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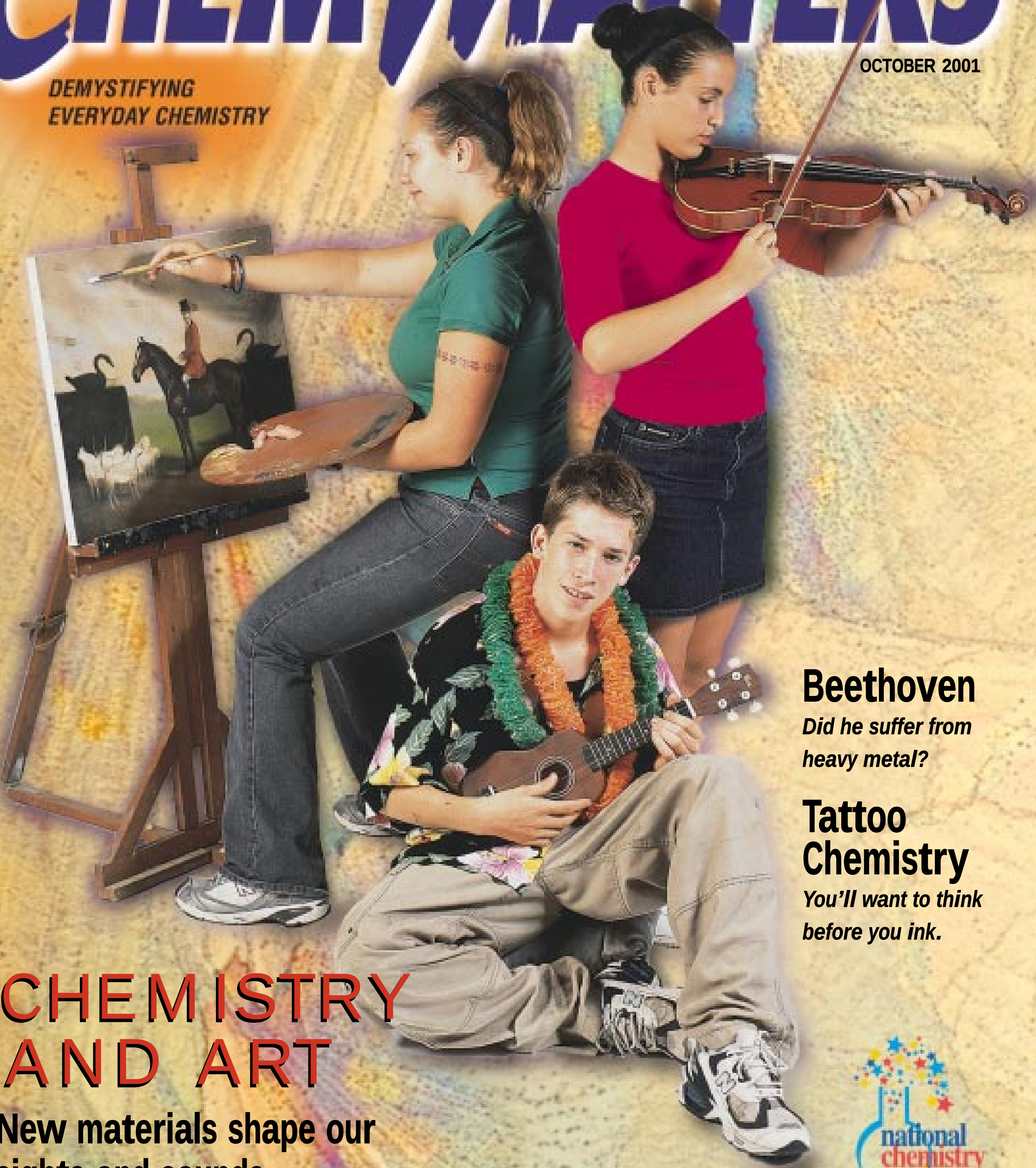
OCTOBER 2001



Beethoven

Did he suffer from heavy metal?

Tattoo Chemistry

You'll want to think before you ink.

CHEMISTRY AND ART

New materials shape our sights and sounds.

national chemistry week

Question From the Classroom

By Robert Becker

Q. Who invented the ballpoint pen, and how does it work?

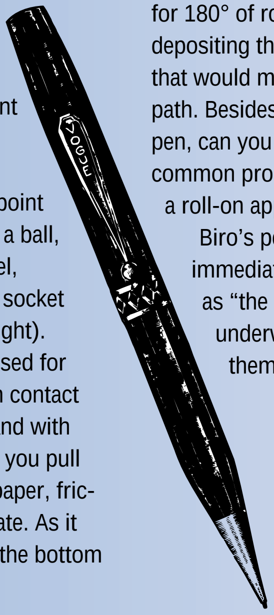
Will your ballpoint pen write underwater? Try it.

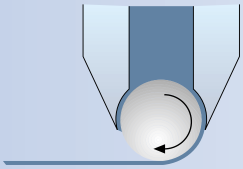
PHOTO BY MIKE CIESIELSKI

A. We certainly take them for granted, yet we use ballpoint pens every day. They probably spend more time in our hands than any other tool—except maybe for remote controls in the hands of couch potatoes! To take notes in class, pass a note to a friend, write a check, fill out an application, or just doodle—what do we reach for? That wonderful little invention: the ballpoint pen.

In 1943, Laszlo Josef Biro, a Hungarian journalist, visited a newspaper print shop where he was impressed with the high-viscosity (very thick) ink they used. This oil-based ink left the paper smudge-free and dried almost immediately after printing. Biro decided to invent a pen that could take advantage of such a quick-drying ink. Using this kind of ink in an ordinary fountain pen would clog it, so the biggest challenge was to find a different way to dispense the ink.

Here's how a ballpoint pen works. There is a ball, usually made of steel, locked tightly into a socket (see illustration at right). When the pen is poised for writing, the ball is in contact with the ink above and with the paper below. As you pull the ball across the paper, friction causes it to rotate. As it rolls, it pulls with it the bottom layer of ink, which is deposited as a thin line on the paper beneath.





Although there is some degree of attraction between the metal ball and the ink, the pen still relies on gravity to pull the next layer of ink down to make contact with the ball. Imagine a deck of cards held on top of a bicycle wheel. As the wheel is pushed forward, the cards would shear off one at a time, sticking to the wheel for 180° of rotation before depositing themselves in a line that would mark the wheel's path. Besides the ballpoint pen, can you think of other common products that rely on a roll-on applicator?

Biro's pens were an immediate success. Billed as "the first pen to write underwater", 10,000 of them sold on the first day they were introduced—at Gimbel's department store in New York City, October 29, 1945. The $10 price tag for each pen would amount to about $98 in 2001 dollars. Who knew so many New Yorkers had a need for writing underwater?

In 1953, a Frenchman by the name of Marcel Bich introduced a much cheaper, mass-produced ballpoint pen.

Today, even with the advent of the personal computer and the handheld PC, Bic pens are still immensely popular, with more than 14 million sold each day! However, if you're traveling in Europe, you'll find that the first inventor gets his due credit: Ballpoint pens there are known generically as "biros".

Do they really write underwater? Find out. Hold a strip of paper on the bottom of a pan half-filled with water and try writing on it with a ballpoint pen. It won't work. But then take your wet pen and try writing on a dry sheet of paper. After a few blank scratchy lines, it works just fine. What's going on? Underwater, the ball doesn't carry much ink out onto the paper. Instead, it carries water up into the pen's ink supply! When you take the ink out of the water and resume writing on dry paper, the water layer, with a higher density than the oily ink layer, is first to contact the surface. When you write, the pen deposits water instead of ink for a few seconds. Once the water is gone, the pen goes back to delivering ink.

Most likely, today's pens use a very different ink than the one used back in 1945, or the lines in Gimbel's return department would have been long!

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ChemMatters®

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COVER PHOTO BY MIKE CIESIELSKI

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Art Conservation

Chemistry to the Rescue

By Anne Rosenthal

“I actually surface-cleaned this object using my own saliva,” says Emily Dunn, an art conservator at one of the world’s best known art museums—the Art Institute of Chicago. Dunn’s work combines her knowledge and love of art, science, and technology. Her background includes training in chemistry, studio art, and art history. And she is presently working on a piece of art worth many thousands of dollars. Why the saliva?

Recently, the Art Institute purchased a piece of valuable antique furniture, the “Sideboard and Wine Cabinet” designed by English artist William Burges and painted by Nathaniel Westlake in 1859. But careful examination revealed some damage. First, the entire piece was covered with tiny brown specks—“fly poop to be exact”, says Frank Zuccari, director of the Art Institute’s conservation department. Then there’s the varnish, applied over the gilding nearly 150 years ago. In many spots, it has turned a deep brown, hiding the gilding beneath. Yet another concern is that the contraction of paint over time has created a pattern of cracks akin to alligator skin—not to mention the scrapes and water damage to one of the shelves.

How can conservators get this piece looking like—well—something you’d see in a museum? How can they restore it without betraying the artist’s original intent in the process? As viewers of television’s *Antiques Roadshow* will tell you, one false step, and the value of the piece plunges.

Turns out, spit IS a good place to start because it contains numerous enzymes—protein catalysts that speed up specific chemical reactions. Enzymes help loosen organic matter, including grease, without affecting paint pigments or the varnish layer on top of them. Saliva also contains mucin, a gelling agent that keeps water on the surface, preventing damage to the water-soluble gesso, a plasterlike layer underneath the paint. Not only does saliva make chemical sense, it’s also a traditional cleaning method. In the 18th century, people were actually hired on a temporary basis to provide saliva for cleaning large paintings.


CABINET: ACCESSION NUMBER 1999.262

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Art conservator Emily Dunn checks her work with a light microscope designed for performing eye surgery.

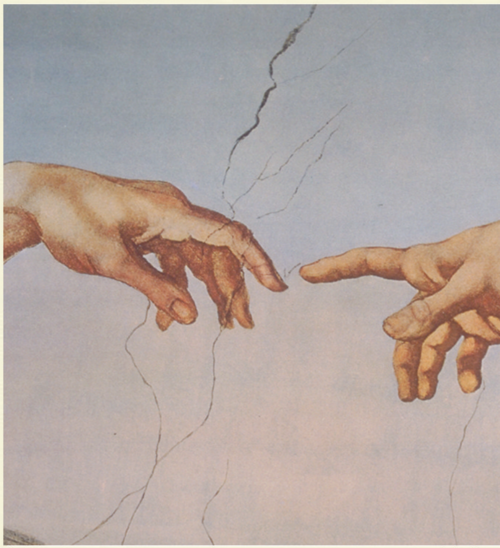
With saliva, Dunn was able to remove the specks and the dirt from the surface, checking her results as she worked with a light microscope developed for eye surgery. With its superb depth of field (distance from the lens that can be in focus at one time), the microscope is ideal for examining artwork surfaces. The microscope, attached to a video camera, feeds images directly to a computer. Dunn imported, photo-enhanced, and stored numerous images for making comparisons before and after each treatment. Her analysis revealed that despite their removal, the fly specks left little bright spots behind. A chemical in the fly excrement had eaten through the surface varnish, exposing the underlying gilding.

Uncovering a masterpiece

Dunn’s next challenge was the yellowed varnish itself. Varnish is a liquid preparation, generally a resin dissolved in a solvent like linseed oil that hardens into a protective, lustrous, transparent coating. Varnishes on old paintings, for example, were usually made with resins from plants. A common one, “damar”, was composed of resin drops from the Far Eastern damar bush dissolved in natural turpentine.

Removing old varnish and applying a new varnish coat is a common step in many art conservation projects. Often, centuries-old masterpieces undergo several rounds of this process. The removal or thinning of yellowed varnish is sometimes the only treatment a painting needs to be restored to its original glory.

Working on tiny areas of the cabinet, Dunn attempted to dissolve the varnish with several solvents normally effective, but without success. Puzzled by the varnish, Dunn approached the staff microscopist, Inge Fiedler, who had a sample of the varnish analyzed by infrared microspectroscopy. Infrared spectroscopy is an analytical method that studies wavelengths of light in the infrared region of the electromagnetic spectrum. By observing their


PHOTODISC

interaction with various known materials, they can use this method to describe the composition of a sample. Spectral features, or wavelength patterns, revealed that this particular varnish was a natural resin, possibly amber or shellac.

No wonder the varnish looked yellow. Even as it was applied, the amber (a fossilized tree resin) or shellac (a resin secreted by an insect) would have had a yellowish color, notes Dunn. "The artist was aiming to tone down the brilliance of the gilding he applied, trying to make it look as if it were from the Middle Ages. The varnish partly functioned as a patina, artificially aging the piece."

Respecting the original artist's intent, Dunn decided against removing the varnish. Instead, she thinned it only in areas where excessive sun exposure had turned it especially dark. She decided to selectively inpaint areas where the paint had cracked extensively.

Damage with age

Many works of art, even best-loved pieces created by the greatest masters, suffer extensive damage as they age. When Leonardo da Vinci created one of the world's most famous paintings, "The Last Supper", in the Monastery of Santa Maria delle Grazie, Milan, Italy, he tried a new technique—painting on top of a type of dried plaster called gesso rather than the time-tested method of applying pigment to wet plaster. As a result, the paint began flaking soon after he completed it in 1498.

While da Vinci's unfortunate choice of technique accelerated the painting's decay, Napoleon's troops added insult to injury. Encamped inside the church some 300 years later after its painting, they used the apostles for target practice, throwing clay bricks at them. Then, during World War II, the entire church became an inadvertent Allied target. Bombs destroyed the ceiling and the other three walls of the refectory housing the famous painting.

In 1978, conservator Pinin Brambilla was charged with restoring the famous painting. Twenty-one years and $7.7 million worth of work later, the results were unveiled in 1999. The team had retouched the painting using reversible water-based paints that do not combine chemically with the original pigments. But some critics objected. Given the extent of the retouching, some branded the painting a "Brambilla" rather than a "da Vinci".

Today, conservators play many roles besides arresting and repairing damage. They might do chemical tests designed to determine whether materials scheduled to share an exhibit case are compatible. For example, the sulfur in a woolen fabric might react chemically with a silver object, turning it black with tarnish, as expressed in the following reaction:

$$Ag^{o} + S^{o} \rightarrow AgS_{\text{(black)}}$$

Conservators also assess whether an art object can travel to other museums without damage, often designing packaging to protect the art in transit from vibration, sudden shocks, and changes in temperature and humidity.

Hidden treasures beneath the surface

Sometimes in the process of examining a work of art, conservators make unexpected discoveries. Since paint changes chemically with age, becoming more transparent, a painting underneath another may become more visible over time. Although many artists reuse canvases, Picasso did an especially large amount of overpainting during his Blue Period, says conservator Bonnie Rimer. At the Art Institute of Chicago, they recently found two unknown Picassos—both underneath a third. If you look at Picasso's famous painting "The Old Guitarist", you can see a faint trace of another painting beneath.

Rimer examined the layered Picasso canvas using both X-rays and infrared reflectography. In the latter technique, light in the infrared wavelengths is bounced off the painting. Depending on the materials used by the painter, the light is absorbed or reflected to various degrees. Reflected light is captured on video, and the image is transmitted to a computer. "Since X-rays and infrared reflectography show different things, they are used together to examine the layer structure of paintings," explains Rimer.

The combination of high-tech images revealed two separate compositions underneath. One contains a cow, calf head, baby, and mother. Later, the composition of the painting was clarified when historical research unearthed a sketch of the painting sent to Picasso's friend Max Jacob in a 1903 letter. "It's essentially like rediscovering a lost painting," says Zuccari.

Science or art?

Bonnie Rimer found a way to do both.

Bonnie Rimer found art conservation to be the perfect way to combine her interests in science and art. She studied chemistry at the University of Illinois, Urbana–Champaign, but chose art history as her major. After reading about the restoration of the Sistine Chapel, Rimer decided to spend her last semester of college in Florence, Italy. That's where she began her studies in art conservation. Her semester abroad convinced her that she had found her career.

After attending graduate school at Queens University, Rimer completed an 18-month internship at the Museum of Modern Art in New York. Currently, she is an Andrew W. Mellon fellow in art conservation at the Art Institute of Chicago.

Anne Rosenthal is a science writer based in Palo Alto, CA. Staff from the Conservation Department of the Art Institute of Chicago contributed to this article.

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TATTOO Chemistry GOES SKIN DEEP

By Brian Rohrig

"Think before you ink," suggests heavily tattooed rock legend W. Axl Rose. Getting a tattoo is serious business. The decision to mark your body for life should not be taken lightly. Only about 1 in 10 teens currently has a tattoo, but no doubt many more have thought about it. Have you? Knowing the chemistry might help you decide.

Tattoos have been around for thousands of years. Heavily tattooed Egyptian mummies have been unearthed. Many ancient tribes marked their bodies as a part of religious rituals. Others throughout history used tattoos to mark a rite of passage or to inform others of their social status. Some societies tattooed criminals for permanent identification and penalty. Today, many think of tattooing as "body art".

In ancient times, getting a tattoo was a particularly painful and dangerous process. Tattooing often involved using crudely fashioned needles made from wood or bone to tap pigments into the skin. It's no surprise that many died from infections.

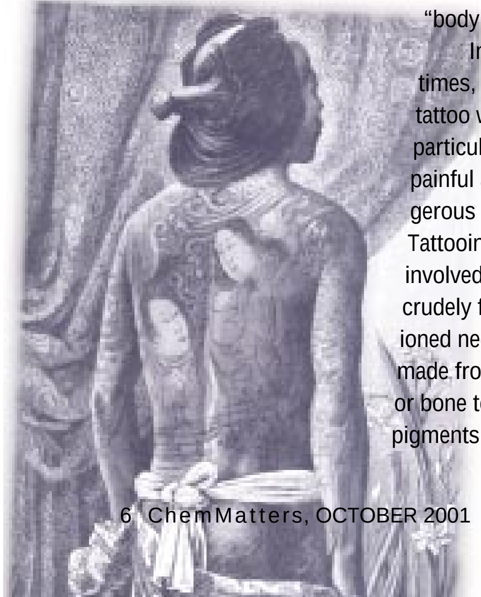

ILLUSTRATION FROM ACS STOCK

Today, the tattooist uses a handheld "gun" resembling a dentist's drill. The design is created by a cluster of electrically powered needles that puncture the skin anywhere from 32 to 3600 times per minute. A burning sensation generally accompanies this process, with some experiencing more pain than others. The most painful place to get a tattoo is where there is not much fat, such as on the head, feet, or hands. These areas are also the most prone to infection.

Applying the pigment

Tattoo pigments must be delivered into the dermis, a layer of skin just below the epidermis. The dermis is made up of blood vessels, hair follicles, nerve cells, sweat glands, and a network of protein fibers known as *collagen*. It's important to inject the pigment deep enough, because the surface layer is continually shedding dead cells. Placed on the epidermis, your tattoo would wear off in a few weeks. But it's also important that the pigments do not go below the dermis into the underlying fatty tissue. Nonpolar tattoo pigments dissolve readily in nonpolar fat. If accidentally injected below the dermis into the fatty tissue, pigment spreads and colors bleed into one another (see Figure 1).

The exact formulas for tattoo pigments are proprietary secrets, but each one begins as a powder to be mixed with a liquid dispersal agent such as glycerin, ethyl alcohol, or propylene glycol. The liquid dispersal agent must be maintained at a neutral pH, since many pigments undergo color changes with pH changes. The powdered pigment does not dissolve but is simply dispersed into a colloidal suspension of particles. The larger the particle size, the better its ability to reflect light. Ideal tattoo pigments must be large enough to reflect enough light to form vivid images.

As soon as the pigment enters the skin, the immune system of the body is activated. Immediately, the body tries to rid itself of these unwelcome intruders. But each pigment particle is huge compared to the size of a bacterial invader! Unable to get rid of these particles, the immune system settles for isolating the intruders from the body. Macrophages—large scavenger white blood cells that search and surround foreign invaders—soon coat every particle. Thus every tattoo becomes a thick layer of macrophage-encased pigments that remains under the skin for life.

Tattoo chemistry

Tattoo pigments commonly contain an iron oxide (Fe_2O_3 and Fe_3O_4) base. Black pigments may also contain carbon black (C) particles. White pigment is usually titanium oxide

PHOTO BY PICTUREQUEST

(TiO_2); reds may be mercuric sulfide (HgS); and yellows, cadmium sulfide (CdS). The potential toxicity of these heavy metal compounds underscores the need for skillful preparation and injection methods. However, a certain percentage of the population may still suffer allergic reactions, resulting in severe rashes or bumpy scar tissues under their tattoos.

It is essential that strict hygiene be observed during the tattooing process. New needles must always be used; in fact, they should always be removed from their sterile packages in front of the customer. Tattoo pigments must be mixed up fresh, never to be reused. All permanent equipment must be completely sterilized in an autoclave, a chamber that kills germs with steam under high temperatures and pressure. The tattooist must always wear new disposable latex gloves. In preparation, the skin area must be shaved and swabbed with antiseptic. Finally, antibacterial ointment must be applied regularly to the new tattoo.

Since there is always bleeding as tattoo needles penetrate into the dermis, there is always a risk for transmitting blood-borne pathogens. A recent study found that people who had received a tattoo were nine times more likely to be infected with hepatitis-C than people who had not received a tattoo. Although no direct link was established between obtaining the tattoo and the infection, few of the infections could be traced to other possible sources such as intravenous drug use or transfusions.

PHOTO FROM ACS DISK STOCK

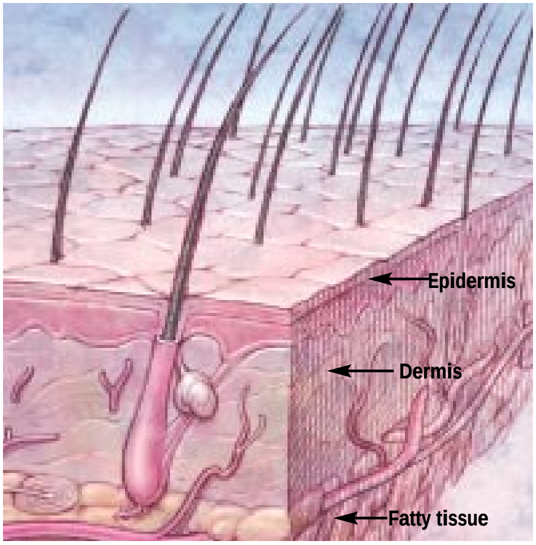

Figure 1. Tattoo pigments must be delivered into the dermis.

Cosmetic tattooing, called *micropigmentation*, is rapidly gaining favor with women. Generally applied by physicians or trained technicians in clinics, cosmetic tattoos can substitute for applied makeup, like eyeliner, eye shadow, or lipstick. Besides being time-saving and convenient, micropigmentation may also be a step in reconstructive surgery, restoring the natural appearance of scarred and damaged skin.

Tattoos aren't for everyone

Cosmetic tattooing is not for everyone. It is an expensive elective procedure that must be done right the first time, since mistakes are hard to cover. Applied to sensitive areas like lips and eyelids, the procedure can be painful. Sun exposure can cause pigments to change color or fade. Over time, black iron oxides, used for eyeliner, can oxidize to form red iron oxides. In other words, your black eyeliner can rust!

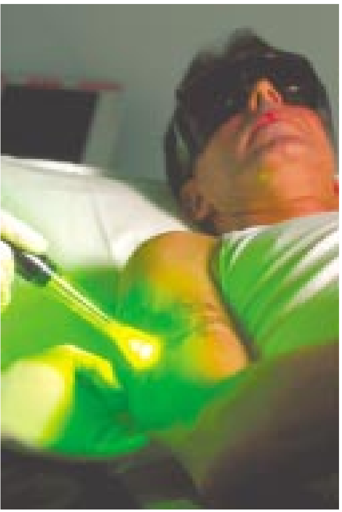

PHOTO BY PICTUREQUEST

Several laser treatments may be required to remove a tattoo.

If you're still debating, the biggest thing to know is that a tattoo is relatively permanent. Consider this. What may look cool at age 18 may not seem quite as cool when you are 30. It is a big decision to put a mark on your body that may last a lifetime. About half of those getting a tattoo wish they hadn't.

Is a tattoo really permanent? Before the advent of laser surgery, the only way to remove a tattoo was to remove part of the skin—thereby replacing your tattoo with a scar. Today, laser treatments are the most effective ways to eliminate unwanted tattoos.

PHOTO FROM PHOTODISC

A laser is a high-intensity beam of monochromatic (one color or wavelength) light. When absorbed by the tattoo pigment, the laser light is converted to enough heat energy to break the macrophage-encased particles into tiny fragments. Some of these small pieces are removed by the immune system; others find permanent lodging in the lymph nodes. The laser-fragmented tattoo pigments may exit the skin only to be distributed throughout the body.

Even with laser treatment, it is rare to experience the complete removal of any tattoo. Permanent eyeliner may even darken with laser treatment. Worse yet, red pigments of iron(III) oxide (Fe_2O_3) can undergo a chemical reduction to black iron(II) oxides. Goodbye lip liner. Hello mustache!

Still thinking about a tattoo? A temporary tattoo may be the way to go. These can look as vivid and colorful as real ones, without any pigment injected into the skin and without the accompanying risks. Placed on the surface of the epidermis, a temporary tattoo wears off after a month or so. Tempted? Try it. Maybe the reactions of your family and your friends will help you decide if you want the real thing.

Brian Rohrig teaches chemistry at Eastmont Academy in Columbus, OH. His most recent *ChemMatters* article "Model Rockets—Chemistry for Liftoff" appeared in the April 2001 issue.

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ACTIVITY:

An Iron-Clad Recipe for Ancient Ink

Probably, some ancient cave dweller dipped a pointed stick into a mineral-rich puddle and used the colorful solution to make pictures on the wall. This primitive "ink", a far cry from the inks in desktop printers or ballpoint pens, had two ingredients still found in all inks today. It had a liquid vehicle (water, in this case) and a mixture of colorful pigments. Today, manufacturers may add other ingredients to modify its chemical and physical properties, but the basic composition of ink remains the same.

Until recent times, all inks were made from naturally occurring materials. Iron–gall ink was the most important ink used in Western history. Leonardo da Vinci wrote his notes using iron–gall ink. Bach composed with it. Rembrandt and Van Gogh drew with it. The constitution of the United States was drafted with it. And, when the black ink on the Dead Sea Scrolls was analyzed using a cyclotron at the Davis campus of the University of California, it was found to be iron–gall ink.

The Roman historian, Pliny the Elder (23–79 AD) wrote that galls were used to produce dyes. He described an experiment that he did using a piece of papyrus that he dipped in gallic acid. He noted that when he dripped a solution of iron salt onto the papyrus, it turned black.

To make iron–gall ink, galls from oak trees were crushed in water to obtain gallotannic acid. The acid was then mixed with water and vitriol (iron(II) sulfate). Water served as the vehicle, and the vitriol–acid combination, the pigment. Gum arabic, a golden sap from acacia trees, was added to keep the insoluble iron product in suspension, thus helping the ink to flow onto the surface. The result was iron–gall ink.

Iron–gall ink was very useful because it did not rub off documents. Unlike paper, parchment, which was made from animal skins, was not absorbent, so carbon-based ink rubbed away easily. Iron–gall ink ate into the parchment by reacting with the collagen content. Iron–gall ink also reacts with cellulose in paper or papyrus, which poses a problem for modern conservators, especially when the ink has eaten all of the way through a document. Some ancient documents written with iron–gall ink have holes where the ink was applied. Some of these texts can still be read by "reading the holes". Others, unfortunately, are destroyed beyond recognition. *Lois Fruen*

Make your own ink

Try making your own iron–gall ink. Find out how it's made the old-fashioned way by going to the home page of the Iron–Gall Ink Corrosion Web site posted by a group of art museums in the Netherlands.

www.knaw.nl/ecpa/ink/index.html

But if you don't want to gather oak galls and wait four weeks for them to ferment, you can try a *ChemMatters* recipe substituting tea bags for oak galls. We adapted ours from directions found in *Chemistry in the Marketplace*, 4th Edition, by Ben Selinger.

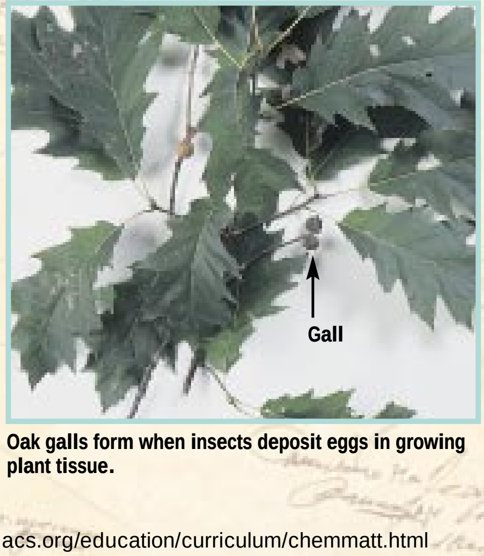

PHOTO BY MIKE CIESIELSKI

Oak galls form when insects deposit eggs in growing plant tissue.

Materials

(enough to supply ink for about 30 writers)

Laboratory apron and safety goggles
Hot plate
Beaker tongs or protective pad for handling hot glassware
200 mL tap water
Two regular tea bags
Three 250-mL beakers
One heat-proof glass funnel that can be supported by a 250-mL beaker
Filter paper (coffee filter works well) moistened with water and shaped to fit funnel
100 mL white vinegar
1 mL of 3% hydrogen peroxide (H_2O_2) (available from a pharmacy)
Small pad of steel wool (plain, no soap) about the size of a large piece of bubble gum
Gum arabic, also called Acacia (available from art supply store in granular or liquid form)
Two 10-mL graduated cylinders
10 small plastic cups
Plastic coffee stirrer for each writer (with a scissors, snip each one to a writing point)
Paper for each writer

Safety

We recommend preparing the ink in a standard chemistry laboratory with safety equipment available. Hydrogen peroxide is sold as an antiseptic. It bleaches clothing, and it is poisonous if swallowed. Allow your vinegar–iron solution to cool to room temperature before adding hydrogen peroxide (you can set it in a shallow container of water to speed the cooling). The ferric tannate solution and your ink product will stain clothing, so take care not to spill. Wear your apron and goggles throughout the preparation procedure.

Make your own ink

Directions

1. Make a batch of very concentrated tea. Pour 200 mL of water into a beaker. Heat to boiling using a hot plate. Remove from hot plate and soak two tea bags in the water for at least 5 minutes. Remove and discard bags. The strong tea will be rich in tannic acid (Figure 1).
2. Make a solution containing iron(II). Pour 100 mL of vinegar into a beaker and add a pad of plain steel wool (Figure 2). Bring to boil and simmer for about 7 minutes. Remove from heat, and pour the liquid into a clean beaker through a funnel lined with a piece of wet filter paper. Allow the iron solution to cool to room temperature.
3. Into the cooled iron solution, pour 1 mL of hydrogen peroxide solution. You should see a dark brownish-red solution indicating the presence of iron(III).
4. Into each plastic cup, pour equal amounts, about 5 mL each, of the strong tea and iron solutions. Stir contents with one of the coffee stirrers and observe the formation of black ferric tannate (Figure 3).
5. Add a few grains (or drops) of gum arabic to keep the ferric tannate in suspension and to bring the ink to the desired thickness for writing. The gum arabic will keep the ink on the surface of the paper just long enough for the pigment to drop evenly to the paper.
6. Dip the pointed end of a coffee stirrer (your “quill”) and experiment with writing on paper.

Details

The chemical composition of tannic acid is complex and nonuniform. It is a naturally occurring organic acid found in bark, fruits, nuts, leaves, and, in the case of the oak, insect galls. There are several forms of the acid, and the *Merck Index* lists other names by which it is known: tannin, gallotannin, gallotanic acid, and coriligan.

Here are the chemical reactions that describe the progress of your ink making:

$$2H^+ + Fe \rightarrow Fe^{2+} + H_2$$

$$2H^+ + 2Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + 2H_2O$$

$$Fe^{3+} + \text{tannic acid} \rightarrow \text{ferric tannate}$$

Discussion

- For the first reaction, what was your source of hydrogen ion? Of iron?
- What happened to cause the iron atom to change into a ferrous ion? Is this an oxidation or a reduction?
- Was there any visible evidence that H_2 formed as a product of the reaction?
- In the second reaction, ferrous ions (Fe^{2+}) are further oxidized to form ferric Fe^{3+} ions. What is the oxidizing agent responsible for that change? What observation showed you that a chemical change took place?
- In the third reaction, the ferric ion reacts with tannic acid to form the pigment, ferric tannate. Is ferric tannate soluble in water? What color is it?

Further investigation

Keep your writing samples and examine them after several days. Did their appearances change? If so, what do you think caused the changes?

Find illustrations in art books showing drawings made by Leonardo da Vinci and describe the appearance of the lines he drew with iron–gall ink. How does ferric tannate pigment change over long periods of time? How would you explain this color change over time?

Try making a batch of ink by just mixing the ferrous solution you made in step 2 with the tea solution. Don’t add hydrogen peroxide. What color is the mixture? Is there a precipitate? Is your writing visible? Let your writing sample sit in the air for a day. Does its appearance change? Explain what you see.

Change the procedure so that hydrogen peroxide is only added as a final step. Does the mixture still turn black? Explain what you see.

PHOTOS BY MIKE CIESIELSKI

Figure 1. Make a batch of tea.

Figure 2. Make a solution containing iron(II).

Figure 3. Mix the two solutions.

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ILLUSTRATIONS FROM ACS STOCK

Lithography Printing

From Rocky Start ...

By Helen Herlocker

Right now, right here, you are reading this printed page. Chances are that you're not the only one in your school with a copy of this issue of *ChemMatters*. And chances are even better that this is not what you would consider a big deal. Colorful printed materials are everywhere you look. So what's the point?

Five hundred years ago, the mere fact that two copies, let alone thousands of copies, of one publication might be in existence was a very big deal. European monks worked long hours in workrooms called "scriptoria", painstakingly copying manuscripts, one letter at a time. It's no wonder that the Latin words *explicuit feliciter* often appeared at the end—"Thank goodness it's finished!"

The invention of the printing press by Johannes Gutenberg in the 15th century is arguably the most important invention of the last millennium. Gutenberg, a jewelry maker, wanted to find a way to mass-produce religious pamphlets. Using his jewelers' tools to carve out metal molds for each letter of the alphabet, he filled them with a molten lead alloy. Next, he aligned the resulting raised metal letters on a frame to construct the text. Finding it difficult to hand stamp the completed message, Gutenberg rigged up a wine press for holding both the paper and the type frame.

Gutenberg then considered his choices of inks to complete his project. Fast-drying, water-based inks were fine for hand copying, but they evaporated too quickly from the metal type for effective printing. He preferred an ink used by woodcut artists—a more viscous, slow-drying mixture of boiled linseed oil and finely divided graphite or *lampblack*. Turning the wine press, he drove the ink deep into the fibers of the paper. Museum examples of these first printings, as well as of his later triumph, the beautiful and costly Gutenberg Bibles, remain sharp and clear to this day.

As important as the invention of movable type was to the advance of modern civilization, barely a trace of it remains in the pressrooms of today. Enter a printing plant, and you'll see a series of giant smooth rollers turning out a steady paper stream of clean colorful text and images—at a speed beyond Gutenberg's wildest imagining.

Lithography

ChemMatters, like most magazines, books, and catalogs, relies on a method of printing called *lithography* or "stone printing". Although you won't find any rocks in a printing plant, the method gets its name from a late 18th-century invention, a classic case of serendipity, in other words—luck.

Aloys Senefelder, a native of Prague and a resident of Munich, wanted to write and print his own plays and musical scores for the theater. He tried etching on steel, copper, and zinc until he ran out of money for these expensive materials. As a last resort, he tried smooth slabs of locally quarried limestone.

The story goes that one day his mother interrupted his work for his list of clothes to be laundered. He picked up a greasy crayon, and wrote the list on a piece of stone. Later, while trying to clean off the crayon marks, he noticed something interesting. Water soaked into the surface of the stone in all of the nonmarked places, but not into the crayon-coated areas. When he applied his oil-based ink to the stone, it behaved in the opposite way. It adhered to the crayon marks but was repelled by the water-soaked areas. When he pressed paper to the inked slab, lithography, "stone writing", was born.

Modern lithography for *ChemMatters*

Senefelder would be amazed at how modern lithography prints the colorful publications we see today. Art director Cornithia Harris assembles an issue of *ChemMatters* on her computer screen by combining edited article text files and colorful graphics. The screen display, easily arranged and rearranged, shows what the pages will look like. When everyone is satisfied with the result, Harris saves the layout on a Zip disk. There is no movable type, no stones—just streams of digital data.

When the disk arrives at the printing company, United Litho in Ashburn, VA, the data are translated into a program for making printing plates—four sets of them, one for each color of ink to be applied to the pages. (More about the four colors later.) In some ways, the photomechanical process for making a plate is the exact reverse of Senefelder's lithography process. Instead of receiving its images from a waxy crayon, the plate comes precoated with a nonpolar film. The computer directs the removal of this water-repelling material from the nonimage areas.

Plates, generally flexible sheets of aluminum, have thin coatings of a light-sensitive emulsion—a mixture of a hydrophobic (water–repellent) polymer and a light-sensitive silver–halide compound. The computer, reading the data as a complex matrix of dots, directs a narrow laser beam to be either “on” or “off” for each dot in its path as it completes its row-by-row scan of the plate. The light is “on” for a nonimage dot. The light is “off” if the dot belongs to the image. Only the light-exposed dots undergo a chemical change. The chemical change makes these nonimage dots soluble to the solutions used in the next treatment.

TO DIGITAL FUTURE

Next, the plate goes through a developer–activator solution. This solution dissolves the laser-exposed photo emulsion, washing it away from these nonimage areas. The unexposed dots in the image areas remain coated with the water-repelling emulsion.

Roll the presses!

The plate is now ready to transfer its inked image. It works like this. The plate is wrapped around a printing roller. During a print run, the plate is predampened with water, which adheres to the hydrophilic (water attractive), nonimage areas only. This water coating repels the oil-based ink, which adheres only to the hydrophobic, nonpolar regions of the plate. The technician, called a “pressman”, controls the balance of water to ink. Too much water prevents the ink from sticking to the image areas; too little, and ink smudges into nonimage areas.

The image from the plate doesn’t go directly to paper, however. Instead, the plate transfers or offsets its ink to more flexible rollers made of rubber. These are better able to supply the pressure necessary to drive the ink deep into the fibers of the paper. A hot “flash” treatment sets the ink, drives off its volatile solvent, and leaves only the colorful pigments behind. Thus, the printing process gets its full name: Offset Lithography (see Figure 1).

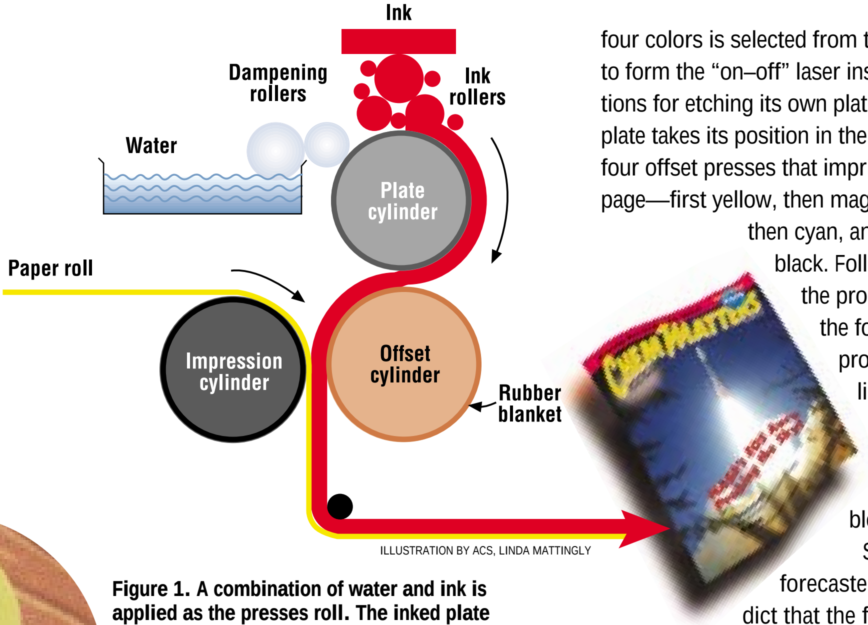

ILLUSTRATION BY ACS, LINDA MATTINGLY

Figure 1. A combination of water and ink is applied as the presses roll. The inked plate cylinder contacts the rubber-coated offset cylinder, which in turn transfers the ink to paper.

End of story? Not quite. Remember that there are four sets of plates, one for each of four ink colors used to print an issue of *ChemMatters*. Only four colors? You are probably noticing many others as you look at the illustrations on this page. But take a closer look with a strong magnifying lens, and the secret of 4-color printing is revealed (see Figure 2). Believe it or not, every color in an illustration is rendered as a display of tiny dots—cyan, magenta, yellow, and black. Add some white spaces from the page, and you have your entire printing palette.

PHOTO BY MIKE CIESIELSKI

Figure 2. Every color is a display of tiny dots.

Before dot patterns are transferred to plates, the digital files undergo a color analysis. The number of dots of each color, their arrangement relative to one another, and the white spaces in between are derived from the file data. Next, the dot pattern for each of the four colors is selected from the mix to form the “on–off” laser instructions for etching its own plate. Each plate takes its position in the series of four offset presses that imprint the page—first yellow, then magenta, then cyan, and finally black. Following the progress of the four-step process is like watching a flower bloom. Some forecasters predict that the future will bring alternatives for media that go well beyond paper, ink, and presses. Imagine reading the same “newspaper” every day, but every day finding different stories, pictures, and links. In fact, your electronic newspaper, a rolled-up page you carry in your backpack, might display one page after another at your command. Lucent Technologies of New Jersey is working on adding complex circuitry to thin sheets of flexible plastic to create this “E-paper” of the future.

Helen Herlocker taught high school science in Carroll County, MD, before joining the staff of *ChemMatters.*

ACKNOWLEDGMENT

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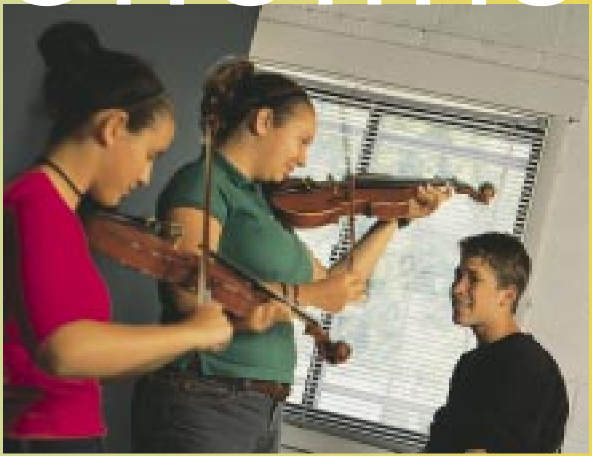
ChemSumer

Stringed Instruments Chemistry

By David Thielk


PHOTOS BY MIKE CIESIELSKI

Imagine listening to a Bach concerto played on two different violins. One, produced in the shop of Antonia Stradivari, is nearly 300 years old. The other is a modern inexpensive factory-made violin. Whether or not you are a trained musician, chances are you could easily pick the Stradivarius by listening to the two being played. But what accounts for the differences in sound? Musicians and scientists have been trying to answer that question for decades.

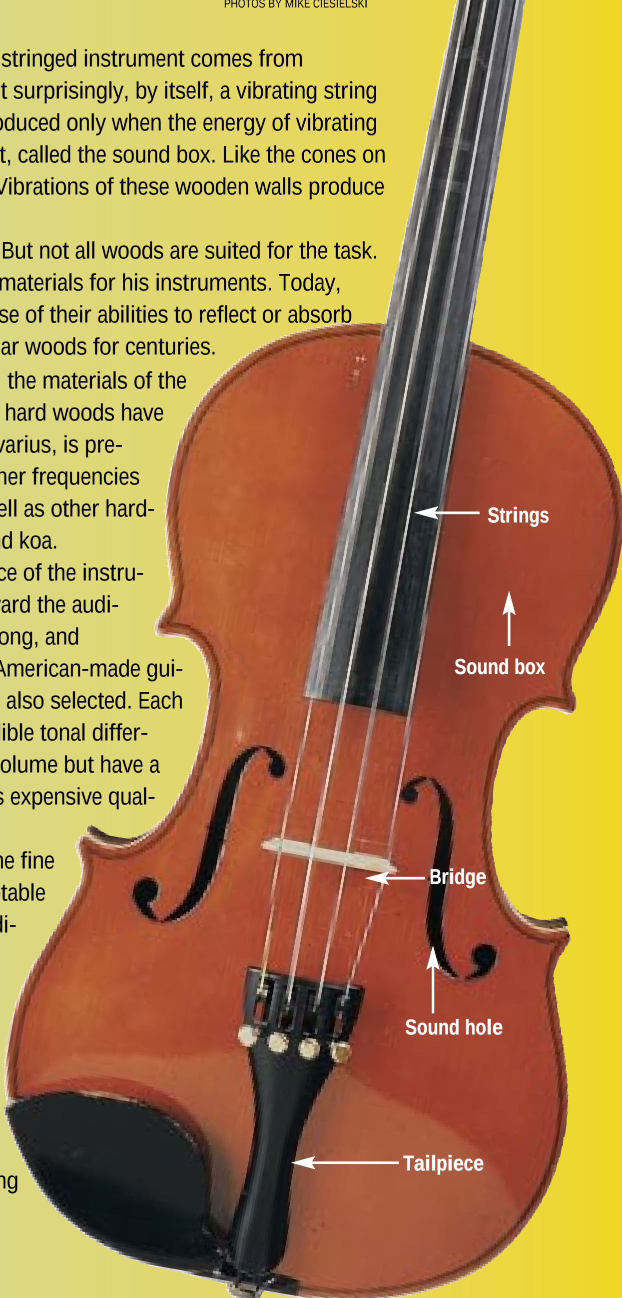
The way a stringed instrument produces sound is no mystery. Sound carries energy, and the initial energy that produces musical tones in a stringed instrument comes from plucking or drawing a bow across a string, causing it to vibrate. But surprisingly, by itself, a vibrating string produces almost no sound. The beautiful sound of a violin is produced only when the energy of vibrating strings is conveyed by air into the main body of the instrument, called the sound box. Like the cones on a loudspeaker, the walls of the sound box are set to vibrating. Vibrations of these wooden walls produce the sounds we hear.

Most violins, and certainly all old violins, are made of wood. But not all woods are suited for the task. Stradivari often returned to the same stands of maple trees to find materials for his instruments. Today, instrument makers still describe certain woods as “musical” because of their abilities to reflect or absorb different frequencies. Instrument makers have prized these particular woods for centuries.

For a guitar or another stringed instrument to have good tone, the materials of the sides and back should reflect rather than absorb sound. In general, hard woods have high reflection properties. Maple, the wood of choice for the Stradivarius, is preferred for mandolins as well because of its ability to project the higher frequencies characteristic of these instruments. Guitar makers use maple, as well as other hardwoods, on the sides and backs, including mahogany, rosewood, and koa.

Rather than reflect sound, the materials used on the top surface of the instrument should absorb and transmit sound from the inside toward the audience. Called tone woods, these woods must be light, strong, and aesthetically pleasing. The most popular tone wood for American-made guitars is spruce, but Western red cedar and mahogany are also selected. Each of these woods has different sound characteristics, resulting in audible tonal differences. Mahogany-topped guitars, for example, produce less bass volume but have a crisp midrange. Mahogany is often the tone wood of choice for less expensive quality instruments.

But if choosing the same type of wood alone could replicate the fine Stradivarius violins, instrument makers would be turning out acceptable clones on a regular basis. What makes the wood in the prized Stradivarius violins so exceptionally responsive? Dr. Joseph Nagyvary, a biochemist at Texas A&M University, believes he has found the answer. His laboratory analyses reveal that Stradivari treated the woods with preservatives made from ingredients as simple as borax ($Na_2B_4O_7 \cdot 10H_2O$), a common ingredient in modern laundry detergents, and alum ($AlK(SO_4)_2 \cdot 12H_2O$), traditionally an ingredient in brine for making pickles. Stradivari, he believes, soaked the woods in mixtures of these solutions for as long



by Ear

as two years before shaping them. It may be that his primary goal for this treatment was to make lasting, durable instruments. Nagyvary thinks that the greatly enhanced tone quality is likely to be its fortunate byproduct.

Although musicians and collectors prizing the estimated 1200 Stradivarius violins remaining today are critical of Nagyvary's conclusions, the biochemist has already applied his methods to making his own line of violins. Many of these Nagyvary violins are highly acclaimed by present-day musicians

In search of vanishing trees

Like Stradivari, traditional violin makers often returned to the same stand of maples to obtain wood year after year. Once a tree was selected and felled, the knowledge and skill of the craftsman came into play. The blocks of wood for violin tops were cut parallel to the grain to produce the best tone. With this cut, the cellulose fibers found extending upward through the tree would be oriented *parallel* to the surface of the instrument, allowing for maximum elasticity and response. Quartersawing, as this is called, is still used today to prepare raw wood for use on the tops of all quality stringed instruments.

The decline in abundance of tropical tone woods has driven up the price of traditional guitars and bows. Brazilian rosewood, also known as jacaranda, is considered to have the best tonal properties of all of the rosewoods used in guitar construction. Unfortunately, this wood is essentially unavailable for modern guitar construction. Adequate but less desirable Indian rosewood is normally used in its place. And the Brazilian wood called pernambuco is still valued as the ultimate choice for a traditional violin bow with its ideal strength to weight ratio. Unfortunately, living pernambuco is nearly nonexistent.

PHOTOS BY MIKE CIESIELSKI

The scarcity of these and other woods is one factor driving instrument makers to seek out new materials.

For thousands of years, humans have been making stringed instruments from plant and animal materials—woods, gourds, skins, hides, bone, and gut. These natural materials were readily available and workable. But today, as desirable woods become rare and as musicians look for new sounds, these traditional materials are being replaced by laminates and composites. The result is a musical revolution.

The synthetic revolution

Imagine a guitar impervious to water. Such an instrument would be right at home at a beach campout. With a little careful balancing, you could use it for a float toy by day, and strum it by the campfire at night. Mario Maccaferri began building such a guitar, entirely of plastic, in the 1950s. A master builder of traditional violins made of wood, Maccaferri was certain that plastics were the wave of the future. After successfully manufacturing a variety of useful plastic items normally made from wood, he began producing his first guitars from Dow Styron plastic in 1953. Maccaferri continued to build plastic instruments for 30 years—ukuleles, guitars, and even violins. Although these instruments sound flat and dull next to quality wood instruments, they are playable and very reasonably priced.

Today, even traditional instrument makers are discovering synthetics. Many musicians are choosing synthetic materials for convenience as well. Polyvinyl chloride glues, which can be made to "unglue" at specific temperatures, have replaced horsehide glue, an unpredictable material that often crystallizes with age. Synthetic glues offer easier and more predictable repairs. "Superglue" (cyanoacrylate), unheard of on traditional instruments, is used today to securely bind pieces that will never have to be taken apart or to fill gaps and seams. (See "Liquid Bandages" in *ChemMatters*, February 2000.)

The use of synthetic materials is affecting the classical music world as well. Finding them difficult to keep in tune, violinists today rarely use animal gut strings. Instead, strings are made from nylon cores wrapped with metal windings. Violin tailpieces are now almost always made of plastic or metal, materials that absorb less sound than the traditional wooden tailpiece.

As tone woods become scarcer and even more expensive, some instrument makers are producing instruments made entirely of synthetic materials. Graphite fiber, used for making golf clubs, fly fishing rods, and other sporting equipment that must be both light and strong, is replacing pernambuco in the production of violin bows, as well as tone woods in guitars.

Redefining music

Will certain sounds always be recognized as music, while others are judged to be noise? If Beethoven were alive today, would he recognize hip-hop as authentic music? Is the difference between music and noise defined by the age in which we live, or will there always be standards to which new forms of music are compared?

As synthetic materials replace traditional materials in stringed instruments, new sounds will be born. The first artists to embrace new sounds will likely be the artistic innovators. Typically, innovators, popular in their day, all but disappear 10 years later. Others, for some indefinable reason, take hold and live on for centuries.

In the science fiction movie *The Empire Strikes Back*, an amusing scene takes place in a "cantina" nightclub with musicians from all corners of the galaxy making tones, barely recognizable as music, on wildly bizarre instruments. Will your grandchildren listen to music played on instruments made of materials beyond your imagination? Will you recognize, let alone appreciate, the sounds they call music? Better hold on to those tapes and CDs. You may need them to explain what real music is supposed to sound like!

David Thielk is a science writer who lives in Port Townsend, WA. His most recent *ChemMatters* article, "Kidney Dialysis—The Living Connection", appeared in the April 2001 issue.

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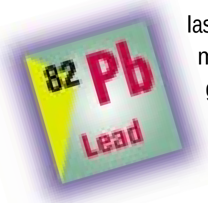
MysteryMatters

Lead—Beethoven's Heavy Metal Ailment

By Jay Withgott

The music written by renowned composer Ludwig van Beethoven is amazing enough, but what's more amazing is that he did it all while living in tremendous pain. From the age of 20, Beethoven was afflicted with a mysterious malady that altered his personality and caused him endless suffering. Despite seeing dozens of doctors, not one of them could cure his abdominal pain, digestive trouble, depression, and irritability, and none of them could figure out what was wrong.

In 1802, he wrote in a letter, "After my death, if Dr. Schmidt is still alive, ask him in my name to discover my disease . . . so at least as much as is possible the world may be reconciled to me."



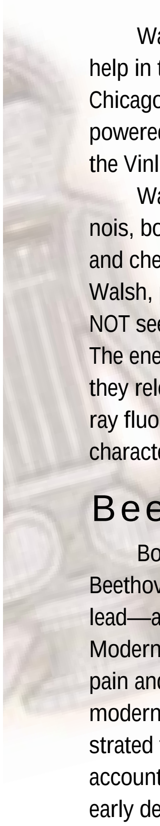
Well, it came 173 years too late, but last year, analytical chemists finally determined what ailed—perhaps killed—the great musician. The culprit? Element number 82 on the periodic table: lead.

The story begins in Vienna one day after Beethoven's death in 1827, when a young music student clipped a lock of the composer's hair, as was customary at the time. The lock of hair was passed down through the generations within the family, and during World War II, it was given as a gift to a Danish doctor who had helped Jews escape Nazi Germany. When the lock of hair was eventually sold at auction in 1994, Beethoven scholars snapped it up.

Two of the buyers, with the improbable names of Ira Brilliant and Che Guevara, wondered whether modern techniques of analytical chemistry could be applied to the hair in order to clear up some long-debated questions about the composer: Did Beethoven contract syphilis? Did he use painkillers to ease his suffering? What killed him? And, most intriguing of all, why did he go deaf at an early age (yet still continue composing incredible music until the day he died)?

Chemical detective work

Brilliant and Guevara enlisted chemist William Walsh, chief scientist of the nonprofit Health Research Institute and Pfeiffer Treatment Center in Illinois, to tackle the project. Walsh was best known for analyzing and finding characteristic patterns in the biochemistry of sociopaths like Charles Manson and those who committed the McDonald's massacre and the Oklahoma post office killings. After years working with coroners, the FBI, and Scotland Yard, Walsh says he was thrilled to direct the Beethoven project because it was "the first time I got to analyze someone who was a GOOD guy!"



Walsh scoured the world for the best people and technologies to help in the analyses. He began by enlisting Walter McCrone, founder of Chicago's McCrone Research Institute. McCrone, an authority in high-powered microscopy, had previously analyzed the Shroud of Turin and the Vinland map, concluding both to be fakes.

Walsh also contacted the Argonne National Laboratory (ANL) in Illinois, boasting the world's most powerful tool for studying the structure and chemistry of ultra-tiny objects. The Advanced Photon Source, says Walsh, provides "the brightest beam of photons anyone's ever seen" (or NOT seen, actually, since it's 100 times brighter than the sun's surface!). The energetic X-ray beam knocks electrons out of atoms. Upon return, they release energy. These units or *quanta* of energy are measured by X-ray fluorescence spectroscopy. Because every element releases its own characteristic quantum pattern, its identity is readily revealed.

Beethoven's chemical profile

Both McCrone's analysis and that of ANL showed the same thing: Beethoven's hair contained more than 60 parts per million (ppm) of lead—about 100 times the amount found in an average person today. Modern patients with such a concentration suffer from severe abdominal pain and other symptoms that Beethoven showed. Thus, the tools of modern chemistry, too late to be of any benefit to the composer, demonstrated that Beethoven suffered from lead poisoning. This condition likely accounted for his personality changes, his physical symptoms, and his early death at 57.

The analyses also answered other questions. In the early 19th century, mercury was the treatment for syphilis. Because no mercury was found in the hair sample, it's likely that Beethoven did not have the disease. And an assay of the hair by a collaborating Los Angeles researcher revealed no traces of opiates, the drugs he would most likely have used to dull his pain. Walsh concludes that Beethoven, keeping his mind clear for music, doggedly worked through his pain.

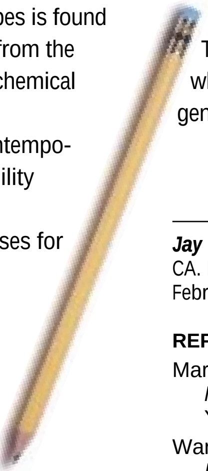
Beethoven's deafness remains a mystery. Deafness only rarely results from lead poisoning. Walsh speculates the composer may also have suffered from a bone disorder called Paget's disease.

How and why did Beethoven get lead poisoning? Answering this question may fall to historians rather than chemists. Sources of lead abounded for the average 19th-century European. One potential source was drinking water, likely to pick up trace amounts of lead from the lead pipes through which it flowed. Even today, lead solder in pipes is found in some older houses. Indeed, the term "plumbing" comes from the Latin word for lead, *plumbum*—the origin of the element's chemical symbol: Pb.

Ignorant of the dangers of poisoning, Beethoven's contemporaries saw lead as a useful material. Its high luster, malleability (shaping ability), ductility (ability to be drawn out into thin strands), and its resistance to corrosion suggested many uses for technological and practical applications.

Lead poisoning today

In more recent decades, lead has been used for a wide variety of products, including paint, batteries, glass, ceramics, ink, electric cable sheathing, protective shielding against X-rays and radioactive substances, jewelry, stained glass, car radiators, tanks, food cans—even foil caps on wine bottles. Don't worry about the pencil that you may be chewing. Early manufacturers thought that the "lead" in pencils was exactly what the name implies. But we now know that "lead pencils" contain graphite, a form of carbon, not lead.



PHOTOS BY MIKE CIESIELSKI

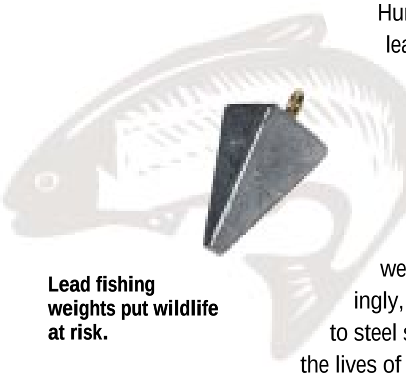
It has only been in the past few decades, however, that we have learned enough about the threats of lead to human health to take serious steps to eliminate or reduce it in the products around us. Lead-based paints, particularly dangerous to young children who put objects in their mouths, were common until 1978, when they were banned in the United States. Leaded gasoline was used until the 1970s, when the government began phasing it out by mandating that new cars be made to require unleaded gas.

Because of such steps, atmospheric lead emissions in this country have decreased dramatically. In 1970, lead emissions totaled 223,300 tons, but by 1991, they dropped to only 5467 tons. The percentage of children showing elevated blood lead levels has fallen from 88.2% to 4.4% from the late 1970s to the early 1990s.

The symptoms

Lead poisoning still occurs, and we need to recognize the symptoms. Abdominal pain, nausea, fatigue, slowed reflexes, weakness, vertigo, tremors, and loss of appetite are common physical signs. Mental manifestations include depression, irritability, confusion, anxiety, and learning problems. Lead causes damage to kidneys and other organs; it damages the reproductive tract, the brain, and the nervous system, and it can cause high blood pressure and heart failure.

Children are more susceptible than adults, as their bodies absorb lead more readily. Still developing physically and mentally, children experience damage that is more lasting and severe.



Lead fishing weights put wildlife at risk.

Humans are not the only victims of lead poisoning. Birds and fish are at risk, because hunters' cartridges and fishermen's sinkers have traditionally been made of lead. Waterfowl and fish that ingest shotgun pellets or fishing weights sicken and die. Increasingly, however, hunters are switching to steel shot, which is beginning to save the lives of many thousands of birds.

Beethoven, unfortunately, hadn't a clue about the threat of lead poisoning. If he were alive today, blood tests would confirm the diagnosis, and treatment would be available for ridding his body of lead. That he was able to compose some of the world's greatest music while enduring the pain of his condition makes the work of this great genius all the more remarkable.

Jay Withgott is a science writer, author, and journalist based in San Francisco, CA. His article "Dinosaurs and Iridium—Traces of an Impact" appeared in the February 2001 issue of *ChemMatters*.

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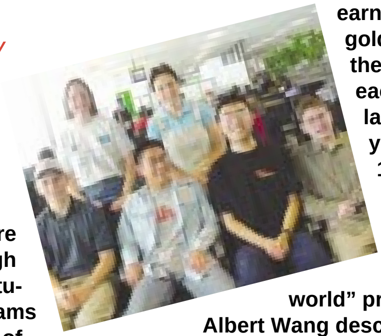
Olympic Chemistry



Studying for an Olympic chemistry exam may not be your idea of a way to spend a summer vacation. But this spring, more than 10,000 U.S. high school chemistry students took local exams for a chance at one of the 20 slots for a two-week June chemistry training camp at the U.S. Air Force Academy in Colorado Springs, CO.

The training was intense. Finally, a four-member team was selected to represent the United States at the 33rd International Chemistry Olympiad (IChO), held this year in Mumbai, India, July 6–15.

Students from 54 nations competed in the IChO, with the U.S. team winning two gold and two silver medals. Sean Kedrowski, of Baylor High School in Chattanooga, TN, and Binghai Ling, of Brighton High School, Rochester, NY, won gold medals. Collin Martin, of the Oklahoma School of Science and Math, and Albert Wang of Bellaire High School, TX, won silver.

Shown from left to right in the photo above, Sean, Albert, Binghai, and Collin await their flight to India with mentors Nadine Szczepanski and Jane Nagurney.

Recent U.S. teams have performed well at the IChO. U.S. team members have earned the top gold medal at the Olympiad each of the last two years. In 1999, the U.S. team garnered the "best in the world" prize.

Albert Wang describes his experience this way: "To label the International Chemistry Olympiad simply as another academic competition is to label the Olympics as another race. For just over one week, teams of students representing some 50-odd nations across the world convened in India for this competition. Interactions between so many different groups, sharing so much more than our common interest in chemistry, gave us a glimpse of our future global community."

To learn more about the Chemistry Olympiad and to test your knowledge and skills on one of the qualifying exams, go to www.acs.org/education/student/olympiad.html. Next year's competition? The Netherlands!

National Chemistry Week Celebrates Chemistry and Art

Mark your calendars for National Chemistry Week 2001, November 4–10. This year the theme is "Celebrating Chemistry and Art".

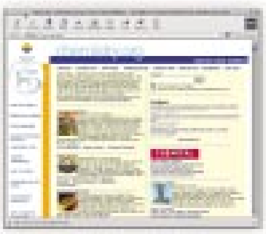
Each year, the American Chemical Society's (ACS) Office of Community Activities designates the first full week of November for this lively community-based event. Member volunteers nationwide engage thousands of individuals in activities and events to help people better understand the nature and importance of chemistry in their everyday lives. Some of these events may be taking place in your school or even in your favorite shopping mall.

This year, local ACS sections are planning poster contests, museum events, and displays to demonstrate the importance of chemistry in the world of art. *ChemMatters* is pleased to be part of the celebration.

If your class or your science club would like to get involved, contact your local section of ACS to find out how you can join in on their plans for the celebration. You can find local leadership information at chemistry.org/localsections.

To learn more about this year's National Chemistry Week theme, go to chemistry.org/ncw.

chemistry.org



ChemMatters always links you to a selection of Web sites for more information about the important chemistry in your life. This month, we invite you to enjoy the sites in our own neighborhood. The American Chemical Society (ACS) has a new Web presence at chemistry.org with links to a wide variety of useful information. We hope you'll make it a regular stop for browsing through current magazines and journals, reading about the most useful products that affect your life, getting the latest career information, and researching topics for your class assignments and projects. While there, use the site map to find *ChemMatters* under Educational Resources. You'll find articles from recent issues online, and if you want more in-depth information on any of the recent articles, you can link to the Teacher's Guide (it's allowed!).

If you have comments about the ACS Web site, or about anything you have read in *ChemMatters*, we would like to hear from you. You can reach us at chemmatters@acs.org.

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Reach Us on the Web at
www.acs.org/education/curriculum/chemmatt.html