen before printing gives even a casual photographer unprecedented power to print only the images they want.

There are two basic types of printers that can print photos: laser and inkjet. The laser printer works by using static electricity. The underlying principle involves positively charged toner sticking to negatively charged paper, since opposite charges attract. A laser



beam projects a negatively charged image of whatever is to be printed onto the light-sensitive drum. The drum is then coated with positively charged toner, which is attracted to the negatively charged image on the drum. An analogy would be writing a message on the outside of a coffee can with glue, and then rolling it in flour. The flour will stick to the glue but not to the “unglued” parts of the can.

A piece of paper then passes over a charged roller, giving it an even stronger negative charge than the drum. The drum then rolls over the sheet of paper. The strongly negatively charged piece of paper pulls off the positive toner from the drum. Finally, the paper passes through a pair of heated rollers known as the *fuser*, which fuses the toner to the paper. After the paper attracts the toner from the drum, a discharge lamp bathes the drum in bright light, erasing the original electrical image.

Color printers work the same way, except the above process is repeated four times. Four types of toner are used: cyan (bluish), magenta (reddish), yellow, and black. By combining tiny dots of these four colors, nearly every other color can be created.

A photocopier works according to the same basic principle, except the electrostatic image that forms on the drum is formed by bright light that reflects off the paper to be copied. The drum is manufactured with a photoconductive material on its surface that makes it sensitive to light. White areas of the paper are reflected onto the drum. The black ink on the paper to be copied absorbs light, so parts of the drum do not receive an electrical charge. These uncharged parts of the drum will form the photocopy. Just like in a laser printer, the negatively charged toner is attracted to the positively charged image imprinted by light on the drum. A strongly positively charged piece of paper then attracts the toner from the drum. Your copy is com-

plete once it passes through the heated rollers of the fuser.

Inkjet printers, as the name implies, work by spraying tiny droplets of ink onto the surface of the paper. Each drop is very tiny, being only about 50–60 micrometers in diameter. A micrometer ( $\mu\text{m}$ ) is a thousandth of a millimeter. A human hair has a diameter of

about 70  $\mu\text{m}$ . There are two main types of inkjet printers on the market today. Bubble jet printers use heat to vaporize ink to form a bubble. This expanding bubble forces some of the ink onto the paper.



employed in a color printer. Other types of photo printers use a dye sublimation technique. Sublimation is the process of changing phase from a solid to a gas, skipping the liquid phase altogether. Heat is used to vaporize solid dyes, which permeate the paper before they return to the solid form. Thermal autochrome photo printers require the use of special paper that already contains the ink. A print head delivers various amounts of heat to the paper, causing various pigments to appear.

Amazingly, experts agree that digital photography is still in its infancy. We will no



**Inkjet printers work by spraying tiny droplets in ink on the surface of the paper and tend to produce better quality photos.**

When the bubble pops, a vacuum is created, causing more ink to flow from the cartridge into the print head. A piezoelectric printer works using piezo crystals (such as quartz). Piezoelectric crystals generate an electric field when distorted, but conversely, they can be distorted by an electric field. Thus, to get the nozzle to deform and eject the ink, an electric field is applied. This electric charge causes the nozzle to vibrate, forcing ink out on the paper.

Digital photos can be printed using either laser or inkjet printers, but inkjet printers tend to produce better quality photos. An inkjet photo printer will generally use six colors as opposed to the four that are normally

doubt see huge advances in digital quality and convenience in the near future. Will digital cameras completely replace conventional cameras? There are photographers who remain devoted to the artistic and visual effects of developed film and darkroom processing. For most of us, it's nice to know we have plenty of options available for recording lasting images of our big moments. And it's all due to—you guessed it—chemistry! ▲

**Brian Rohrig** teaches chemistry at Jonathan Alder High School in Plain City, OH. His most recent *ChemMatters* article “There’s Chemistry in Golf Balls” appeared in the October 2005 issue.



## Real or Fake? *The James Ossuary Case*

By Lois Fruen

**C**SI (criminal scene investigation) is not limited to murder. Recently, a crime team was assembled to examine a controversial and potentially priceless bone box and black stone tablet. Although the bone box may have once held skeletal remains, the team was not interested in DNA or fingerprint evidence. They focused on a grimy buildup, called patina, on the surface and in the inscriptions of the box and tablet. If proven to be fake, the patina could expose a forgery ring that has faked inscriptions on ancient objects found in museums all around the world.

The inscription on the bone box claims that it once held the bones of the brother of Jesus, while the tablet reports ancient repairs to Solomon's Temple in Jerusalem. Too good to be true? The Israel Antiquities Authority thinks so. But what did the crime team find?

Dr. Elizabetta Boaretto at the Weizmann Institute radiocarbon  $^{14}\text{C}$ -dated the tablet, using samples of patina from the inscription. Patina is the coating that builds up on ancient objects over long periods of time. The main component of the patina in the inscription is calcium carbonate ( $\text{CaCO}_3$ ), called calcite by geochemists. Calcite contains carbon, which can be  $^{14}\text{C}$  tested. Dr. Boaretto reported that the patina dates to 390–200 BC. This makes it tempting to declare the tablet authentic, but  $^{14}\text{C}$  dating is not enough to prove it is real. Expert forgers know that scientists use  $^{14}\text{C}$  dating to authenticate pieces, so they concoct patinas using ancient carbon (charcoal) found at archaeological digs. Dr. Boaretto reported that  $^{14}\text{C}$ -dating the bone box would not provide any better proof of authenticity than she obtained for the tablet.

### Carbon Dating

**Plants and animals take in small amounts the radioactive isotope  $^{14}\text{C}$  when alive. When an organism dies, replenishment of  $^{14}\text{C}$  stops and  $^{14}\text{C}$  steadily decreases at a known rate. The longer the organism is dead, the less  $^{14}\text{C}$  remains. One important fakery note— a pencil made yesterday from a tree cut down 2000 years ago will appear to be 2000 years old. But a tree cut down last year will not!**

Above: Bone box that may have held the bones of the brother of Jesus.



Next, Professor Yuval Goren at Tel Aviv University examined the tablet and the bone box. He tested hardness and density and did microscopic analysis of the mineral composition. He determined that the tablet is greywacke, a stone found in western Cyprus and northern Syria, not Israel. Because the tablet is supposed to be from the 9th century



Dr. Avner Ayalon from the Geological Survey of Israel examines the controversial bone box.

BC, it seems less likely that imported stone would have been used instead of local stone. With further investigation, Professor Goren found that the surface patina is a silicate that firmly adheres to the surface. He pointed out that it was unlikely that a silicate patina formed in the calcite environment of Jerusalem. Even more suspicious, the patina in the inscription is different from the surface patina. It is calcite and soft enough to be easily removed with a toothpick. This softness is a hallmark of recent patina formation. He concluded that the inscription was added in recent times.

Professor Goren also analyzed the bone box and determined that it was made of native limestone ( $\text{CaCO}_3$ )—a stone that was commonly used to make bone boxes in the 1st century AD. That finding and his analysis of the surface patina convinced him that the box is genuine. It was the patina in the inscription that concerned him. On close inspection, he found the inscription cut through the surface patina, so he was suspicious that it had been faked in modern times.

Dr. Avner Ayalon from the Geological Survey of Israel took the investigation further. Using mass spectroscopy, he analyzed the oxygen isotope composition ( $\delta^{18}\text{O}$ ) of patina from both the bone box and the tablet. Oxygen isotope analysis measures the ratio of  $^{18}\text{O}$  to  $^{16}\text{O}$  in a sample, compares the ratio to a standard, and then expresses the finding as per

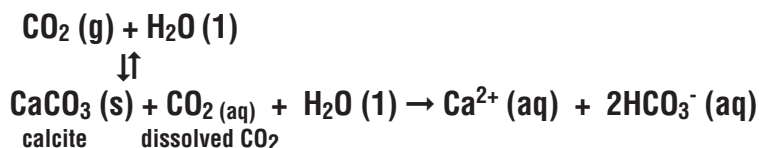
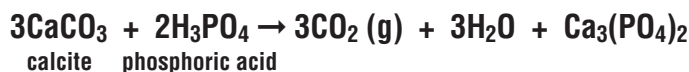
mil  $\delta^{18}\text{O}$ . In this notation, the lower case Greek letter delta ( $\delta$ ) signifies the relationship between the measured  $^{18}\text{O}$  and the  $^{18}\text{O}$  found in a standard. You can think of the delta value as the number of atoms per 1000 that the heavy isotope in the sample differs from the heavy isotope in the standard. To calculate a value, investigators use this formula:

$$\delta^{18}\text{O} = \left[ \left( \frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{standard}}} \right) - 1 \right] \cdot 1000$$

To find the  $\delta^{18}\text{O}$ , Dr. Ayalon reacted samples of patina with phosphoric acid ( $\text{H}_3\text{PO}_4$ ). This reaction produces  $\text{CO}_2$  gas, seen in the reaction below. The  $\text{CO}_2$  gas was ionized in the mass spectrometer, and then the

were between  $-4.1$  and  $-6.7$  per mil  $\delta^{18}\text{O}$ . These matched results for surface patina on the bone box in question. But,  $\delta^{18}\text{O}$  readings of patina from the inscription were between  $-5.8$  and  $-10.2$  per mil  $\delta^{18}\text{O}$ , with all but one of the readings falling outside of the acceptable range. He concluded that the box itself was real, but the inscription was forged.

Oxygen isotope analysis was the nail in the coffin for the bone box. It convinced Dr. Ayalon that the inscription was forged. The reason had to do with the temperature at which the patina in the inscription formed, which he determined from  $\delta^{18}\text{O}$  values. Natural calcite patina forms in much the same way crusty scale slowly builds up in hot-water pipes and inside kettles, sealing oxygen isotopes in as the patina dries. The process of calcite patination starts when groundwater picks up  $\text{CO}_2$  from air trapped in soil. When this  $\text{CO}_2$ -rich



oxygen isotopes were separated by mass by a strong magnetic field.

Dr. Ayalon compared  $\delta^{18}\text{O}$  for patinas on the bone box to  $\delta^{18}\text{O}$  of patinas from 1st century AD bone boxes that he knew were authentic. He found  $\delta^{18}\text{O}$  of authentic boxes

groundwater comes in contact with calcite, it dissolves it. Although calcite is not very soluble in pure water, the higher the concentration of dissolved  $\text{CO}_2$  in water, the more calcite will dissolve, shifting the equilibrium to the right.

When calcite-rich groundwater is exposed to air in a burial cave, the equilibrium shifts back, releasing  $\text{CO}_2$  gas into the cave and precipitating calcite.

If the patina on the bone box is authentic, the patina could have formed in one of two ways. First, it could have recrystallized from water that seeped into the burial cave. Water entering the burial cave would have absorbed  $\text{CO}_2$  gas from the cave environment, formed a thin film of water on the bone box, and reacted with the surface. (This reaction is the same as above because the box is made of limestone,  $\text{CaCO}_3$ ). When the film of water evaporated, it would have left behind a white film of calcite patina on the surface of the box. However, if the bone

**The Reason  $^{18}\text{O}$  is concentrated in the calcium carbonate relative to water is because of quantum mechanical effects: The carbonate has more vibrations whose energies depend on the mass of the oxygen atoms, and the carbonate with the  $^{18}\text{O}$  isotope has lower-energy vibrations and overall energy.  $^{18}\text{O}$  prefers to be in the carbonate. The importance of this energy difference is lessened at higher temperature because it's an exothermic reaction—the reaction becomes less favorable as the temperature increases.**



Stone tablet that reports ancient repairs to Solomon's Temple in Jerusalem.

Next, Dr. Ayalon checked the patina on the tablet. From the  $\delta^{18}\text{O}$ , he determined that two different calcite patinas had been used in the inscription. The first gave  $\delta^{18}\text{O}$  values between  $-7.3$  and  $-8.4$  per mil  $\delta^{18}\text{O}$ , while the second had higher values between  $-0.9$  and  $-1.7$ . Dr. Ayalon speculated that the patina was concocted by grinding a carbonate material like chalk with a carbonate that contained fossils. He suggested that the forger then dissolved the mixture in hot water and spread it onto the surface of the inscription. Ms. Orna Cohen, an expert conservator who specializes in identification and restoration of ancient patinas, concurred with him that the patina was forged. She reported that when the patina was removed from the inscription, it appeared freshly cut.

ings, which had convinced the Israel Antiquities Authority that the bone box was forged, could have come from cleanser!

Further doubt was raised by Andre Lemaire of the Sorbonne in France. He suggested that the fluorine found in the inscription of the bone box could have resulted from cleaning with tap water. He also suggested that fluorine might be present in patinas of many authentic antiquities, since the antiquities may have been exposed to groundwater containing modern-day runoff.

Recently,  $\delta^{13}\text{C}$  data for the bone box patina have been released.  $\delta^{13}\text{C}$  is a comparison of  $^{13}\text{C}$  to  $^{12}\text{C}$  isotopes in a sample and is determined using mass spectroscopy. Readings for the surface patina on the bone box varied from



The inscription on the bone box reads, "Ya'akov bar Yosef ahui d'Yeshua," which translates "James, son of Joseph, brother of Jesus".

box had been buried in a shallow grave, the patina would have precipitated directly from the groundwater water onto the surface of the box by  $\text{CO}_2$  degassing from the groundwater.

In either case, if groundwater or seepage water were cold, the patina would have contained more  $^{18}\text{O}$  than  $^{16}\text{O}$  isotopes, giving higher  $\delta^{18}\text{O}$  readings.

Conversely, calcite patinas that form from hot groundwater have lower  $\delta^{18}\text{O}$  values. The very low  $\delta^{18}\text{O}$  readings obtained for the patina found in the inscription of the bone box suggest the patina formed from very hot water. In fact, Dr. Ayalon reported that the water temperature had to be between  $40$  and  $50^\circ\text{C}$ . Because groundwater temperatures in caves and shallow graves in the Jerusalem area are between  $18$  and  $20^\circ\text{C}$ , it would have been impossible for a patina with such a low  $\delta^{18}\text{O}$  values to have precipitated naturally.

On the basis of this evidence, Dr. Uzi Dahri, Deputy Director of the Israel Antiquities Authority, declared that the inscription was a forgery. To further support his case, he reported that fluorine was found in the patina in the same percentage as fluorine added to tap water in Jerusalem to prevent tooth decay. Since drinking water was not fluoridated until modern times, Dr. Dahri concluded that the patina had been faked using modern-day tap water. Things were not looking good for the bone box.

The forgery case seemed airtight. The Israeli police arrested the owner of the bone box, who is an antiquities dealer, on a charge of knowingly conspiring with intent to defraud. And that's when things took a turn.

## Muddying the waters

Dr. James Harrell, professor of Archaeological Geology at the University of Toledo, suggested that the low  $\delta^{18}\text{O}$  readings could have come from a cleanser that was used to clean the bone box. He pointed out that antiquities dealers and collectors often clean artifacts to increase value, and the patina in the inscription "looks and feels exactly like what one would expect from a powdered cleanser". Cleansers contain ground-up limestone ( $\text{CaCO}_3$ ) abrasives and baking soda ( $\text{NaHCO}_3$ ), which serves as the cleansing agent. Both limestone and baking soda react with  $\text{H}_3\text{PO}_4$  to produce  $\text{CO}_2$  used in  $\delta^{18}\text{O}$  analysis. Intrigued, Dr. Harrell decided to have an oxygen isotope analysis done on four widely used cleansers from Israel.

The Georgia Center for Applied Isotope Studies tested the four Israeli cleansers with interesting results. Three of the four cleansers produced results lower than the  $-4.1$  to  $-6.7$  per mil  $\delta^{18}\text{O}$  range set by the Geological Survey of Israel for authentic carbonate patina. And, the most popular cleanser had a  $\delta^{18}\text{O}$  of  $-8.5$  per mil, consistent with the patina in the inscription of the bone box. The low  $\delta^{18}\text{O}$  read-

$-1.2$  to  $-7.7$  per mil  $\delta^{13}\text{C}$ . However, unlike the  $\delta^{18}\text{O}$  results, the  $\delta^{13}\text{C}$  readings for the inscription patina were almost identical to the values for the surface patina, ranging from  $-1.1$  to  $-7.4$  per mil  $\delta^{13}\text{C}$ .

Are the bone box and stone tablet fakes? If they are, they could expose a forgery conspiracy that has been operating for years. In fact, the Israel Antiquities Authority has warned that many forgeries from this conspiracy could be in museums in Israel and around the world. The forgery trial was scheduled to begin on September 4, 2005. But, even if the defendants are found not guilty or the case is dismissed, doubt will linger about the authenticity of the tablet and bone box. Scientists will continue to disagree about analyses and interpretations of results. Methods to test antiquities will improve, and it is likely that new examinations will be undertaken.

More importantly, even if one day the inscription on the bone box were to be proven authentic, the names James, Joseph, and Jesus were common in the 1st century AD, so the inscription could refer to a family other than the biblical one. You can follow the ongoing controversy on the bone box by clicking on the "Update" section at [www.bib-arch.org](http://www.bib-arch.org). ▲

**Lois Fruen** teaches chemistry at the Breck School in Minneapolis, MN. Her most recent article "Liquid Crystal Displays" appeared in the October 2005 issue of *ChemMatters*.

# Super fibers

Carbon nanotubes could be the key to spinning the future's hottest threads.

By **Christen Brownlee**

Imagine you're a soldier of the future. As you scan the horizon for possible threats to your platoon, the day heats up, but you stay cool. Tiny air conditioners placed strategically within your shirt turn up the juice before sweat makes its first appearance.

But that's just the start of the laundry list of things your new standard-issue attire might do.

For example, sensors integrated into the fabric could take minute-by-minute health readings to make sure you're fit, calm, and well hydrated. Radios woven right into the cloth might communicate your position and status back to the home base. Your camouflage could instantly morph to hide you in any background, not just the usual forest greens or desert browns. All of these powerful applications might be fueled by light-weight capacitors, or batteries, twisted right into the threads. To top it all off, your shirts and pants might stop projectiles on their own, without the help of extra bullet proof materials.

Think these revolutionary duds are "mission impossible"? Think again. Scientists are currently working on developing super fibers made of powerful carbon nanotubes. These ultra-thin threads can be less than one-ten

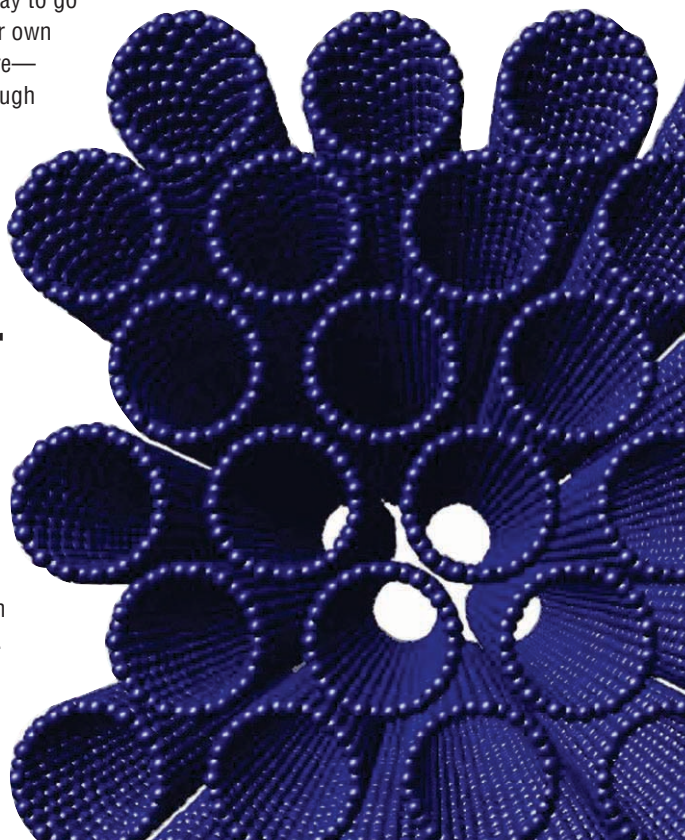
thousandth the width of a human hair, and they come with a bevy of interesting chemical properties such as super strength, and super electrical and thermal conductivity. Woven into a fabric, these fibers could turn any article of clothing into extraordinary wired attire.

The research still has a long way to go before you'll be able to pick up your own super shirt at the army surplus store—chemists need to work out some tough kinks in manufacturing the right kind of nanotubes at the right length for these applications. But with the science marching swiftly ahead, an army of super-tailored soldiers won't be long behind.

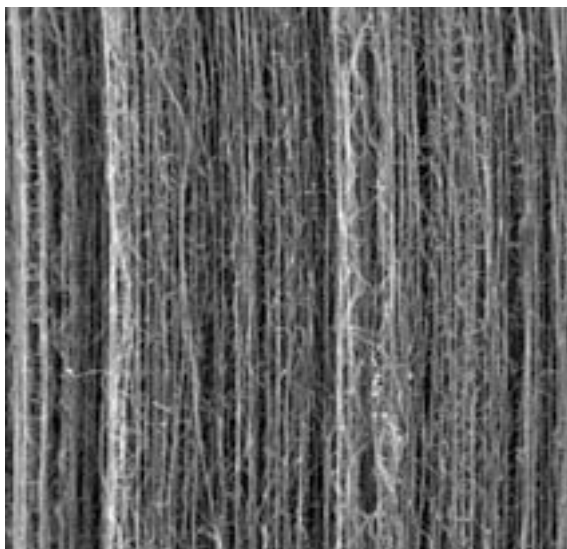
## Strong character

Despite scientists' long-range scheming over possible applications, carbon nanotubes are still a relatively new technology. They were discovered by chance in 1991 by researcher Sumio Iijima at Japan-based NEC Laboratories while he was examining other carbon structures for unrelated applications.

Iijima and his colleagues knew they had something special. They immediately saw how the structure of the tubes, which look like rolled-up chicken wire at the molecular level, gives them unique chemical features that scientists haven't seen in any other material.



COURTESY OF OAK RIDGE NATIONAL LABORATORY



COURTESY OF NASA SEM IMAGE OF CARBON NANOTUBE FIBERS



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VANSON

Carbon nanotube fibers are 4 times stronger than spider silk and 17 times stronger than the Kevlar used in bullet-proof vests.

According to Matteo Pasquali, a chemical engineer at Rice University in Houston, TX, like every covalent network solid, every atom in a carbon nanotube shares electrons with its neighbors. Sometimes, this property gives them the ability to conduct electricity extremely efficiently. The tubes' honeycomb lattice and cylindrical structure also allow them to channel heat effectively and retain their shape.

Carbon nanotubes conduct heat better than any known material and are many times stronger than any known fiber. Plus, they are extremely lightweight, making them perfect for adding these special qualities to other materials without adding extra pounds.

"To some extent," says Pasquali, "they're the Holy Grail of fibers." But much like the original Holy Grail, he adds, good carbon nanotubes are extremely tricky to find.

When Iijima's group discovered nanotubes, they noticed that the tubes spontaneously arise from a variety of combustion reactions. For example, nanotubes emerge every time you light a candle. But this run-of-the-mill production makes nanotubes that aren't suitable for anything useful, says Pasquali.

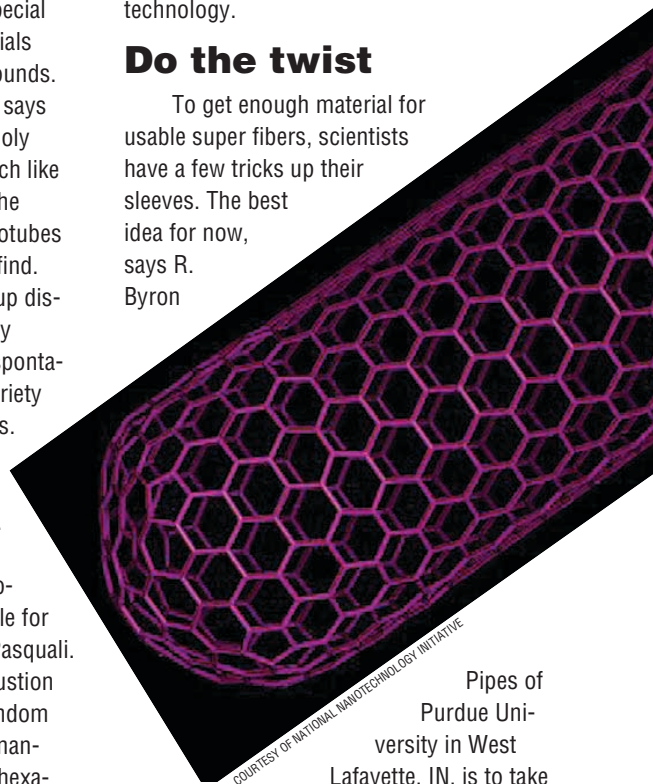
First, many combustion reactions produce a random mishmash of different nanotube structures—the hexagons in the tubes' chicken-wire structure may be rolled up at different angles, for example, giving them different properties. This slipshod production also spews out various assortments of nanotube types. Single-walled nanotubes, the hose-like structures that seem to have

the most benefits, are often mixed in with multiwall nanotubes, which look like tubes rolled up within tubes. To get the most reliable properties, scientists need to work with a uniform batch of tubes that perfectly match each other.

Second, the manufacturing techniques available today—such as knocking carbon off of a surface with a laser, for example, or discharging bits of carbon by zapping carbon rods with electricity—can only produce nanotubes that are usually only a few micrometers long. "If you interrupt the nanotube, then you interrupt their properties," says Ray Baughman of the University of Texas at Dallas. The most bang for chemists' buck lies in learning how to manufacture individual, extra-long nanotubes. However, many scientists agree that it will be a big stretch to produce single nanotubes much longer than the current limits with today's technology.

## Do the twist

To get enough material for usable super fibers, scientists have a few tricks up their sleeves. The best idea for now, says R. Byron



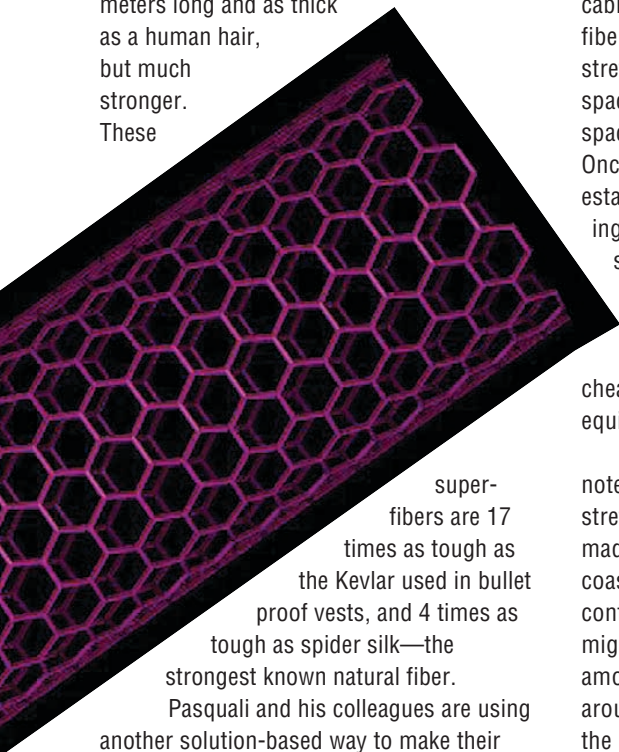
COURTESY OF NATIONAL NANOTECHNOLOGY INITIATIVE

Pipes of Purdue University in West Lafayette, IN, is to take many short nanotubes and bundle them into yarns. Although the resulting yarn has less than 1% of the theoretical strength, heat conductivity, and electrical conductivity, the end product still has some intriguing possibilities.

"For many centuries, man had only discontinuous fibers at his disposal, like flax and cotton. But we've made yarn, rope, and cloth, twisting fibers so they become

strong,” says Pipes. “Most people think that if the elements aren’t continuous then it’s not strong, but that’s not true.”

For example, Baughman and his coworkers have manufactured carbon nanotube yarns by distributing billions of nanotubes into a detergent solution. The scientists keep the tubes from bunching together by blasting the solution with high-frequency sound waves. Feeding a thin stream of the solution into a whirling bath, the scientists have twisted yarns up to 200 meters long and as thick as a human hair, but much stronger. These



super-fibers are 17 times as tough as the Kevlar used in bullet proof vests, and 4 times as tough as spider silk—the strongest known natural fiber.

Pasquali and his colleagues are using another solution-based way to make their own nanotube yarns. Dumping their individual nanotubes into sulfuric acid, the researchers found that electrical charges within the acid distributed the tubes evenly without the high-frequency sound waves. Pasquali’s team simply pressed the nanotube solution through a syringe into a coagulating bath, pushing out meters of super-strong nanotube cables.

## Next big thing

Researchers are now testing the new fibers to see exactly what kind of physical properties they possess. If they can tweak the properties of these yarns to even one-tenth of an individual nanotube, then scientists will be in business for a number of opportunities.

Clothes for a futuristic soldier will be only the tip of the iceberg, says Baughman.

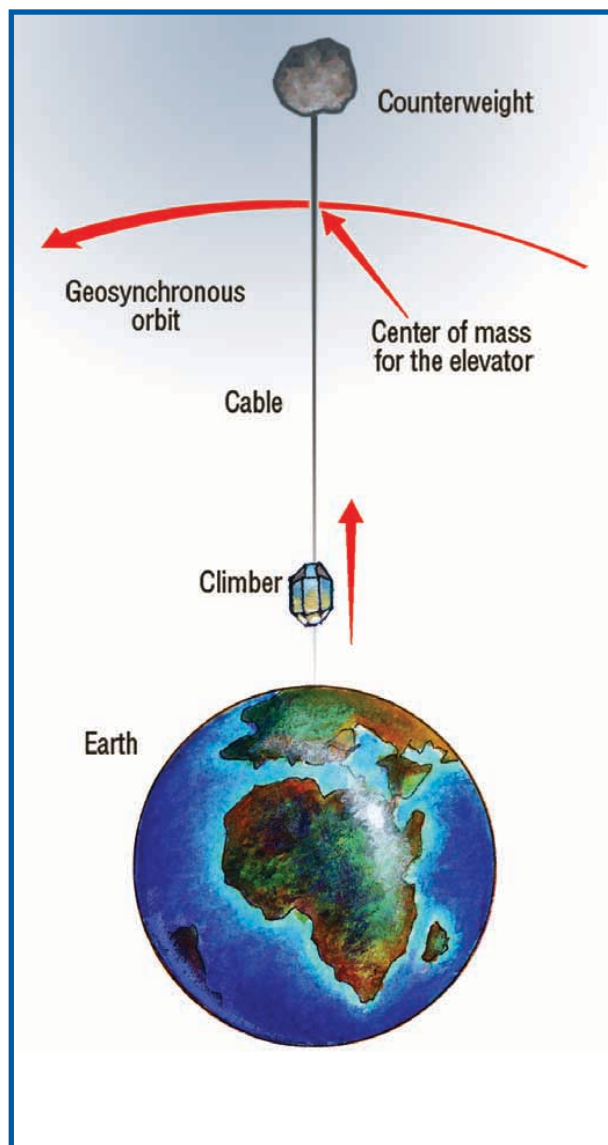
They could play a major part in building stronger vests for police officers and artificial muscles that twitch with electricity. These are two super fiber possibilities that he and his team are talking about.

Many scientists are dreaming much bigger; for example, some researchers believe that an extra-long cable spun of carbon super fibers might someday stretch all of the way to space, tethering an orbiting spacecraft to the earth. Once the initial thin cord is established, a small climbing machine could strengthen and thicken the line, eventually creating a space elevator that could cheaply carry people and equipment into space.

On a more practical note, Pasquali thinks that stretching electrical cables made of super fibers from coast to coast—or even continent to continent—might save an enormous amount of electricity around the world. “One of the big problems with power is that, for the most part, you can’t store it,” says Pasquali. “You continuously have to produce the power that’s needed.”

Right now, loads of electricity are wasted as power plants churn away through the night, supplying electricity for just a few night owls. But at night in one part of the world, it’s daytime in another. If scientists could move electricity instantly from one half of the world to another, energy production’s efficiency would dramatically improve.

Traditional cables won’t work for such an expansive application—right now, they lose about 50% of the energy that’s produced through resistance while just moving it around. However, a cable woven of carbon super fibers could be a perfect fit for the job, notes Pasquali.



Some researchers believe that carbon superfibers may someday stretch to space.

ACS STAFF

Although the phenomenon has been only demonstrated over a distance of a micrometer, it’s an exciting result. He estimates that some of the applications of carbon super fibers could be here in a mere 10 to 20 years.

In the meantime, he and other carbon nanotube chemists will keep spinning longer and longer superfibers, weaving their dreams toward reality. ▲

*Christen Brownlee* is a contributing editor to *ChemMatters*. Her article “Flaking Away” also appears in this issue.



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# salting roads

## THE SOLUTION FOR WINTER DRIVING

By Doris R. Kimbrough

**M**ost of you are probably planning to be in a car at some point this winter, so be sure to wear your seatbelt, obey the speed limit, and be extra cautious in “winter driving conditions”. It is actually physics that makes being in a car on an icy road hazardous; friction is an important part of keeping a car under control. However, your state and local transportation departments make use of some pretty interesting chemistry to keep roads safer for travelers in the winter-time. In addition to plowing, one of the ways that highway workers keep roads clear of ice and snow is by spreading salt on the roads. Even though salt can cause rust and corrosion on cars, bridges, and other parts of the highway, it more than makes up for this costly damage by saving lives. Let’s take a look at how it works.

### Freezing point depression

Pure water freezes at 0°C; adding salt to water depresses or lowers the freezing point below zero. When you remove heat from water (or any substance), the molecules slow down. The freezing process occurs when the molecules stop sliding and tumbling all over each other (liquid phase) and settle into fixed positions in a large network called a *crystal lattice*, which is the solid phase. The molecules are still moving, but in the solid phase that motion involves bonds stretching and compressing or the atoms wiggling a little bit. This is called vibrational motion.

When a solution of salt in water is cooled to a low enough temperature, the water molecules begin to stick together in an organized way to form solid crystals. The crystal framework tends not to include the salt ions because the ions would disturb this

organization. So when you cool a solution enough, the ice crystals that start to form are made of pure frozen water. You can actually purify salty water like this, by freezing a portion of the solution and washing the salty water off of the ice crystals and then thawing the ice to produce pure water. Eventually, if you cooled it enough, the whole solution will freeze, but it does not have a sharply defined freezing temperature. Getting the water molecules organized into a crystal from a solution requires that you remove more energy (actually free energy) than if you are freezing pure water, so the water in a solution typically does not start freezing until it reaches a lower temperature than the normal freezing point. This is true of all solutions, not just those made with water.

The difference in temperature between where the pure solvent (water in our case) freezes and where the solution starts to freeze is called the *freezing point depression*. How low



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you go depends upon what the solvent is and how concentrated the solution is. The more concentrated the solution, the lower the freezing point. This is why if you freeze a solution completely, you have to keep lowering the temperature. As the pure water freezes away from the solution, the concentration of the solution remaining increases. How does your Department of Transportation use this chemistry to keep roadways clear of snow and ice in the wintertime?

## Salting roads

Highway workers use salt in two ways: 1) to melt ice that is already on the roadway and 2) to prevent ice from forming on the roadway. The second one is a little easier to understand, so we will start there. Let's say a snowstorm is forecast for your town. Municipal workers get out and spread salt on the roads. As the storm hits, snow starts to fall, but the road surface is warmer than the air, so the first flakes melt. As they melt, the salt dissolves in the liquid water. Now you have a solution of salty water, which has a lower freezing point than pure snow, so that even though the additional snow might cool the road enough to "stick" to the road surface, the temperature will not get cold enough to freeze the solution the way it could freeze pure water. In the end, the real snow removal is done by the plows, but salt plays a crucial role in preventing snow and ice from bonding to the pavement.

"Hold it!" you say. Suppose the tempera-

ture does get cold enough to freeze the solution. Or suppose that enough snow falls so that the salt water solution gets too dilute to work, what happens then? In both of those cases, snow could build up on the road. This

tals, water molecules do not have the same stable arrangement they have on the interior; they are more mobile and more reactive. So the surface ice reacts with the surface of the salt crystals, allowing a small amount of salty



MIKE CIESIELSKI

Sodium chloride and calcium chloride.

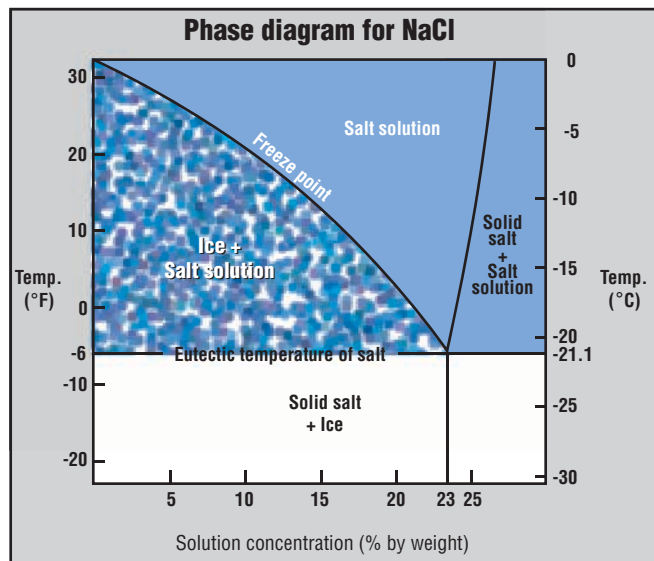
is why your highway workers are out there round-the-clock, plowing and spreading more salt as long as the storm is in the area. Communities with really cold temperatures, like parts of Canada and Alaska, where it can get to  $-20^{\circ}\text{C}$  (below zero on the Fahrenheit scale), don't even bother with salting the roads, because it doesn't help. They typically plow off as much as they can and use gravel or sand to add traction.

How does it work if the road already has snow or ice on it? You may have seen how spreading salt on an icy sidewalk will cause the snow or ice to melt. The very beginning of the melting process begins where solid ice contacts solid salt. At the surface of ice crys-



MIKE CIESIELSKI

Water freezes at lower temperatures when it is saltier. But solubility of salt in water decreases with decreasing temperature. So at some point, a solution is too cold to hold the salt that keeps it from freezing. The *eutectic* temperature is the lowest temperature at which a mixture of two or more substances can stay liquefied. For a NaCl and water mixture, the eutectic temperature is  $-21.1^{\circ}\text{C}$ . For road ice,  $-10^{\circ}\text{C}$  is the practical limit for salt.



This phase diagram illustrates the impact of NaCl concentration and temperature on the phase of an aqueous NaCl solution.

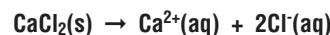
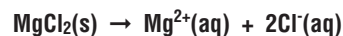
solution to form. This first step is relatively slow, but then the growing solution continues to dissolve more salt and melt more ice. Passing vehicles warm the slush through friction, which speeds the dissolution of the ice and may crush the salt and ice together, which will increase the surface areas of the particles in contact with each other. Some communities use “prewetted” salt (usually rock salt with a CaCl<sub>2</sub> solution sprayed on it) to speed the process.

## Road salt history, fun facts, and current technology

Putting salt on the roads to lessen the buildup of snow and ice began in the 1930s, and by the 1960s, it was used by most communities where snow and ice are a problem. Concerns about the effect of the use of sodium chloride (common table salt) on the environment have prompted some state and local road crews to explore the use of more environmentally friendly salts, such as magnesium chloride and calcium chloride. These two salts have the advantage of being more effective at lowering the freezing point and there is some interesting chemistry behind this benefit.

As you probably know, sodium chloride has the formula NaCl. When it dissolves in water, it dissociates into its ions: Na<sup>+</sup> and Cl<sup>-</sup>, producing two ions in solution for every NaCl for-

mula unit. Magnesium chloride (MgCl<sub>2</sub>) and calcium chloride (CaCl<sub>2</sub>) dissociate to three ions each because the metal has a 2<sup>+</sup> charge and there are two chlorides per metal ion:



It is the number of dissolved particles that determine the extent of the lowering of the freezing point of a solution. So although NaCl produces two ions, MgCl<sub>2</sub> and CaCl<sub>2</sub> each produce three, making them more effective. Other variations include mixtures of the magnesium and calcium chlorides, as well as magnesium and calcium acetates, Mg(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub> and Ca(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>.

	Practical Melt Temp.	Eutectic Temp.
CaCl <sub>2</sub>	-32°C	-56°C
MgCl <sub>2</sub>	-15°C	-33°C

The technology of salting roads has become fairly sophisticated. Often, these salts are dissolved in water or some other solvent so that they can be sprayed onto the road surface. Having the deicing substance in a solution (i.e., fluid) form makes it possible to pump through hoses, which allows for a more targeted application. In addition, various anticorrosive substances are added to protect highways and cars from the damage the salts can cause over time. Some 15 million tons of deicing salt is used each year in the United States and about 4–5 million tons in Canada.

You may have seen signs that warn about bridges freezing before road surfaces. This is because bridges are more exposed and not insulated by the ground from underneath like the rest of the highway. Some high-tech highway bridges have been constructed with deicing sprayers built right into the pavement, complete with sensors that detect when conditions are right (e.g., cold temperatures, high wind speeds, high humidity) for ice to form. The sensors detect the possible formation of ice, and the deicing sprayers go to work to keep the roadway from freezing.

Highway engineers have been working with other interesting variations. One deicing material that is currently on the market mixes magnesium chloride with sugar cane or sugar beet molasses. The sticky molasses keeps the magnesium chloride from getting blown or washed off the road surface. There are also substances that are added directly to the top layer of concrete or asphalt when the road is built or repaved that help prevent ice from forming. Highway workers can then get away with using less salt than before, which is cheaper, easier on the environment, and helpful in preventing corrosion. Scientists and engineers continue to develop new ways to keep winter highways safe while minimizing expense and environmental harm. Just another way that chemistry is keeping you out of harm's way. ▲



MIKE GIESIELSKI

**Doris Kimbrough** teaches chemistry at the University of Colorado-Denver. Her last article, “Einstein’s Miraculous Year”, appeared in the December 2005 issue.





**From Ferraris to Ford Pintos, almost every car is fighting a losing battle to rust.**



**By Christen Brownlee**

**T**he old-style Volkswagen Beetle: Is it a classic car, or an endangered species? The answer depends on where you live. Although there are few classic cars hanging around the northern states or on the coastlines, plenty of vintage automobiles still exist in the mild southern climates and in America's interior states.

The reason that Volkswagen Bugs and other older cars are dropping like flies isn't the typical habitat loss or human encroachment that's plaguing other endangered species. Classic car fleets are constantly shrinking due to a chemical reaction that you're no doubt already familiar with: rusting.

But why does rust unequally strike cars in the snowy states and coastal towns but leave vehicles elsewhere virtually untouched? And more importantly, how can you keep your beloved grocery-getter safe, no matter

what parking place you call home? Read on to get the lowdown on how rust works and what measures you can take to stop corrosion in its tracks.

### **Electron swap meet**

Like all types of corrosion, rust is actually a chemical bargain, with two reactions in one: reduction, in which some atoms gain electrons, and oxidation, in which other atoms lose electrons. With all those electrons flowing from one place to another, rust-making is also considered an electrochemical reaction. According to John Scully, a

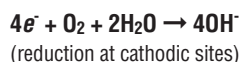
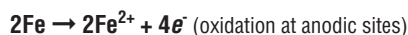


corrosion expert at the University of Virginia in Charlottesville, the redox reaction that forms rust needs just three ingredients to take place: an anode, or metal that readily gives up electrons; a cathode, or substance (in this case, oxygen) that easily accepts electrons; and an electrolyte solution, which shuttles ions between cathode and anode.

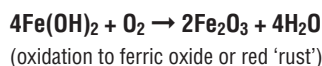
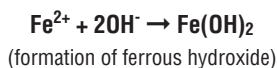
Most cars are made mostly of steel, a tough mixture of iron, carbon, and small amounts of other ingredients like manganese, silicon, phosphorus, and sulfur. It's the iron part of steel that corrodes to make rust.

Iron doesn't hold onto its electrons very tightly, says Scully, making it the perfect anode for an electrochemical reaction to take place. Other metal atoms in the steel mixture, or even another point on the piece of iron, make excellent cathodes. Steel has a nonuniform surface because the chemical composition is not completely homogeneous. Also, physical strains leave stress points in the metal. These defects create anodic regions where the iron is more easily oxidized than it is at others (cathodic regions). However, without a bridge to connect potential anodes and cathodes, rusting would be such a time-consuming process that cars would virtually last forever.

The water on the steel surface is a solvent for ions produced when the iron metal at the anodic region loses electrons (is oxidized to form ferrous ions) and the electrons are conducted through the metal to the cathodic region where they react with water and oxygen from the air to form hydroxide ions, as shown in these equations:



The ions in this electrolyte solution can migrate together and react to form ferrous hydroxide, which reacts further with oxygen from the air to oxidize the ferrous ion and form insoluble ferric oxide, the chemical name for rust, as shown in these equations:



The movement of ions through the electrolyte solution completes the electric circuit that allows the electrons from iron to move from the anode to the cathode.



**A redox reaction on wheels. The bumper of this vehicle wears the product of the reaction between iron and oxygen—rust!**

But all this still doesn't explain why colder climates and coastal areas get an unfair share of rust. The magic ingredient that both areas share—which is missing in the basic recipe for rust—is a high abundance of salt. Coastal areas have plenty of salt sailing through the air from ocean spray, and with each cold, snowy winter, northern states smear tons of rock salt on roads to lower the freezing point of water and help keep roads free of ice and snow. [See "Salting Roads: The Solution for Winter Driving" in this issue]

Salt speeds rust's redox reaction along by making water a better conductor. "Salt allows the anode and cathode to be in touch even better," says Scully, making corrosion happen even quicker. Also, chloride ions form very stable complex ions with  $\text{Fe}^{3+}$ , which helps dissolve iron and accelerate corrosion.

## Costly corrosion

Scully points out that iron can't help rusting—existing as an oxide in its thermodynamically favored state. In fact, the metal rarely exists in a pure state in nature. Before it becomes a side panel in your car, engineers must convert rusty iron ore into a pure metal.

With rust being iron's favored state, it is of little use trying to fix rust after it has already happened. By putting energy into rust, it's possible to plate metal back onto a

car, says Scully. However, it's also incredibly costly and impractical. Plus, by the time most car owners notice a rust spot, a significant amount of iron has already sloughed off of the car, lost to wind and rain.

One solution to stopping iron's thermodynamic conversion, says Scully, would be to make cars out of a metal that doesn't corrode, such as gold or silver. "Converting to an oxide isn't thermodynamically favorable





MIKE CIESIELSKI

**It's not only cars that are rusting away. Corrosion costs the United States a whopping \$276 billion per year!**



MIKE CIESIELSKI

**This student investigates the role of salt on the rate of rusting by putting nails in various salt water solutions.**

Today's high tech paints have evolved far from being just a simple barrier, says Scully. Researchers are currently working on paints that release rust inhibitors on demand when paint's seal on steel is breached, for example, when the paint on a car is scraped or scratched. Other "smart paints" that ooze together to close gaps whenever a car's panels get scratched are also in the works.

Although rust is a big deal for car owners, it's an even bigger deal for industries that rely on machines with metal parts, ranging from farm tools to factory equipment to fighter jets. According to Scully, corrosion costs the United States a whopping annual toll of about \$276 billion in lost goods and services. With the exorbitant cost of new military equipment, the Department of Defense (DOD) is one of the largest investors in antirust research, says Scully. Scientists at the DOD hope they can keep the aging Blackhawk helicopters and B52 bombers that are currently in use running smoothly for decades to come—a cost savings of millions of dollars per machine.

But one military asset sometimes harmed by corrosion is extremely difficult to put a price on, says Scully. "If a soldier goes to war and the rifle he's using to protect himself doesn't fire when he needs it to, how do you estimate the cost of corrosion then?" ▲

reaction for these metals, so they won't corrode spontaneously," he says. "Archaeologists can dig up gold coins that have survived through the ages without corroding."

But while driving a gold car might make you feel like a million bucks, making such a vehicle would cost substantially more. Not to mention the fact that these soft metals would be unable to support the car's weight and would squash like putty in a collision!

Even using noncorroding metals that are cheaper than gold or silver, such as stainless steel that Deloreans are made of, is still more expensive than using the plain steel that most cars are made of today.

The best way to prevent corrosion is still the cheapest. A good coating of paint removes the connection between anode and cathode by preventing water from making contact with steel. Without water, rusting slows down to a snail's pace.



GETTY IMAGES

*Christen Brownlee* is a contributing editor to *ChemMatters*. Her article "Super Fibers" also appears in this issue.

## With a flash of light, nanotubes ignite!

Shine light on some materials and they will make an audible sound. This interesting phenomenon is known as a photoacoustic or optoacoustic effect.

The photoacoustic effect was first discovered by Alexander Graham Bell and reported to the world in 1880. While working on the photophone, he inadvertently discovered that if a beam of light was focused on a selenium cell and then rapidly interrupted by a rotating disk, the cell produced an audible sound. He further demonstrated that the strength of the photoacoustic effect is dependent on the strength of light absorbed by the material.

Shine light on some new nanoscale materials and they'll not only sound off, but they actually ignite under an ordinary camera flash. Enhanced photothermal properties are one of the many unexpected properties that researchers are discovering as they delve into the realm of nanoscale materials.

## Single-walled carbon nanotubes

Last year, researchers at Rensselaer Polytechnic Institute in

Troy, NY, reported in *Science* that single-walled carbon nanotubes (SWNTs) of a dry, "fluffy" nature ignite when exposed to a conventional flash at close range.

Similar materials such as C60, fluffy carbon soot, and multiwalled carbon nanotubes do not ignite.

The researchers believe the nanotubes must have an enhanced ability to absorb light and convert it to heat (a photothermal effect). In the "fluffy" bundles, the heat does not dissipate and reaches an estimated 1,500°C—more than enough to ignite the SWNTs. Other researchers have hypothesized that part of this effect might rely on metal impurities present from the manufacture of the SWNTs.

See SWNTs ignite and burn after exposure to an ordinary camera flash.

<http://www.sciencemag.org/cgi/content/full/296/5568/705/DC1>

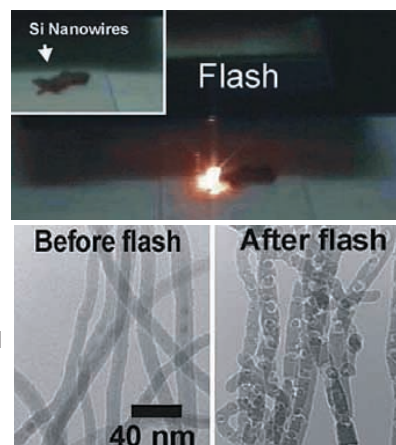
## Silicon nanowires

In an article in *Nano Letters*, researchers at the University of Science and Technology in Hong Kong have described a similar phenomenon involving enhanced photothermal effect in Silicon (Si) nanowires. When these nanowires are hit by a

light, they make an audible pop. If the flash has sufficient power the Si nanowires ignite. Like SWNTs, the researchers see evidence that the Si nanowires experience temperatures of approximately 1500 °C during the flash.

The figures on the right show Si nanowires before and after a flash under an inert atmosphere. The nanowires don't ignite, but they get hot enough to melt Si. The authors believe that "the optical absorption in Si nanowires was enhanced by their special structure." The same effect is not observed in bulk silicon material, and yet the absorption spectrum of Si nanowires and pure Si single crystals is similar. The mechanism is unclear, but the Si nanowires must clearly "trap an incredible amount of energy from the flash." The ignition of the Si nanowires is distinct from carbon nanotubes because there is no metal impurity in Si nanowires.

Because of the unexpected ability to confine photoenergy, Si nanowires may find uses in "smart ignition systems, self-destructing



systems for electronic devices, nanosensors, and nanostructural or nanophase reformation for nanotechnology."

See Si nanowires resist burning in gas flame, only to ignite after a flash of light at:

<http://www.chemistry.org/portal/resources?id=3f136aba6e8711d7f03f6ed9fe800100> ▲

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