CHEMMATTERS

DEMYSTIFYING
EVERYDAY CHEMISTRY

FEBRUARY 1998

A Splash from the Past!

ChemSurf

Fizzies—A Splash from the Past

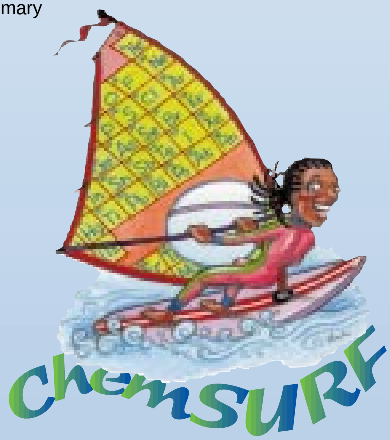
- **Fizzies**
  www.fizzies.com
  The official home page for Fizzies has more from Premiere Innovations.
- **The American Dietetic Association**
  www.eatright.org/asweeteners.html
  This page records the position of the ADA on the use of nutritive and nonnutritive sweeteners.

Lindow Man—Murders in a Bog

- **The Bog Page**
  www.jamesmdeem.com/bogpage.htm
  This Web site by James Deem, *Bodies from the Bog*, catalogs and discusses bog bodies.
- **Science at Work**
  www.campus.bt.com/CampusWorld/pub/ScienceNet/slup/Interviews/vincentd.html
  This site includes a discussion of the preservation techniques used for Lindow Man.

Color in a Capsule

- **Silly Putty on the Web**
  www.vern.com/sillyputty
  This page lists some interesting trivia, uses, and history of Silly Putty.
- **The Art and Science of Microencapsulation**
  www.swri.org/3pubs/ttoday/summer/microeng.htm
  This article from *Technology Today* is a nice summary of the microencapsulation industry.



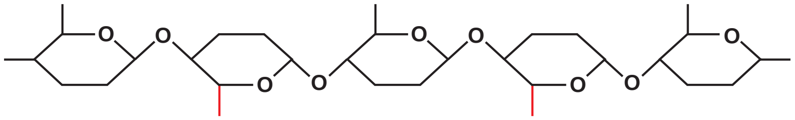
Ozone Out of Bounds

- **Ozone Transport Assessment Group**
  www.epa.gov/oar/otag/otag.html
  This Web site addresses OTAG and its concerns for ground-level ozone.
- **Georgia Tech Atmospheric Sciences**
  www-wlc.eas.gatech.edu/wlc.html
  This Web page by William Chameides, Regent's Professor, goes into more detail on research of ground-level ozone.

Other Fun and Interesting Sites

- **MAD Scientist Network**
  madsci.wustl.edu
  Some 500 scientists are working in this network to answer about 250 questions from students a week in 26 areas of science. You can ask a question by completing the form under Ask A Question. However, check the archived questions or answered questions first to see if your question has already been answered. Just click on Recently Answered Questions or The MadSci Archives to check. If you are interested, you can browse the answered questions in a given area and check the ones that look interesting to you. This is not a site to ask homework questions.

Correction: An error occurred in the illustration of cellulose appearing in the article, "Counterfeit Detecting Pens" (October 1997, p. 14). The hydroxymethyl group appears on the wrong side of the molecule in every other molecule. A corrected version of the polymer appears below.



Cellulose

SomeMatters

A Different Approach

In this issue—the first in our 16th year—we unveil new departments for *ChemMatters*. One of our goals for *ChemMatters* is to keep up-to-date, and so we are striving for the look and feel of the current trends in magazine publishing. This new look includes the ChemSurf department we introduced in the last issue and another department called SomeMatters devoted to editorial notes, including these comments. This department will also include your letters and comments, special announcements, and updated information on articles from previous issues.

You will still see the familiar four "feature" articles. From past evaluations, we have noted that most of you enjoy reading about mysteries and consumer products. In response, we are making a commitment to present articles of these types in each issue. In this and future issues, two of the articles are presented as departments—MysteryMatters and ChemSumer.

In these two departments, you will see the use of symbols from the Periodic Table of the Elements. We think it is appropriate to connect *ChemMatters* articles with something familiar to all of us—the elements—and how they relate to the articles. Look for links between the article and the element.

A fifth and final department—still in the planning stage—will seek more involvement from you. We want to print questions from you on a chemical topic you have always wondered about. If your question is selected, it will be answered in a future issue.

Your comments and suggestions are valuable. We like to hear from you, and we welcome your questions as well. Send your questions or comments to me with your name and school affiliation to e-mail: ChemMatters@acs.org; or write: *ChemMatters*, American Chemical Society, 1155 16th St., NW, Washington, DC 20036-4892.

Michael Shea
Michael Shea

CHEMMATTERS February 1998

DEPARTMENTS

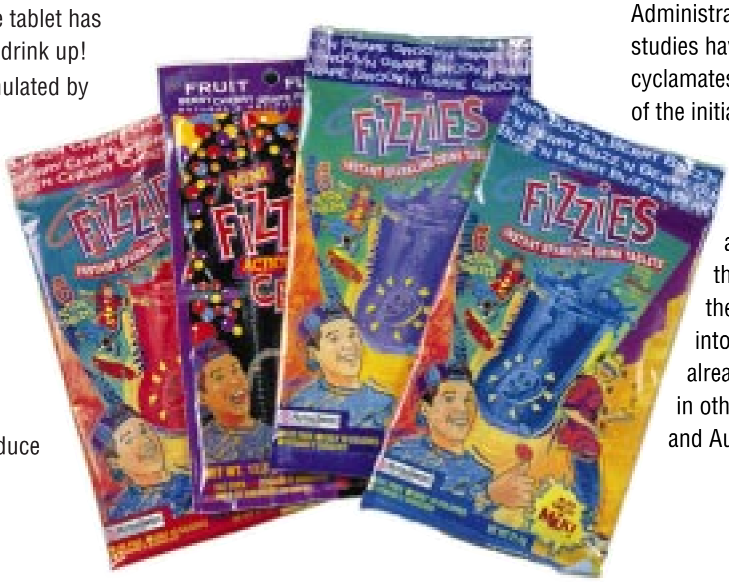
FEATURES

Fizzies—A Splash from the Past

By Brian Rohrig

They're baaack . . . a splash from the past! Fizzies instant sparkling drink tablets, popular in the 1950s and 1960s, are now back on the market. What sets them apart from other powdered drinks is that they bubble and fizz when placed in water, forming an instant carbonated beverage. Simply place a tablet in a glass of water and watch it fizz for a minute or so. After the tablet has completely dissolved, drink up!

Fizzies were formulated by scientists at the Emerson Drug Company in the 1950s. The researchers had been working with substances similar to today's Alka-Seltzer, a popular antacid. Alka-Seltzer tablets, when dropped in water, produce the distinctive "plop, plop, fizz, fizz" sound for which they have become famous. These scientists thought it would be great if they could duplicate this effervescence and create a tablet that would make instant soda pop when dropped into water. Thus, Fizzies sparkling drink tablets were born. They first appeared on the market in 1957 and became wildly popular, sweeping U.S. and international markets.



In search of a sweetener

In 1968, Fizzies were removed from the market in the United States because they contained cyclamates, an artificial sweetener. Cyclamates were banned because of a study that found a possible link between this substance and cancer in laboratory rats. However, according to the U.S. Food and Drug Administration (FDA), 75 subsequent studies have failed to demonstrate that cyclamates are carcinogenic. Because of the initial study, however, all products containing cyclamates had already been removed from the market. Cyclamates are currently under review by the FDA, which is considering their possible reintroduction into the U.S. market. They are already in use on a limited basis in other countries such as Canada and Australia.

Several years after Fizzies were banned, the formula was purchased by Premier Innovations, Inc. The company immediately began searching for a suitable substitute for cyclamates. An artificial sweetener was essential, because such sweeteners are much sweeter than ordinary sugar (sucrose) and only very small amounts are needed. Cyclamates are almost 45 times sweeter than sugar.

Today's Fizzies are made with aspartame, often marketed as NutraSweet, which is about 200 times sweeter than sucrose. If sugar were used in Fizzies, each tablet would be the size of a hockey puck, making it difficult to fit into a glass! After many years of research, the newly reformulated Fizzies were put back on the market in 1995 and have steadily gained in popularity.

The fizz in Fizzies

The fizz in Fizzies is caused by bubbles of carbon dioxide (CO_2) gas that are released when the tablet is dropped into water. Careful observation reveals that these bubbles always rise to the surface because CO_2 gas is much less dense than water. However, not all of the CO_2 gas rises to the surface; some of it dissolves in the water. The dissolved CO_2 can react with water to form carbonic acid, H_2CO_3 (see Reaction 1).

$$H_2O(l) + CO_2(aq) \leftrightarrow H_2CO_3(aq)$$

Reaction 1. The fizz in solution

The pH of the Fizzies drink registers between 5 and 6, showing that the resulting solution is clearly acidic. Carbonic acid is found in other carbonated beverages as well.


PHOTO COURTESY OF PREMIERE INNOVATIONS, INC.

These values are averages; relative sweetness depends on temperature, pH, and other substances in sweetened food. For example, aspartame and saccharin decompose at high temperatures; consequently, they cannot be used for cooking. Cyclamates, however, can withstand the high temperatures of cooking.

One of the ingredients on any soft drink label is carbonated water, which is another name for carbonic acid. However, in the production of soft drinks, the CO_2 is pumped into the solution under high pressure at the bottling plant.

The directions for Fizzies state to add the tablet to cold water. Milk can also be used, producing something like an instant root beer float! Although Fizzies sparkling drinks taste better cold, what happens when you drop a tablet in warm water illustrates some interesting chemistry.

$$H_3C_6H_5O_7(aq) + 3NaHCO_3(aq) \rightarrow Na_3C_6H_5O_7(aq) + 3H_2O(l) + 3CO_2(g)$$

citric acid **sodium bicarbonate** **sodium citrate** **water** **carbon dioxide**

Reaction 2. The reacting ingredients in Fizzies

At higher temperatures, less gas is able to dissolve in a liquid. If Fizzies are made with warmer water, less CO_2 remains in solution, and the drink tastes "flat." If you don't drink up right away, much of the dissolved CO_2 gas will diffuse into the air, leaving behind a fizzless sweet liquid.

The Fizzies label does not list CO_2 as an ingredient because the CO_2 is formed *in* the drink as a result of a chemical reaction between the first two ingredients listed: citric acid and sodium bicarbonate. As soon as a tablet hits the water, a gas is released, indicating that a chemical reaction has occurred (see Reaction 2).

The other ingredients in Fizzies, such as artificial flavors, aspartame, and ascorbic acid, combine with the products of this reaction, to give Fizzies their unique taste.

Neutralizing Fizzies

A bubbling glass of Fizzies drink is a good example of a neutralization reaction. An acid and a base combine to form three products—sodium citrate (a salt), water, and CO_2. However, because some of the CO_2 combines with water to form carbonic acid, the final product registers an acidic pH. The tablets are enriched with vitamin C (ascorbic acid), which also helps to lower the pH.

For the reaction between citric acid and sodium bicarbonate to take place at an appropriate rate, large numbers of citric acid molecules and bicarbonate ions must be able to collide with each other. In the solid powdered state, the reactants lack mobility, so fewer effective collisions occur and the reaction is slow. After dissolving in water, each molecule and ion is freed and can move about independently in the solution. This allows a much greater number of tiny, highly mobile molecules and ions to collide.

The term *aqueous solution* (aq), used in Reactions 1 and 2, is another way of saying that a substance is dissolved in water; thus, it exists either in the form of molecules or ions. Fizzies are stored in sealed pouches with a

Mini-Fizzies Activities

You can do some activities to learn more about how Mini-Fizzies behave.

- ***Which dissolves faster, whole Mini-Fizzies or tablets crushed into many pieces?***
- ***Does temperature play a role? Try Mini-Fizzies in different temperature water.***
- ***Does concentration matter? Try dissolving Mini-Fizzies in an already acidic drink like coffee or orange juice.***
- ***Why does the candy always rise to the surface before it finishes dissolving?***

PHOTO COURTESY OF PREMIERE INNOVATIONS, INC.

The original packaging for Fizzies

foil lining to keep the tablets dry and prevent a premature reaction with water from the air.

Fizzies versus Pop Rocks: What's the difference?

Fizzies are also available as a candy that can be popped into your mouth, known as Mini-Fizzies. Each packet contains five flavors: berry, cherry, grape, punch, and orange. You put a single Mini-Fizzie on your tongue, and it immediately reacts with saliva and begins to fizz, for a very interesting tingling sensation. A chemical reaction in your mouth—the water in the saliva causes the citric acid and sodium bicarbonate to react—produces CO_2.

So what's the difference between Mini-Fizzies and Pop Rocks? Pop Rocks do funny things in your mouth too; in fact, they also give off CO_2 gas. But take a look at a Pop Rocks label; CO_2 is one of the ingredients. CO_2 bubbles are manufactured inside the candy, and as the sugar dissolves in the mouth, the gas is released, producing a popping sound. This is a physical change: No chemical reaction here!

Brian Rohrig is a chemistry teacher at Aurora High School in Aurora, OH. He has just written a book called *150 Captivating Chemistry Experiments Using Household Substances*. This is Brian's first article in *ChemMatters*.

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Lindow Man—Murders in a Bog

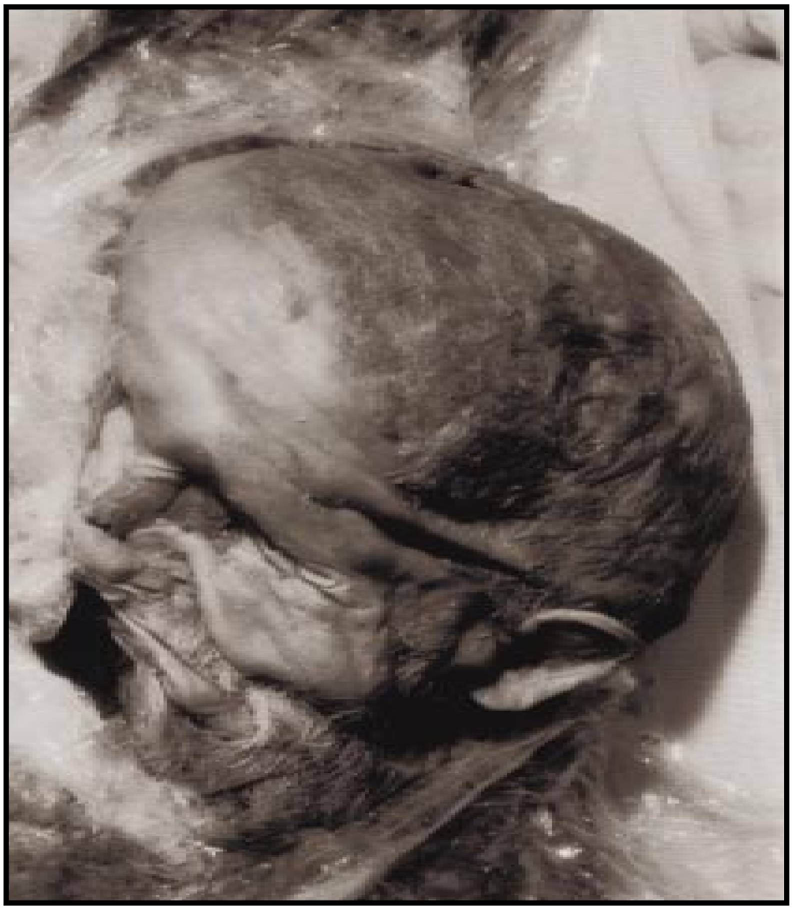


PHOTO: ©THE BRITISH MUSEUM

By Lynn Sibley

On May 13, 1983, Andy Mould and Stephan Dooley were working the shredder at the Lindow Moss Peat Company in Cheshire County, England. It was their job to watch for rocks or large pieces of wood that might jam the shredder. They spotted what appeared to be a burst football and, picking it up, joked that it might be a dinosaur's egg. As they handled it, the peat that was stuck to the "egg" began to fall away. Curious, they hosed it off, and it became clear that the object was a human skull—hair clung to the scalp, the left eyeball was still intact, and brain tissue was visible inside the cranial cavity. They called the police.

The police were intrigued by the discovery. When the preliminary forensic report found that the skull was that of a European female between the ages of 30 and 50, the police arrested Peter Reyn-Bardt for murdering his wife some 20 years earlier. Faced with what appeared to be irrefutable evidence, Reyn-Bardt confessed that he had killed his wife, dismembered her, and buried her in the Lindow Moss bog. Subsequently, the Oxford University Research Laboratory for Archaeology analyzed the skull by using a dating technique involving radioactive ^{14}C and determined that the skull was not Mrs. Reyn-Bardt's but that of a woman who had died about 1,750 years earlier. Based on the strength of his confession, however, Mr. Reyn-Bardt was convicted of murder.

More body parts

On August 1, 1984, Andy Mould was again scrutinizing the peat as it moved toward the shredder. He grabbed what he thought was a large piece of wood and tossed it toward his partner where it fell hard on the ground, exposing a well-preserved human foot.

55 BCE Romans invade Britain

20 BCE Lindow Man entombed in Lindow Moss

98 Roman historian Tacitus writes about bog bodies

230 Lindow Woman entombed in Lindow Moss

406 Romans leave Britain

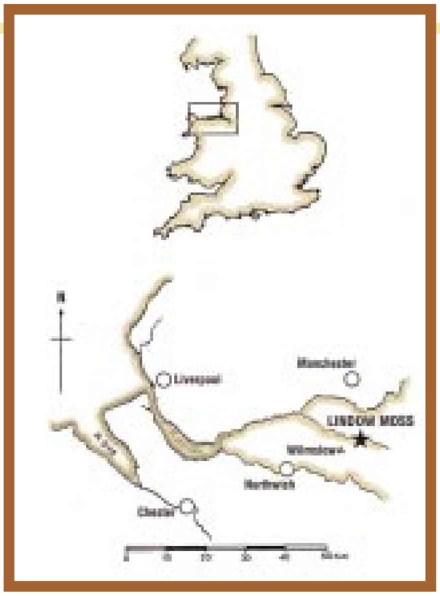
700 *Beowulf* is written

The Acid Test

The Lindow bodies did not rot in the peat bog. Normally a dead body is broken down by bacteria in a process called *putrefaction*. It didn't happen in this case because of three important factors: The water in the bog was anaerobic (no free oxygen), which prevented bacteria from growing; it was highly acidic (around pH 4), which preserved the Lindow Man's skin, hair, and fingernails; and it was extremely cold, which refrigerated his body and arrested decay.

Bogs are unbalanced ecosystems—they produce more vegetation than they decompose, causing a buildup of material called peat. Peat is made up of these partially decayed plants; humic and fulvic acids produced by this decay; and small amounts of insects, algae, yeasts, and fungi. This plant accumulation prevents oxygen from reaching deeper water.

There are different types of bogs, depending on weather and terrain, but most form in basins that have little or no drainage because the underlying bedrock is impermeable. As the water level rises, vegetation growing along the bank drowns and decays, forming soils that dam incoming streams. With no flowing water, the soil becomes waterlogged. Floating vegetation, primarily sphagnum moss, spreads over the water like an insulating blanket. Sphagnum moss extracts positively charged ions, such as calcium and magnesium, from water in the soil and releases hydrogen ions. Because the hydrogen ions are not flushed by flowing water, the environment becomes extremely acidic.



Location of Lindow Moss in Great Britain

The next morning Rick Turner, a Cheshire County archaeologist, began a search of the area. Walking along an uncut section of the bog, Turner noticed a flap of skin jutting from a wall of peat. The skin, coffee-colored with visible pores, was flexible except for the tip that had been exposed to the air for several months. Turner wondered whether it was Mrs. Reyn-Bardt or another ancient body.

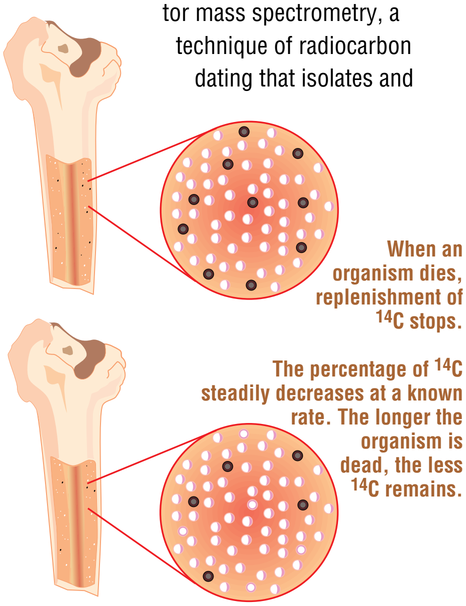
Turner's discovery brought a team of scientists to the Lindow Moss. Turner was convinced that the body was ancient because it was resting in undisturbed peat 2.5 m below the bog's original surface. The police were not so sure.

Fingernails still attached to the right hand

PHOTO: ©THE BRITISH MUSEUM

On August 6, the team began to trim away the peat. The remains occupied a small space, 0.7 m by 0.55 m, and Turner feared that only a portion of the body had survived the peat-cutting machines. The team slid a sheet of plywood under the block of peat containing the body, lifted it out, protected it in plastic sheeting, and drove it to the mortuary at a nearby hospital. The coroner placed it in a refrigerated box kept at 4 °C, the standard morgue temperature.

The autopsy was conducted by London's British Museum, but the coroner would not release the body until it was proven to be ancient. Researchers at the Atomic Energy Research Establishment, using accelerator mass spectrometry, a technique of radiocarbon dating that isolates and counts ^{14}C atoms, tested some bone fragments. On August 17, they announced that the body was at least 1,000 years old. More careful analysis later revealed that it was about 2,000 years old—from Celtic times.



Carbon dating

An unusual autopsy

On September 24, a team of archaeologists, chemists, surgeons, and others began the autopsy. They started with the flap of skin Rick Turner had first spotted. Using small brushes, scrapers, and squirts of distilled water, they cleared away the peat, removing the excess water with a dental vac-

1078 Construction begins on the Tower of London

1150 Oxford University is founded

1215 Magna Carta is signed

1242 Bacon describes a formula for making gunpowder

1386 Chaucer writes *The Canterbury Tales* uum. As Turner suspected, the lower body had been chopped off by the peat-digging equipment. However, the upper intestines and stomach survived, their contents preserved by the bog's high acidity (see The Acid Test).

When the face was cleaned, they knew for certain that the body was that of a male—the shape of the bone in the upper eye socket, the prominent mastoid bone (the bump behind the ear), and the beard were male traits. His head slumped downward, facing his right shoulder. The right arm, in good condition, was outstretched, with four well-manicured nails. The left forearm, in poor condition, was frayed above the wrist, exposing bone. Scanning electron microscopy (SEM) analysis of the beard and mustache hairs revealed "stepped" ends, indicating they had been trimmed with shears and not with a single blade. He was naked, except for a fur armband. The fur—short (5–10 mm), ginger-colored, and round—was fox fur. His upper body muscles were developed evenly on both sides which suggested, along with his well-groomed appearance, that he had done no manual labor.

Human sacrifice?

A chill came over the team as they rinsed away more peat—this man had met a violent death. His skull was fractured in two places, and his throat slit on the right side through the jugular vein. A leather thong dug into his neck; he had been garroted. X-rays showed that his neck was broken, which accounted for his head's unusual slump.

Why was the Lindow Man so brutalized? Anne Ross, an anthropologist who specializes in Celtic traditions, says that aspects of his death suggest that he was a victim of Druidic sacrifice. One clue is that he died a threefold death. Another clue is the analysis of the stomach contents, which contained burned cereal grains (see Lindow Man's Last Meal). Fried griddlecake was part of Celtic rituals, Ross says, and the blackened crust was fed to a sacrificial victim.

Full frontal excavation of Lindow Man

PHOTO: ©THE BRITISH MUSEUM

Preserved again

The next task was to preserve the body. Could modern technology do a better job than the acidic waters of the Lindow Moss? The team decided to freeze-dry the Lindow Man. Freeze-drying removes moisture from organic materials by sublimation. Water is turned into ice, then converted to vapor and removed. This method preserves the original structure and avoids excessive shrinkage. The team experimented first with pigskin. When they found the right method, they placed the body in a freeze-drying machine. When it was removed, the body was gradually adjusted to a room temperature of 19 °C and a relative humidity of 55%. The body shrank less than 5% and retained enough flexibility to be handled easily.

Today the Lindow Man rests in a display case in the British Museum in London. Unlike his grave in the bog, he lies on his back, face up—his eyelids closed over empty sockets, his lips pulled open from the autopsy. The fur armband is still wrapped around his arm, and the sinew garrote circles his throat. ▲

Lindow Man's Last Meal

The Lindow Man's stomach contained sphagnum moss spores; crushed wheat, bran, and barley grains; and mistletoe pollen. Electron spin resonance (ESR) spectroscopy showed that he had eaten burnt griddlecake before he died. ESR can determine thermal decomposition in organic matter by detecting atoms with unpaired electrons. When food is cooked, the reactions that take place create molecules with unpaired electrons. The food's molecular structure changes according to the intensity of the heat. From ESR spectra, it is possible to estimate the highest temperature the food reached while being cooked: boiled, 100 °C; baked, 200–300 °C; or hotter, if burned.

Lynn Sibley is a writer and former managing editor of *ChemMatters* magazine.

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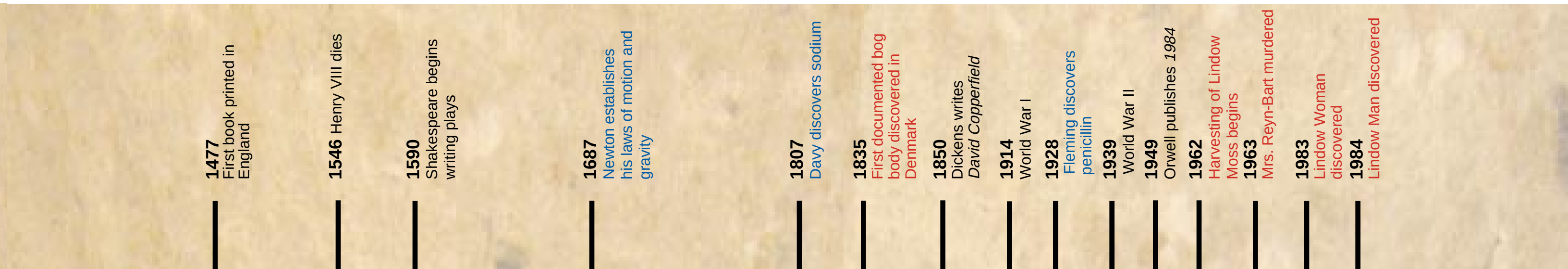


Color in a Capsule

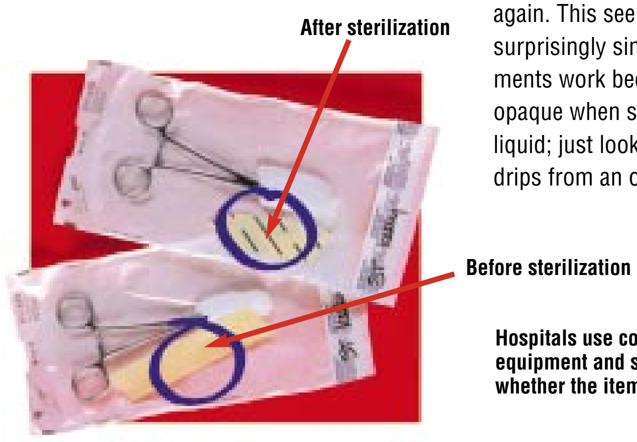
By Bruce Goldfarb


PHOTOS BY MIKE CIESIELSKI

Color-changing Silly Putty is an example of a dazzling new technology that changes the way we see things. In the past few years there has been an explosion of color-changing products—coffee mugs, T-shirts, pencils, stickers, and even battery testers.

Many of these products use thermochromic pigments and dyes that change color according to temperature. Simple irreversible thermochromic pigments have been around for a long time. For decades hospitals have used indicator strips or tape that develops a dark stripe when exposed to steam heat for a length of time. Because of this color change, hospital workers can tell just by looking at an item whether it has been sterilized.

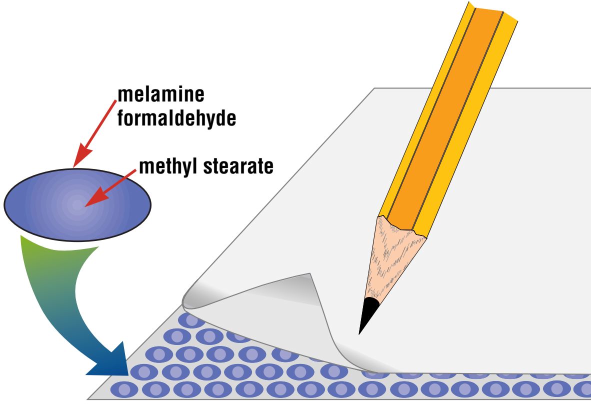
The pigments used in Silly Putty and similar products are different from these thermochromic products. They include a "reversible" microencapsulated pigment that cycles from a color to colorless and back again. This seemingly amazing stunt has a surprisingly simple explanation: The pigments work because waxes and fats are opaque when solid and transparent when liquid; just look at the clear melted wax that drips from an opaque candle.



Hospitals use color-changing indicator strips on equipment and supplies so that they can tell whether the item has been sterilized or not.

Big things in small packages

Microencapsulation was developed in the late 1930s at the National Cash Register Company and introduced in carbonless paper in 1954. The paper is coated with microscopic spheres containing chemicals that are pigment precursors—two colorless substances that turn dark when combined. The weight of a pen crushes the microcapsules, allowing the chemicals to mix and make colored ink.



ILLUSTRATIONS BY CESAR CAMINERO

Carbonless paper uses microencapsulation technology.

Microencapsulation is used in everything from scratch-and-sniff samples to deodorants. In the case of color-changing pigments, the microcapsules are composed of melamine formaldehyde—the same material as Formica—filled with a lipid (a fat) such as methyl stearate, according to Lyle Small, president of Chromic Technology, Inc. (Colorado Springs, CO).

The microcapsule contains a dye that is barely visible when the lipid is liquid but is vividly bright when the methyl stearate solidifies. A jar of pure microcapsules has a pale color. When the pigment is diluted in an ink or paint medium and spread in a thin layer during printing, it becomes essentially invisible.

By altering the combination of lipids in the microcapsules, color-changing pigments can be made to cycle at almost any chosen temperature, within a range of only about 5 °F. Like all lipids, color-changing microcapsules are subject to oxidation, ultraviolet radiation, and other degrading effects. Small says that the reaction may eventually stop cycling, but under most conditions, it will continue indefinitely.

From novelty to security

Color-changing microcapsules come in a palette of about a dozen colors. Two different dyes are typically used in printing and other applications—one is a permanent ink and the other a translucent color-changing pigment. For example, if red ink is mixed with a blue color-changing pigment, it will appear purple when cool. As you warm it, the blue color melts away, turning the purple to red.

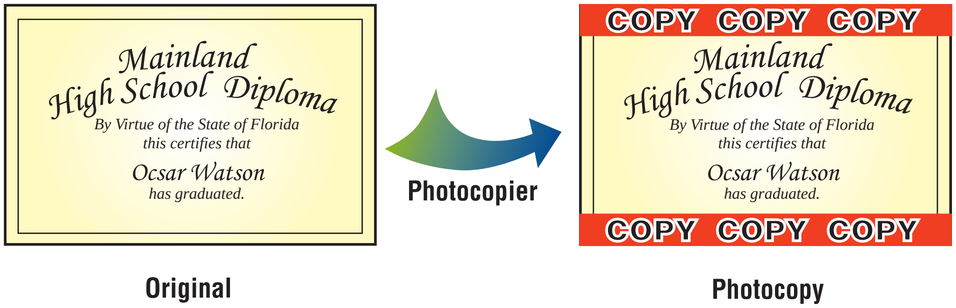
Small's creation of a thermochromic pigment in a sturdy microcapsule led to the development of inks that could be used on standard printing presses. These color-changing inks have opened new avenues of creativity that are limited only by the imaginations of designers and artists.

The next wave of development will take color-changing pigment from a novelty to a security device. There is growing interest in the potential for color-changing inks among security and law enforcement agencies, says Fred Davis, president of Davis Liquid Crystals (San Leandro, CA). Because color-changing ink is more costly than regular inks, it is usually used as a "spot" color in a small area or a stripe. You can make copy-proof paper by treating it with a pigment that is colorless on the paper but turns dark upon exposure to the heat of a photocopy machine. After an original is removed from the photocopier, the darkened area returns to colorless, but a copy shows the darkened area; therefore, you can tell very easily whether you have an original or a copy.

Color-changing pigments are beginning to be used in passports, certificates, licenses, tickets, and other official documents. It is going to make it much more difficult to get a fake ID, for example. Color-changing ink is "quick and easy to add" and difficult to counterfeit, says Davis. However, "no technology is effective forever. The bad guys catch up eventually," he says.

PHOTO COURTESY OF BINNEY & SMITH

Color-changing Silly Putty does everything the original does—and more!



Mainland
High School Diploma
By Virtue of the State of Florida
this certifies that
Ocsar Watson
has graduated.

COPY COPY COPY
Mainland
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Bruce Goldfarb is a science and medical writer in Baltimore, MD. His article "CO control: On the street, in the house, where you live" appeared in the MysteryMatters department of the October 1997 issue of *ChemMatters*.

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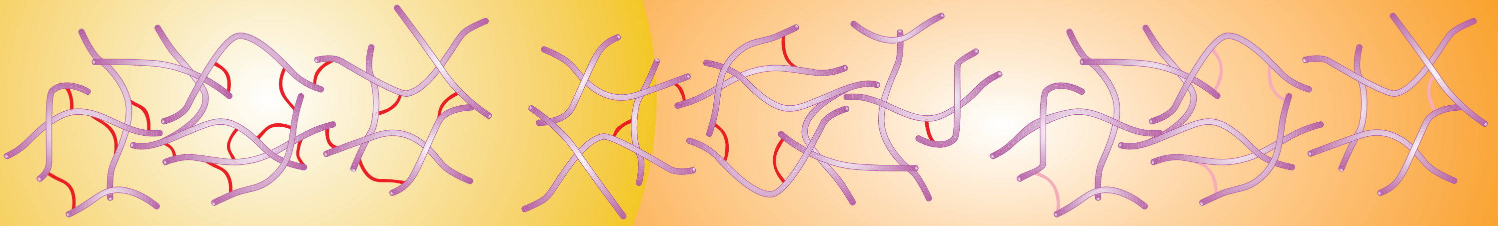
A Successful Failure



Elastomers
An elastomer will be rubbery (left) if it has many cross-link bonds. If it has few cross-link bonds (center), the elastomer behaves like a liquid. When the cross-link bonds are weak and easily broken (right), elastomer behavior is described as dilatant.

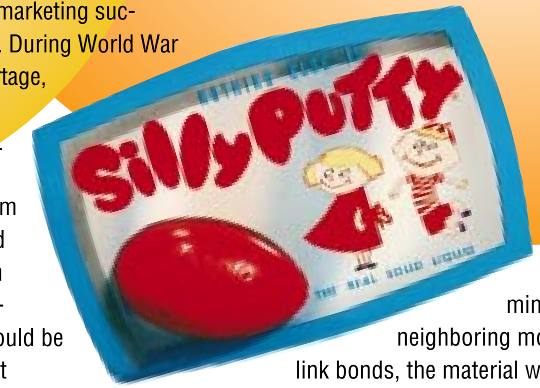
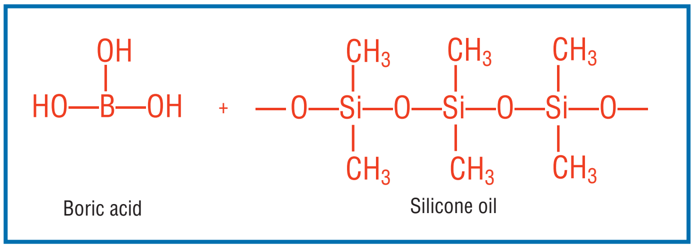


PHOTO COURTESY OF BINNEY & SMITH

Silly Putty—one of America's greatest toy-marketing successes—started out as a complete failure. During World War II, the United States faced a severe rubber shortage, which prompted industry to launch research efforts to develop a synthetic rubber substitute.

In 1943, chemical engineer James Wright was hard at work on the rubber problem at a General Electric (GE) laboratory. He mixed boric acid and silicone oil in a test tube, which was then heated. When polymerized, the compound formed a gooey plastic. The material could be easily molded, but refused to keep its shape. It flowed like a liquid but would snap if pulled quickly. You could roll it into a ball and bounce it off the floor: Interesting stuff, but worthless as a rubber substitute.

GE sent samples to engineers and scientists, hoping that somebody might think of a use for this material—and perhaps make a profit for the company. Dozens of the most creative scientific minds could not think of a single practical use for Wright's plastic.



$$\mathrm{HO{-}\overset{\displaystyle OH}{\overset{|}{B}}{-}OH \quad + \quad {-}O{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{Si}}{-}O{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{Si}}{-}O{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{Si}}{-}O{-}}$$

Boric acid	Silicone oil

Silly Putty ingredients

The bouncing blob was passed around as a novelty in industrial and scientific circles, eventually falling into the hands of a toy shop owner Ruth Fallgatter. An advertising consultant, Peter Hodgson, suggested that Fallgatter market the material as a toy for adults. In 1949, she bought a quantity of the goop, packaged small pieces, and sold them for $2. The following year, when she lost interest in the plastic, Hodgson decided to market it himself. Hodgson borrowed $147 to buy a batch of the goop, which he packaged in inexpensive plastic eggs. He chose "Silly Putty" from a list of a dozen names and sold the one-ounce wad for $1.

Silly Putty made its debut at the 1950 International Toy Fair in New York. A full-fledged fad emerged after Silly Putty was mentioned in *The New Yorker*. Within three days, Hodgson received more than a quarter-million orders.

Silly Putty is an elastomer, a substance that regains its original shape after being stretched or deformed. This is what gives Silly Putty its bounce. The molecules that make up the plastic are long and slender, mingling together like a bowl of cooked spaghetti. Its behavior is determined by the number of chemical bonds linking neighboring molecules. If the molecules have a lot of cross-link bonds, the material will be quite rubbery. If there are only a few cross-linking bonds, the plastic molecules easily slide past each other and flow like a liquid.

Usually, the cross-links in polymers are strong covalent bonds. But Silly Putty has weaker coordinate bonds (bonds in which both electrons are donated from one of the two atoms)—bonds that are easily broken. If you pull Silly Putty slowly, it will flow and stretch. Pull it faster, and Silly Putty will snap right in two. Liquidlike materials that act like a solid under short-term stress are described as *dilatant*.

After Hodgson's death, the rights to Silly Putty were bought by Binney & Smith, makers of Crayola crayons. The pink plastic is a fixture in American culture. More than 200 million eggs of Silly Putty have been produced since 1950. Silly Putty is recognized in 97% of American homes and has been purchased by almost 70% of households, according to Binney & Smith marketing information.

Silly Putty was a familiar pink color until 1990, when Binney & Smith unveiled fluorescent colors to celebrate its 40th anniversary. Glow-in-the-dark Silly Putty was launched the following year. Binney & Smith introduced color-changing Silly Putty in 1995.

Color-changing Silly Putty uses a nifty chemical trick that is more complicated than other color-changing inks but still based on melting points. The Silly Putty contains microcapsules 15–35 micrometers (µm) wide that hold a two-part dye and a temperature-sensitive solvent. The dye consists of two chemically bonded molecules. When the Silly Putty is warmed, the solvent melts and separates the dye molecules so they no longer create a color.

One variety of Silly Putty turns from orange to yellow when warmed; the putty is colored yellow and mixed with microencapsulated red pigment. When the Silly Putty is cool, you see the yellow and red pigments as orange. As you play with the Silly Putty and warm it with your hands, the red melts away, leaving only the yellow.

There's a lot of science packed in a $1.50 plastic egg, proving that you can learn from failure. When Peter Hodgson died in 1976, he left a $140 million estate—a tidy fortune for selling a completely useless product.

OZONE OUT OF BOUNDS

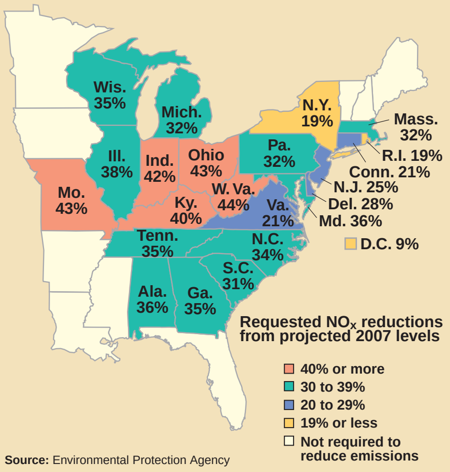
By Harvey Black

It's a hot, sticky July day in Chicago. Pedestrians trudge through the city's clammy streets, mopping their brows with handkerchiefs. The air seems heavy and unpleasant. It's a perfect day for ozone (O_3). In the air we breathe, ozone—the product of volatile organic compounds (VOCs) mixed with nitrogen oxides (NO_x) in the presence of warm sunlight—makes life unpleasant.

Temperatures in the 30s on the Celsius scale (90s on the Fahrenheit scale) are needed to supply heat for ozone formation, says Michael Koerber of the Lake Michigan Air Directors' Consortium. That's why ozone isn't a winter problem, even though winter days can be very sunny. Ozone makes breathing more difficult. In fact, when there's too much, local governments issue ozone alerts to warn people with breathing disorders such as asthma to stay inside.

Last year the Environmental Protection Agency (EPA) tightened its ozone regulations, further curtailing the amount allowed in the air. Those limits can affect anything capable of producing emissions that increase ozone in our atmosphere, such as trucks, automobiles, power plants, and factories. Under previous EPA standards, about 100 places in the United States were identified as nonattainment areas: Ozone levels in their air exceeded the standards. Chicago was one of these areas. The new standards have not been in place long enough for new nonattainment areas to be named.

EPA wants substantial cuts in NO_x emissions in 22 states.

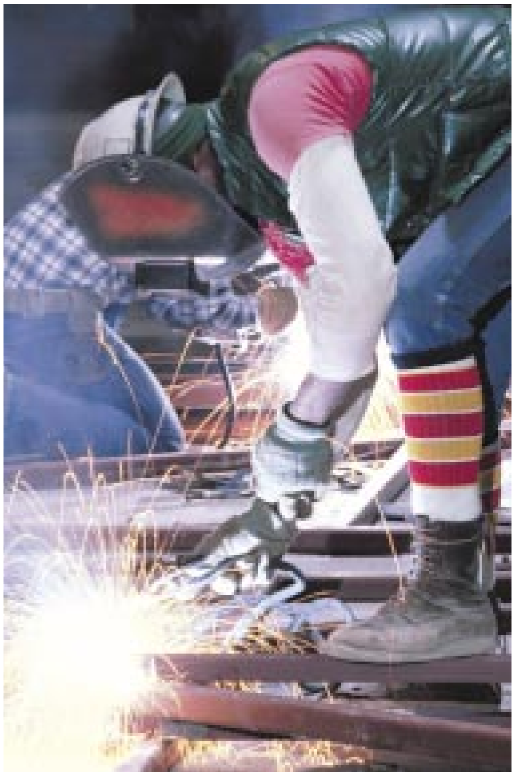


Source: Environmental Protection Agency

Understanding the chemistry of ozone is crucial to controlling it, and ozone chemistry is nothing if not complex and potentially confusing. The problem of ozone, or photochemical smog, as it was once known, was first described by California Institute of Technology scientist Arie J. Haagen-Smit more than 40 years ago. However, atmospheric chemists have only recently begun to grasp the sometimes maddening complexity behind the spawning of this noxious compound.

Understanding what's behind ozone formation pushes the limits and the imagination of scientists, notes William Chameides, who directs Georgia Tech's School of Earth and Atmospheric Sciences. Although the ingredients of ozone seem simple, they are anything but. Hundreds of VOCs can be involved in ozone formation, and that means a whole set of complex chemical reactions going on. "We don't understand the chemistry of every one of those compounds," says Chameides. "Each one contributes to ozone formation in different ways depending on the specific environmental conditions surrounding it."

Furthermore, "All those compounds influence one another in nonlinear ways," says Jay Odum of Georgia Tech. "You can't change just one and get a corresponding change in the way that ozone is formed." Moreover, notes Odum, the number of chemical products created when a VOC breaks down to form ozone can be



You can smell ozone in the air around welding.

enormous. Consequently, notes Chameides, scientists must use mathematical models—sets of equations—to approximate what they think is going on. Sophisticated though these models may be, they are still at least one step removed from reality.

Key to setting off ozone formation is the OH, or hydroxyl, radical. The OH radical is a free radical—it has one unpaired, or free, electron in its outer shell—and therefore it can undergo a process called *energetic rebounding*.

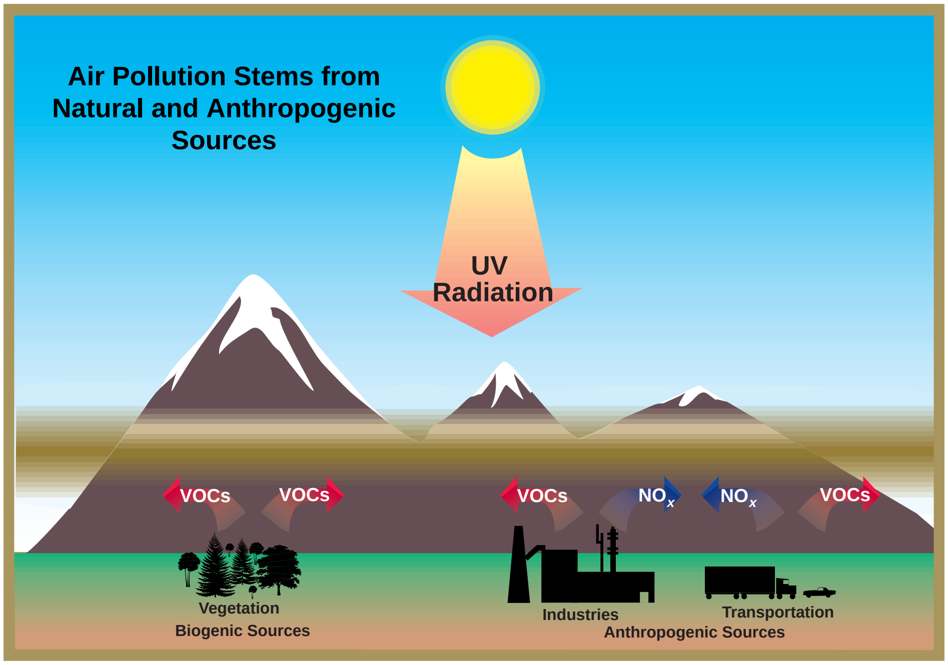
"It's going to grab an electron from another chemical and, in that process, it's going to cause a chemical reaction," says Chameides. "Free radicals are very reactive things in the environment."

What the OH radical is doing, says Chameides, is enhancing what the atmosphere normally does. Our atmosphere is oxygen rich—about 20% oxygen. So if compounds go into the atmosphere with little oxygen, our atmosphere kindly offers it to them.

VOCs don't have much oxygen, meaning they are in a reduced state, so they are perfect candidates to receive oxygen donations. Chameides emphasizes that oxidation of reduced compounds is an entirely natural process. For instance, methane is put into the air naturally as part of decomposition processes and oxidizes over time to carbon dioxide and water. "What's happening with air pollution is we dump a lot of reduced compounds into the atmosphere in a concentrated form in a given location; that causes the oxidation process to speed up. In the process, we produce ozone," he says. Therefore, ozone formation is an acceleration of a normal process.

The third major player in ozone creation is NO_x. Whereas VOCs and sunlight are the fuel for ozone, NO_x is the "catalyst" that leads to ozone, explains Chameides. Two forms of NO_x, nitric oxide (NO) and nitrogen dioxide (NO_2), are produced by the combustion of gas and oil, which means cars and trucks put it into the air.

Keeping track of NO_x is tricky, explains Barbara Finlayson-Pitts, a chemist at the University of California-Irvine. "The major form of NO_x that comes from combustion is NO. To produce ozone, it has to be oxidized to NO_2, which then photolyses to give an oxygen atom, which leads to more ozone." At the point where NO is being emitted, it will react with oxygen to form NO_2. However, air masses move. "As the NO_2 goes downwind, it clobbers the next guy [with ozone]. It's transferring the problem elsewhere," she says. Finlayson-Pitts points to California as a prime example of this phenomenon. Although NO_x emissions are high in Los Angeles, the ozone problem is downwind.



Numerous organizations from the public and private sectors are studying ozone nationwide. Over the past couple of years, the Ozone Transport and Assessment Group, an East Coast consortium, has examined weather conditions, such as wind movements, temperature, and humidity, in an effort to understand how ozone-causing pollutants travel through the air and bring ozone pollution to areas several hundred miles away from where they are emitted.

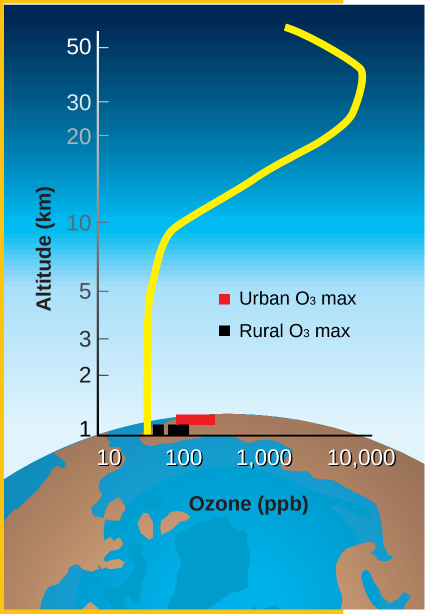
Obviously sunlight can't be controlled to limit ozone. Therefore, efforts to rein in ozone center on limiting VOCs and NO_x. VOCs come from two major sources—human activity (anthropogenic) and nature (biogenic). Anthropogenic VOCs result from manufacturing processes as well as car and truck fuel combustion. Biogenic VOCs, such as isoprene and terpenes, are produced by plants and trees. NO_x is a bit simpler: It comes from smokestacks and, as mentioned before, tailpipes.

Here's where limiting ozone can make air pollution controllers sprout gray hair. What researchers have found over the years is that a kind of give-and-take occurs between NO_x and VOCs. Consider, for example, the city of Atlanta, GA. Not only does it have lots of VOCs produced by cars and factories, it has forests of oak trees emitting isoprene. In short, it has a high VOC/NO_x ratio. Early attempts at controlling ozone in Atlanta focused on trying to control VOCs from human activity. It didn't work. Nature produced so many VOCs that the amount regulators took out of the air was equivalent to a

Where Ozone is Good for You

Although ozone near the ground can make life unpleasant, when it's between 10 and 30 miles above us—in the stratosphere—it's important, if not downright vital to our lives. It prevents harmful forms of solar ultraviolet (UV) radiation (such as UV-B, which can cause skin cancer) from reaching the earth. This high-altitude ozone is generated when sunlight hits molecules of oxygen (O_2), creating two oxygen atoms. These single atoms can then combine with oxygen molecules to form ozone (O_3). The sunlight or UV radiation responsible for splitting the molecules of oxygen is at wavelengths of <240 nanometers (nm). Ozone, however, is unstable and is itself easily broken down when free radicals such as the OH radical, bromine, or chlorine, which occur naturally in the stratosphere, combine with it.

But, as was shown by Nobel Prize-winning scientists F. Sherwood Roland and Mario Molina, humans have had an important role in breaking down the protective ozone of the stratosphere. Chlorofluorocarbons (CFCs), synthetic chemicals designed to be coolants, have leaked into the stratosphere. There, high-energy UV radiation breaks them down, freeing the chlorine, which can destroy ozone. The amount of chlorine generated this way dwarfs the naturally occurring amount in the stratosphere. CFCs in the lower atmosphere are inert. Their only activity is to slowly migrate upwards, where they can do damage.



SOURCE: GEORGIA INSTITUTE OF TECHNOLOGY

few buckets of water from the ocean. It didn't make much difference.

Put in more scientific terms, when the VOC/NO_x ratio is high, NO_x is the limiting factor. Control NO_x and you might be able to limit the production of ozone. Reverse the situation—a low VOC/NO_x ratio—and the opposite strategy should work. VOCs are the limiting factor; therefore, regulations controlling them should reduce ozone.

Scientists such as Finlayson-Pitts and Odum argue that for ozone to be effectively limited, both strategies—NO_x control and VOC control—must be used. If VOCs are to be controlled, the "different propensity" of each to form ozone—their reactivity—must be considered, says Odum. But control of those VOCs depends on more than just knowledge of the particular compound. "The problem is that reaction conditions for, say, toluene in one city might be different in another," he says. "It depends on what time of day the compound is released—in the middle of the day, when ozone is reaching its maximum value, in the morning, throughout the day, and so forth."

Teasing out the chemical complexities of ozone is a demanding and frustrating effort, but understanding the complexities behind its formation is crucial to controlling it and having clean air.

PHOTO COURTESY OF NATIONAL CENTER FOR ATMOSPHERE RESEARCH/ UNIVERSTIY FOR ATMOSPHERIC RESEARCH/NATIONAL SCIENCE FOUNDATION

Ground-level pollution from all sources can be a problem around major cities.

REFERENCE

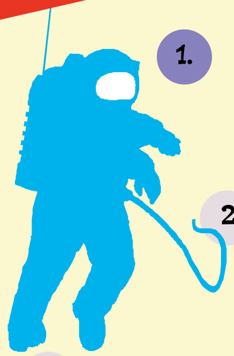
Raber, Linda. "EPA calls for NO_x emissions cuts." *Chemical & Engineering News*, Oct. 20, 1997, p. 14.

Harvey Black is a freelance science writer living in Madison, WI. His article "Surprising Citronella" appeared in the February 1997 issue of *ChemMatters*.

Elemental Punishment

by Robert Becker
Kirkwood High School
Kirkwood, MO

Use the clues to fill in the crossword puzzle using the names of 15 different elements. Some of the clues contain a double-entendre. Circle all that you find.
For example, This metalloid is used in transistors—think about that as you drive along our scenic highways listening to your radio! The element is arsenic and the double-entendre is "our scenic," which sounds like arsenic. (Answers are on page 3.)



1. Without this noble lightweight, scuba divers would be bent out of shape and doctors might be unable to heal them.

2. Critical mass of this fissionable material can blast you to the outer limits of the solar system!

3. Nothing is as effective as stating the obvious—with less than 1 ounce of this halogen on Earth, it's not very abundant.

4. Cinderella owes her good fortune to this semiconductor.

5. Has your car been acting up? You may want to check the antifreeze, oil, or gasoline.

6. Hamlet's soliloquy pondered whether or not this metalloid was diatomic.

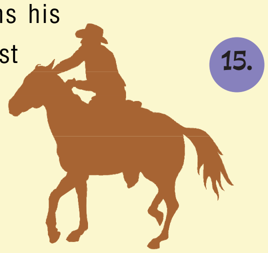
7. Man can easily survive (and so can woman) without Ag or Au, but don't take away this trace dietary mineral.

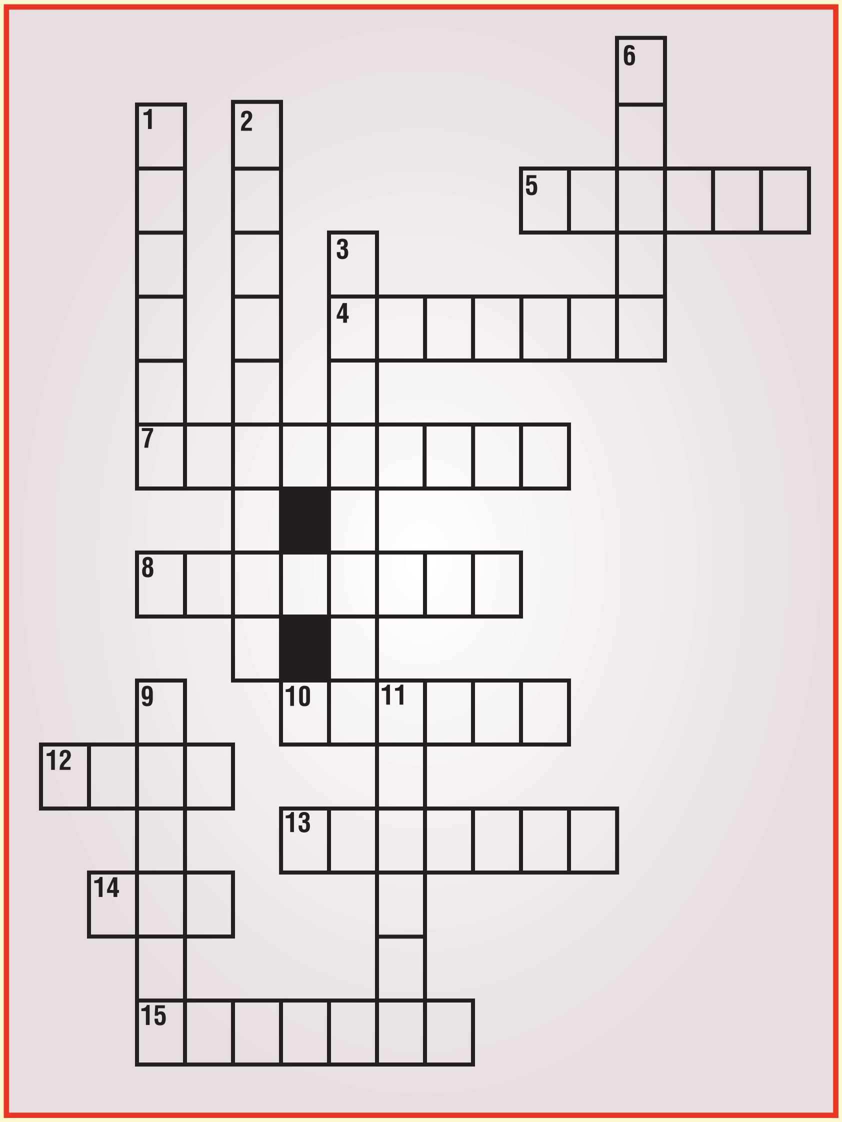
8. Although this is the most abundant metal in the Earth's crust, all you minimal waste advocates have to remind everyone to stop treating it like trash.

9. This alkaline earth metal is toxic by itself, but doctors instruct patients to drink a thick shake of its sulfate helping to prevent burying them.

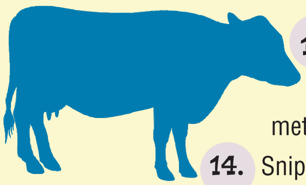
10. This metal is named for its sky blue spectral lines and is used in atomic clocks that are accurate to 1 s in 60 yrs.

11. When the Lone Ranger photographs his horse's fillings in the mirror, he must wonder why this metal is still considered second best by most athletes.





12. This metal is in stained glass windows and old paint, but not in pencils, as some might lead you to believe.



13. Dairy farmers see milking machines as quick extractors of this alkaline earth metal, but I bet the cows see them differently.

14. Snips can cut this metal into tiny pieces. It is used for solders and soldiers.

15. Nick-named "quick silver," this dense and toxic liquid metal is used in barometers and electrical switches. It's hard to imagine a more curious metal.

Answers