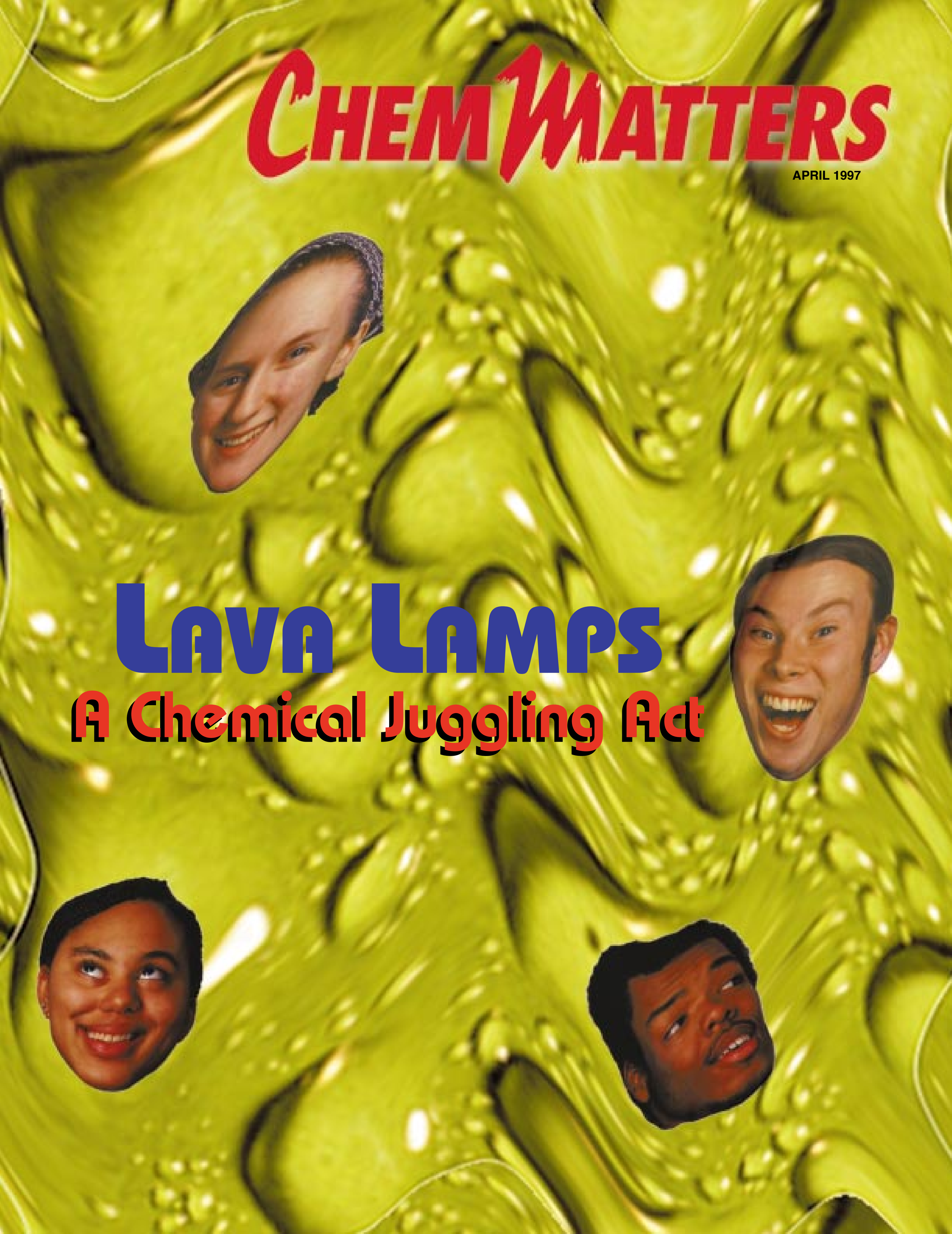
ChemMatters
APRIL 1997

Lava Lamps
A Chemical Juggling Act



COMMENTS FROM THE EDITOR

Two of the articles in this issue of *Chem Matters* rely on information from the U.S. Patent Office. The article about lava lamps and the article on human pheromones could not have been written without consulting patents. Though the Patent Office contains a gold mine of scientific information, writers and researchers often ignore it—perhaps because of the popular misconception that a patent is some kind of government-protected secret. In fact, the purpose of a patent is to dispel secrecy.

Suppose that you invent a new food-processing technique that eliminates bacteria and makes food safer. If you wish to earn money from this invention, you have two options. Choice 1: You keep the process secret, set up a food-processing factory, sell the safer food at a higher price, and pocket the profit. In addition, you can leave the factory to your children who can continue to guard the secret. Meanwhile, many consumers who could benefit from healthier food might not be able to afford it. This situation can continue for decades if the food process is kept secret. But if the secret somehow leaks out, other factories may start using the process, sell the food at a lower price, and drive you out of business. Clearly, society benefits if the new process is not secret, but you benefit if it is.

Choice 2: You apply for a patent and the government grants it. This amounts to a deal in which the government gives you the legal right to exclude others from using the new process for 20 years (so you don't have to worry about the secret leaking out), but you must *publicly disclose* the details of the food process. In the short term, you are given a monopoly—something the government normally frowns upon. In the long term, society gets access to your process and can begin using it freely when the patent expires.

How can you, a member of society, see these publicly disclosed inventions? It's easy. Just read the fine print on the product you are interested in and copy the U.S. Patent number. Write a note saying, "Please send me one copy of U.S. Patent #1234567"; include your name, address, and phone number; enclose a check for $3.00 made out to Commissioner of Patents and Trademarks; then send the request to Patent and Trademark Copy Sales, Box 9, Washington, DC 20231. When the patent arrives, you can read all the "secret" information. (The patent will arrive in about five weeks; information about faster service is available at www.uspto.gov.)

Many people helped with this issue of *Chem Matters*. Our thanks go to Timothy Erickson of University of Illinois Hospital for clarifying some of the details about the lava lamp and to Haggerty Enterprises for sharing the history of Lava Lites. Robin Merlo of the EROX Corporation provided information about Realm perfumes. Thanks to John Mitchell of New Holland Corp. for answering our questions about patents. Thanks also to Chris Knudsen for loaning us his used cast.

* * *

After 14 years as editor of *Chem Matters,* I am resigning to pursue other interests. Some personal goals: spend more time with my family, energize my teaching, and perhaps resume work on a long-postponed chemistry textbook. I am confident the next editor (not yet identified) will move the magazine forward.

For making *Chem Matters* successful, we thank those who are too numerous to name here: the educators who had the vision to start *Chem Matters*; the ACS staff who kept it operating smoothly; the teachers who offered feedback, suggested articles, and served on the Policy Board; the writers who contributed articles or served on the Editorial Advisory Committee; and the artists and designers who made the magazine appealing. Our very special thanks go to Technical Review Editors Derek Davenport and John Kotz, as well as Managing Editors Lynn Sibley and Mary Olenick. These people gave extraordinary assistance, issue after issue. Finally, we acknowledge the most important parties in this enterprise: the members of the American Chemical Society, who have supported *Chem Matters* financially, and you—the readers—who moved the magazine forward through your close attention, involvement, and loyalty. Thank you!

David Robson
Robson-D@toe.towson.edu

Letter to the Editor

I liked Dan Scott's article on the Vinland Map in the December issue. However, I did not like the ending where he asked Tony Cantu to decide, based on the data, whether the map is or is not genuine. Cantu's conclusion that an independent researcher should see if he can repeat my results using my techniques is an insult. The data I have published are sufficient to prove my case. In short, I have published and proved that (1) There are two inks, one yellow to simulate a yellow stain along the black ink line that would have developed naturally over five centuries. That alone suggests, and likely, by itself, proves the map is a fake. (2) I identified, in the yellow ink, a substance that did not exist, and could not have existed in 1440. My published data prove this substance to be the anatase form of titanium white—a post-1920 commercial product—present in the ink. Also, many analytical chemistry problems require analytical methods that are able to see, characterize, and identify very tiny samples. Cahill's (PIXE's) ability to detect titanium [in large] millimeter size pieces is useless for an authenticity study of the Vinland Map.

Walter C. McCrone, McCrone Research Institute

"Aha, Dr. Mecklenberg, noted research scientist, we meet again!"

ChemMatters April 1997

Lava Lite®
A Chemical Juggling Act

by Mike McClure

The tentacle of waxy goop stretched upward from the bottom of the glowing bottle. As the sinewy red mass ascended through clear fluid, a bizarre blob formed at the tip, broke loose, and floated upward. Then cooling and contracting, it spiraled downward in slow motion to be engulfed by the pulsating goo.

Some other-worldly life form emerging from the primordial ooze? Hardly! The glowing bottle, waxy material, and watery fluid are the basic components of every lava lamp.

In 1963, Craven Walker, an English engineer, invented a “display device”, which consisted of a glass vessel containing water and mineral oil. When illuminated by a lightbulb in the lamp base, the oil would nearly jump off the bottom, rising and falling in weird patterns that were fascinating and relaxing to watch, especially if the liquids were brightly colored. Whether Walker’s invention was a carefully planned experiment or a serendipitous discovery is not known. What we do know is that two American entrepreneurs bought the marketing rights for the lamp at a German trade fair soon after its invention. By 1965 Haggerty Enterprises of Chicago, a company specializing in novelty products, had begun production, and Walker’s device had a new name—the Lava Lite Lamp.

Maybe you’ve seen lava lamps in novelty stores or specialty shops. But the original lamps from the

PHOTO BY MIKE CIESIELSKI

Big again. A fad in the 1960s, lava lamps are enjoying a resurgence of popularity in the 1990s. Three decades ago, the lamps were stylish enough to be used as a table centerpiece for a fancy dinner (opposite page).

late 1960s are nowadays commonly found only in flea markets and antique shops. Collectors who stumble upon a classic "Century" model, first introduced in 1965 and sold for $25, consider it a great find. The Century weighed 7 pounds and stood 17 inches high. A tapered glass bottle sat inverted on a golden metallic base punctured with tiny holes that sparkled like starlight in the dark. In one model, a saffron–yellow liquid filled the globe, and a blue blob of oil oozed up from the glass bottom like some alien life form.

PHOTO COURTESY OF LAVA WORLD INTERNATIONAL HAGGERTY ENTERPRISES, INC.

Haggerty Enterprises marketed the first lamps as home accessories, hoping to attract individuals who enjoyed watching late-night TV. Unlike the brightness of most lamps, Lava Lites glow feebly in the dark and give just enough light to read by. Company officials believed this TV night-light idea would appeal to traditional middle-age shoppers.

But the 1960s were anything but traditional. As expressed in a popular song, this was the "Dawning of the Age of Aquarius." And with this "Age" came new fads, attitudes, and looks. This was when the Beatles were hot, bell bottom pants stylish, and "Wow" was not only in, it was "Far out!" Maybe it was the lamp's unconventional shape. Maybe it was the wild combination of color, light, and motion. But whatever the reason, Lava Lites captured the freedom-loving mood of the times and became forever associated with the hippie counterculture of the 1960s.

Oil and Water Still Don't Mix

Craven Walker had created "a motion for every emotion" from simple laboratory chemicals. The exact recipe used in commercial lamps is a carefully guarded secret. Haggerty Enterprises will only admit that 13 mysterious chemicals are carefully blended to produce those goopy lava shapes. Although we may not know Haggerty's secret formula, we do know that the basic components are oil and water along with a slew of specially selected chemicals to improve safety, appearance, and performance. In fact, lava lamps would be boring if the only two ingredients were water and oil because both are clear and colorless. To brighten things up, engineers add light-absorbing dyes. Dyed lava gunk comes in almost every color of the spectrum. There is yellow gunk, red gunk, green gunk, and even neon pink gunk. The water, oil, dyes, and additives all work together to create the lamp's visual charm and special animated effects. The secret of how lava lamps work can be traced back to the molecular nature of oil and water.

Water is a vital ingredient in lava lamps. The clear liquid that the blobs swim through is mostly water. The molecular structure of water is directly related to its chemical and physical properties. Each tiny V-shaped water molecule is made of two hydrogen atoms covalently bonded to oxygen. Because oxygen has a greater attraction for electrons than hydrogen, the electrons between these two atoms are not shared equally. Imagine the electrons as a rope with oxygen and hydrogen pulling at each end. In this atomic tug-of-war, oxygen is most powerful, and its prize is a slight negative charge. Both hydrogens relax their grip on the electron rope and finish positively charged. These permanent electrical charges are responsible for water's unique polarity.

Walker knew water is a polar substance. And he knew the solubility rule that "like dissolves like." Many substances dissolve in water because they also have polar molecules. Ethyl alcohol, for example, has a polarized oxygen–hydrogen bond and, consequently, mixes freely with water. But to create those weird lava shapes, Walker needed something water could not dissolve. That substance turned out to be paraffin.

The paraffin used in Walker's lamp had waxlike properties but was not a true wax like carnauba or beeswax. Carnauba wax, which is from a plant, and beeswax, which is secreted by bees, are esters; their molecules contain some oxygen. Paraffin is a hydrocarbon; it contains only hydrogen and carbon atoms. You don't have to look far to find hydrocarbons. Mineral oil, kerosene, and Vaseline are just a few common hydrocarbons.

In nature, paraffins exist as mixtures. A typical hydrocarbon in this molecular soup may contain 20 to 30 carbons and more than twice that number of hydrogens. And unlike electron-greedy oxygen, carbon shares electrons equally with its hydrogen partners, making paraffins nonpolar. This means that water and paraffin have completely different properties. Like oil and vinegar, they don't mix or dissolve. This difference in polarity is what Walker used to turn his idea into a wacky invention.

Let There Be Lava

When a lava lamp is turned on, an ordinary 40-watt bulb illuminates and warms the contents of the glass globe. The solid paraffin melts, changing into a thick molasses-like liquid. As the temperature increases, the blob of paraffin expands, like a soap bubble. When the paraffin's volume goes up, its density decreases; and when the density of the paraffin falls just below the density of water, an interesting phenomenon happens. Struggling to float in the surrounding water, an expanding pillar of brightly colored gunk squishes upward. Usually a glob of paraffin breaks loose, wobbles into a sphere and rises like a hot air balloon to the top of the globe. As it rises, the paraffin releases some of its heat to the surrounding water and cools. When this happens, the lava shrinks and its density increases. Soon the blob becomes denser than water and sinks slowly back to the bottom where the cycle begins again.

Successful operation of any lava lamp depends on this relationship between the density of water and wax. The water and paraffin must begin with nearly the same densities so that, with just a little heating and cooling, the paraffin becomes less dense than water, then more dense. The density of water is 1.00 g/mL. Ordinary paraffin has a room temperature density of about 0.90 g/mL. Because its density is less than water, the paraffin will float at room temperature, even before it's heated. At first this seems contradictory to what we observe in the lamp. Something must be in the paraffin to make it heavier than water.

Haggerty Enterprises keeps that information top secret, but we know from Walker's original patent that chlorinated hydrocarbons were added to the paraffin. Because they contain heavier chlorine atoms, these organic compounds are much denser than water. Because these chlorine-rich substances are nonpolar, they dissolve easily in the paraffin but will not dissolve in the water. By adding just the right amount of chlorinated hydrocarbons to the paraffin, the density of the paraffin mixture can be made just slightly greater than the density of water when the paraffin mixture is at room temperature. When warmed, the density changes, and the paraffin rises.

Walker also dissolved some polyethylene glycol, a polar compound, in water. Polyethylene glycol has two effects. First, it increases the viscosity of the water so the paraffin blobs rise and fall more slowly. Second, when heated, polyethylene glycol expands more rapidly than pure water, so the delicate balance of densities is not disrupted when the lamp heats up. At operating temperature, the density of paraffin changes just slightly more than the density of water; and the paraffin blobs rise and fall, rise and fall in what seems like perpetual motion.

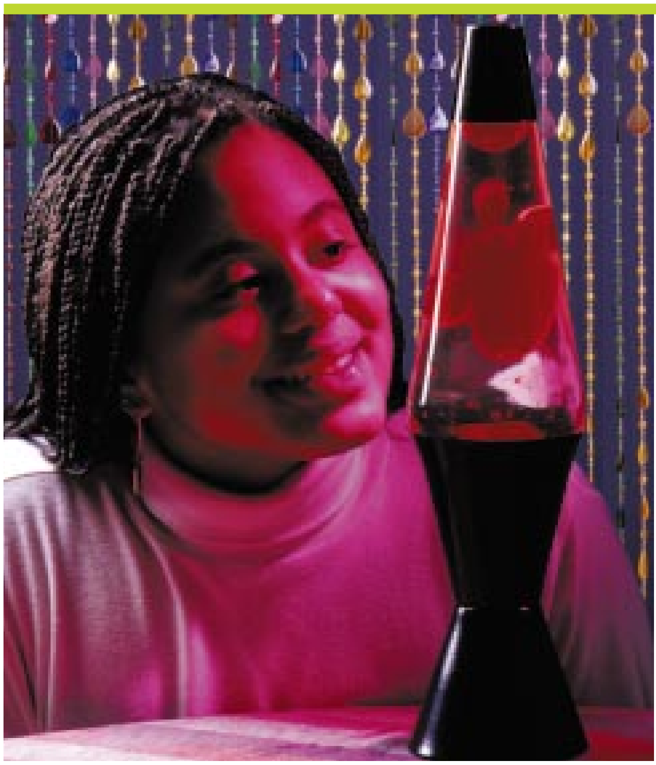


PHOTO BY MIKE CIESIELSKI

Lava Market Ups and Downs

Getting paraffin and water to perform this chemical juggling act was not the only challenge facing Haggerty Enterprises. Another problem was competition. Several copycat companies tried to recreate the secret formula and construct their own version of the lava lamp. One Japanese imitator marketed a lamp shaped like a flying saucer that is now a collectors' item. And a company

Analysis by Accident

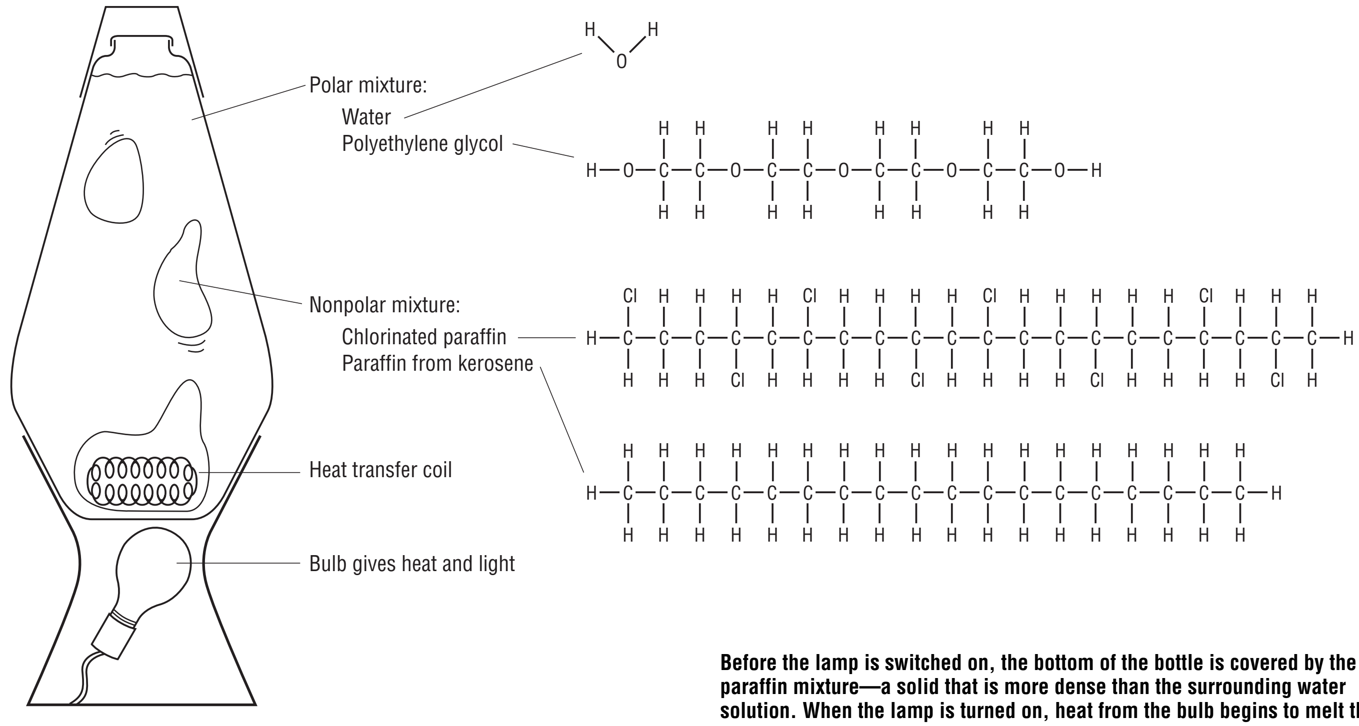
In 1993, the wall of secrecy surrounding the chemical ingredients of the lava lamp was accidentally breached by a Chicago alcoholic. The 65-year-old man was taken to the emergency room at University of Illinois Hospital because he was unresponsive and lethargic. He had rapid pulse and respiration. Blood tests showed starvation, dehydration, excess positive ions, malfunctioning kidneys, and a blood pH of 7.32 (normal is 7.40). Although he was given intravenous fluids, his condition declined and, three days later, doctors began dialysis to clear his blood of some of the chemicals that his kidneys could not handle.

At this time his family reported that, in an apparent search for alcohol, he had opened a cool lava lamp and drunk most of the liquid in the lamp and some of the solid. His doctors needed to know—immediately—the chemical composition of the lava lamp. The lamp was sent to Hinez Veteran's Administration Hospital where chemist Ralston Reid promptly analyzed the remaining material by gas chromatography–mass spectrophotometry. The lava lamp was found to contain water, 38% by mass; chlorinated paraffin, 36%; low molecular weight polyethylene glycol, 13%; kerosene 7%; and microcrystalline wax, 6%. A similar analysis of the man's blood, saved from the day he was admitted to the hospital, showed some of the same materials.

Finally, the doctors knew how to treat the man, and he made a gradual recovery, which was complicated by alcohol withdrawal. After three months of hospitalization, the man was sent home, although his kidneys did not fully recover. Toxicologist Timothy Erickson and the other physicians who treated this man believe that the most prominent toxic effect was the kidney damage caused by the *low* molecular weight (200 daltons) polyethylene glycol. This chemical can damage the kidneys even though *high* molecular weight polyethylene glycol (3,500 daltons) is safe and is used therapeutically to flush certain toxins from the intestines.

After this incident, the manufacturer changed the design of the lamp so it contains less-toxic ingredients, and the bottle is harder to open.

—D. Robson



Before the lamp is switched on, the bottom of the bottle is covered by the paraffin mixture—a solid that is more dense than the surrounding water solution. When the lamp is turned on, heat from the bulb begins to melt the paraffin. The melting process is slow because paraffin is a poor conductor of heat. The process is speeded up somewhat by the heat transfer coil, a coil of wire that transfers heat from the lightbulb into the paraffin. When paraffin melts, its volume increases about 3%. When this expansion changes the density of the specially formulated paraffin mixture from slightly greater than water to slightly less than water, the paraffin begins to float. A pillar of warm paraffin detaches from the main blob and floats upward. The blob rises slowly because the paraffin mixture is thick and because polyethylene glycol has been added to the water to increase its viscosity. At the top of the bottle the surrounding water is not as hot, so the blob cools, increases density, and sinks. When the blob reaches the bottom, the wire coil helps break its surface tension, so it merges with the paraffin at the bottom. The tapered shape of the bottle guarantees that the water at the narrow top has greater surface area and thus cools faster than the water in the wide bottom.

started by Walker, called Crestworth Trading of London, continued marketing lamps in Europe under the brand name Astro Lamp. Fortunately for Haggerty Enterprises, most of these companies were unsuccessful in creating lava lamps that equaled theirs in quality or performance.

A more serious threat to the business of selling lava lamps came at the end of the 1970s. Hippies and flower children were reluctantly approaching middle age, and the whole hippie culture was fading into history. Attitudes and styles changed. Lamps once proudly displayed in college dorms and hippie communes were relegated to attics, garages, and trash bins. When lava lamp sales dipped to an all time low in 1983, company officials decided to take action.

The classic Century was given a facelift, and new models sporting sleeker, high-tech shapes were brought to market. In addition to the redesigned Century, there are now the Aristocrat, Enchantress, Midnight, Silver Streak, Princess, and Elek-Trick with eight shades of lava. In the early 1990s, these changes met a wave of 1960s nostalgia that brought renewed popularity to the globes of glowing goo.

In 1995 Haggerty Enterprises hosted a party celebrating the 30th anniversary of its star product. Aging hippies mingled in the mellow glow of hundreds of lava lamps. Some danced. Some traded lava lamp stories. Others gathered to admire a specially constructed 3-foot-tall lamp that oozed ruby red blobs the size of footballs. One guest gazing mesmerized into this giant lava lamp, expressed her feelings in one word...Wow!

Note: The current issue of *the Chem Matters Classroom Guide* contains a simplified recipe for making a demonstration lava lamp from laboratory chemicals.

Mike McClure worked for several years as a chemist at a veterinary diagnostic laboratory, investigating unusual animal deaths. He now teaches chemistry at Hopkinsville Community College in Kentucky and is a regular contributor to Chem Matters *magazine. The editors appreciate the author's careful and painstaking laboratory work to uncover the secrets of lava lamps!*

REFERENCES

"Cool sign of the 1960s glows again." *New York Times*, May 7, 1990, Section B, p. 12.

Erickson, Timothy B. et. al. "Acute renal toxicity after ingestion of lava light liquid." *Annals of Emergency Medicine* **1996**, *27*(6), 781.

Hubscher, Ralph. "Build a lava lamp." *Popular Electronics* **1991**, *8*(3), 31.

Walker, Edward C. U.S. Patent 3,570,156, March 16, 1971.

PHOTOS BY MIKE CIESIELSKI AND ASC PHOTO FILE

Human Pheromones: The Nose Knows

by Amy Kimball

What makes a male moth drop everything to pursue a sexually receptive female moth? Pheromones—chemicals that carry messages to other members of the same species. Pheromones can guide a column of ants to a distant food source or cause a group of aphids to flee when a predator eats one of them.

That's all very well if you're a moth, but do human pheromones broadcast messages of desire? Do humans even *have* pheromones? Perfume companies would love to know, to find them, and to bottle them.

Craig Warren, vice president and director of fragrance science at International Flavors and Fragrances in Union Beach, New Jersey, says that companies have been "very actively looking for human pheromones since the early 1970s." But the search for a human pheromone hasn't been easy. Experimental methods that led to the identification of hundreds of insect pheromones can't be used on humans. Humans bring memory and personality to new situations and evaluate their environment by using several senses. Many scientists believe that the complexity of human behavior is beyond the reach of chemical messengers.

Yet recently published, exciting work suggests that humans may respond to pheromones after all. It was a belief in human pheromones that led David Berliner, a former anatomy professor and entrepreneur, to raise $14 million to start EROX Corporation, the company that now sells perfumes called Realm Women and Realm Men. The Realm promotional material proclaims that these are "the only fragrances with a synthesized human pheromone component." Evidence that the active ingredients in the Realm perfumes are human pheromones was convincing enough to persuade the U.S. Patent Office to grant patents to Berliner for "fragrance compositions containing human pheromones." But not everyone is convinced.

The search for human pheromones

Interest in pheromones heated up in the 1970s when the first mammalian pheromone was found. That molecule was isolated from the saliva of boars and was shown to induce mating behavior in sows. After extensive search for human pheromones, many abandoned the hunt. According to a 1995 research report by Catherine Dulac and Richard Axel (Columbia University, New York), "It has been difficult to identify human pheromones that elicit behavior . . . since behavior in humans is far more likely to be tempered by learning and experience."

Earlier, in the 1960s, Professor Berliner became interested in the possibility of human chemical communication and began looking for molecules on skin cells. Casts that had been worn by skiers with broken bones were a source of naturally shed cells. Although Berliner published papers describing the chemicals he isolated from skin, he didn't test his hunch that some of these molecules were pheromones. He did, however, save the solutions that contained these puzzling chemicals.

In 1968 Berliner left the University of

Utah to become vice president of Research and Development at ALZA Corporation, a biotech company. Berliner spent the next 20 years investing in and founding a variety of pharmaceutical companies. Eventually, believing that his skin extracts contained pheromones, he founded EROX Corporation. In his new lab, Berliner thawed out the old extracts and with chemist Clive Jennings-White did some additional purification. Several androstene and estrene steroids were identified, and the researchers set out to determine whether the molecules were pheromones.

Berliner focused his attention on an obscure organ that is present in snakes and rodents. This vomeronasal organ (VNO) is a tiny pouch in the nose that detects pheromone signals from other members of the species. The human VNO was discovered in 1703. It is located on the septum and is about 2 mm wide; it has long been considered inactive in humans.

PHOTOS BY MIKE CIESIELSKI

The scientist who first isolated human pheromones used a solvent to extract the chemicals from skin cells that were collected from the inside of used casts.

Berliner recruited colleagues Luis Monti-Bloch and Larry Stensass from the University of Utah, who in turn recruited a group of volunteers. The scientists used a slender probe that could be inserted into the volunteer's nose. Just 1 mm wide, the probe contained a fragrance delivery tube, an electrode, and an aspirator to monitor the activity of the volunteers' noses. The researchers positioned the probe in either the olfactory epithelium, the nose tissue that detects aromas, or in the VNO.

When the researchers delivered a fragrance, such as clove oil, through the tube to the olfactory epithelium, the electrode detected a response in the nerves leading from that tissue. When an unscented compound was delivered, there was no response. When some androstenes and estrenes (isolated from skin) were delivered to the olfactory epithelium, there was no electrical response. Yet when these same molecules were delivered to the VNO, several elicited electrical responses. Conversely, the VNO gave no response when it was exposed to fragrance molecules. Thus, it seems that the human nose houses *two* sensory systems: one that detects aromas and another that detects a class of molecules that have no aroma.

There were critical differences in the way volunteers responded to aromas and VNO stimulants. Subjects could always tell when an aroma had been delivered to the olfactory epithelium. But they had no conscious awareness of when a pheromone had been delivered and sensed by the VNO. Furthermore, scented compounds were detected with similar sensitivities by males and females. In contrast, the estrenes, which elicited strong responses by males, were barely detected by females. The androstenes, which females sensed, went almost undetected by males.

The VNO may send a message to a different part of the brain than the olfactory epithelium does. Unlike aromas, VNO responses trigger slight changes in body temperature, indicating changes in the body's state of relaxation. Indeed, a few subjects reported feeling calm, comfortable, or confident after being given a VNO stimulant. But there are no data showing that the compounds that stimulate the VNO affect behavior or mood.

A bottle of Realm Women perfume (about $60) and a tube of Realm Men after-shave lotion (about $20). In addition to conventional solvents and aroma compounds, Realm products contain some compounds that are said to stimulate the VNO and act as human pheromones. Realm advertising claims that it makes the wearer feel attractive because of the pleasant smell of the aroma ingredients and the enhanced feelings about one's self caused by the pheromones. The manufacturer, EROX Corporation, likes to call the detection of pheromones a "sixth sense."

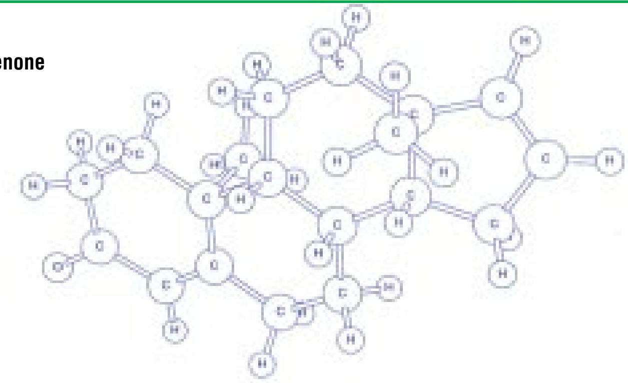
Making and marketing *Realm*

In December 1993, Berliner and EROX received the first of two patents. The patents include a discussion of the human VNO and data showing VNO stimulation. They describe how to chemically synthesize skin compounds and related molecules that also stimulate the VNO.

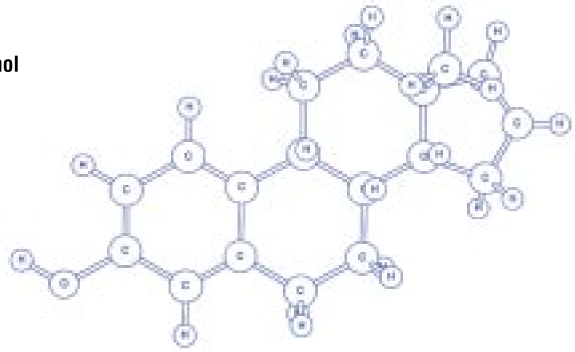
EROX introduced the Realm perfumes in the fall of 1994. Scientific papers published by the EROX scientists don't contain any data on mood or behavior. However, press releases and an infomercial describe the mood-altering properties of human pheromones. They explain that human pheromones, unlike animal pheromones, "do not arouse sexual desire. Instead, they help you feel more attractive by enhancing positive feelings such as comfort, security, well-being, and confidence."

Guided by this view, EROX formulated products whose pheromone content is intended to work on the wearer. Thus, Realm Women "is a softly beautiful, sophisticated Floriental scent" that also contains androstenes. Realm Men is a "traditional, quietly bright scent" containing

Androstadienone



Estratetraenol



These are two of the compounds that have recently been discovered to be human pheromones. Androstadienone (top molecule) is detected by the vomeronasal organ (VNO) in the nose of women, whereas estratetraenol (bottom) is detected by the VNO of men. The pheromones seem to confer feelings of calmness and well-being.

estrenes. The EROX Corporation likes to call the detection of pheromones a "sixth sense." Realm advertising claims to make the wearer feel attractive because of the scent and the pheromonal enhancement of positive feelings.

Of course, perfumes attract extravagant advertising. Realm has been promoted with scent strips placed in expensive catalogs and attractive packaging. EROX also ran a TV infomercial that described their pheromone research. Retail store employees were given a training video.

EROX is a small company but it is growing. A million dollars worth of Realm was sold in 1994, $9 million in 1995, and twice that amount was anticipated for 1996.

The proof is in the replicate

The EROX scientists believe that an electrical response by the VNO proves that a molecule is a human pheromone. Researchers outside of EROX say that more data are needed. The tissue response alone doesn't prove that a message is received by the brain. A true pheromone would give a behavioral response.

Although it might not be feasible to study human sexual behavior, a variety of psychological tests are commonly used to evaluate a person's mental state. Until the 1990s, the only evidence EROX had produced to show that a pheromone message goes to the brain was a slight change in body temperature and a slight change in skin resistivity. But the temperature measurements were taken in a nonstandard way that makes them difficult to evaluate.

The Galvanic skin response—sweat test—"has a bad reputation," says Tyler Lorig, a physiological psychologist at Washington and Lee University in Lexington, Virginia. The test "is sensitive to everything," and the results are difficult to interpret.

Furthermore, in the first scientific papers published by EROX, the active molecules were given code names. Researchers in the field of mammalian pheromones and human sensory systems have reserved judgment on the current standing of human pheromones.

Now that patents on the molecules in Realm have been issued, the chemicals have been identified publicly; Dulac and Axel cloned genes that code for proteins in the VNO that bind to pheromones. In a June 1996 paper in the *Journal of Steroid Biochemistry and Molecular Biology* (*58*(3),259), EROX scientists show that exposure to VNO stimulants leads to altered hormone levels.

This is an active field and during the next few years we'll learn much more about human pheromones: Are they real? Do they occur in places other than the skin? Do other pheromones cause different kinds of feelings?

In the meantime, maybe it doesn't matter if Realm contains actual pheromones. Perhaps all that is necessary is that the wearer *believes* the perfume contains ingredients that will make them feel "more romantic, more attractive, and more alluring."

Amy Kimball has a PhD in biochemistry and has recently completed a postdoctoral fellowship at Johns Hopkins University in Baltimore. This is her first *Chem Matters* article.

REFERENCES

Arrigo, Joseph T. "Mystique of Musk." *Chem Matters*, April 1991, p.12.
Berliner, David L. U.S. Patent 5,272,134, Dec. 21, 1993.
Berliner, David L. U.S. Patent 5,278,141, Jan. 11, 1994.
Goldman, Bruce. "The essence of attraction." *Health* **1994**, *8*(2), 40.
Linner-Luebe, Marilyn. "Perfumes." *Chem Matters*, February 1992, p. 8.
Monti-Bloch, L.; Jennings-White, C.; Dolberg, D. S.; Berliner, D. L. "The human vomeronasal system." *Psychoneuroendrocrinology* **1994**, *19*, 673–86.
Moran, D. T.; Monti-Bloch, L.; Stensass, L. J.; Berliner, D. L. "Structure and function of the human vomeronasal organ." In *Handbook of Olfaction and Gustation*; R. L. Doty, Ed.; Marcel Dekker: New York, 1996.
Schulz, S.; Toft, S. "Identification of a sex pheromone from a spider." *Science* **1993**, *260*, 1635–37.
Taylor, Robert. "Brave new nose: Sniffing out human sexual chemistry." *Journal of NIH Research* **1994**, *6*, 47–51.
Taylor, Robert. "The sixth sense." *New Scientist* **1997**, January 25, 36–40.
Wright, Karen. "The sniff of legend; human pheromones?" *Discover* **1994**, *15*(4), 60.

ACKNOWLEDGMENTS

Thanks to Joe Arrigo, Clive Jennings-White, Tyler Lorig, Kevin McCarty, Robin Merlo, and Craig Warren for sharing their expertise; to Melissa Kimball, David Robinson, David Schmickel, and Nancy Touchette for suggestions on the manuscript.

FIRE IN THE HOLD

by Robert Mentzer

The hatch cover blew off the number 5 hold at 10 a.m. on a chilly winter day in 1996. The Turkish ship *MV B. Onal* had been riding at anchor in Delaware Bay with a cargo of iron ore in the hold. The surprised crew asked themselves, "Can iron ore explode?"

Obviously it had, and the explosion had been powerful enough to lift a 2-ton hatch cover and move it 5 ft sideways. One look into the hold revealed an even bigger problem. Several square meters of the black iron pellets were glowing red.

Radio messages confirmed that the nearest available port was Wilmington, Delaware, 90 miles up the Delaware River. The *MV B. Onal* took on river pilot Earl Eggers who guided them toward Wilmington. Eggers said the fire "looked like a giant charcoal grill with little blue flames dancing on the surface." They soon accumulated a convoy of ships, some from the Coast Guard and some merely curiosity seekers. It was midnight when they reached the docks at Wilmington with the fire still burning in the hold.

Awaiting them were members of the Delaware Emergency Management Unit, headed by Sean Mulhern. Many phone calls had established that the cargo was not a simple iron ore but a potentially reactive form called "direct-reduced iron" (DRI).

NOT ALL IRON IS CREATED EQUAL

Traditionally, iron ore is shipped from the mines to steel mills where it is chemically reduced to iron metal and then processed to make steel. Iron ore is an oxide such as Fe_2O_3. To reduce it to iron, the ore is heated with carbon and a limited amount of air. The carbon reacts to form carbon monoxide, which reacts with the iron oxide in a series of steps to form liquid metallic iron and carbon dioxide. This is done in 10-story-tall units called blast furnaces.

$$2C + O_2 \rightarrow 2CO$$

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$$

During the past 25 years, a competing process has captured part of the world market for iron. Smaller refining plants have been established, sometimes near the iron mines. The new plants use less energy by converting iron ore directly to iron without having to heat the materials to the melting point of iron. In the new process, chunks of iron ore are heated to 850 °C in the presence of carbon monoxide and hydrogen gas. The iron oxide is reduced to iron with the formation of carbon dioxide or water. The resulting pellets of almost pure iron are DRI, which can be shipped to steel mills anywhere in the world with lower shipping costs.

$$Fe_2O_3 + 3CO \rightarrow 2Fe + 3\,CO_2$$

$$Fe_2O_3 + 3H_2 \rightarrow 2Fe + 3H_2O$$

These pellets are not inert chunks of iron. DRI pellets are extremely porous and full of many tiny airways that permit oxygen molecules to come into contact with a large percentage of iron atoms. In contrast, during traditional high-temperature refining, the iron melts during the molten stage, collapsing the airways. After cooling, the solid iron has relatively few iron atoms exposed to air.

Under the right conditions, DRI pellets can be reoxidized back to iron oxide. In most cases, oxygen reacts with iron slowly and the resulting heat can readily escape. If water is present, however, the oxidation rate is speeded up 100-fold and releases more heat. If the pellets are more than 1 m deep, as in the hold of a ship, the heat cannot escape as fast, and the temperature rises. This speeds up the oxidation reaction and generates more heat that can't escape—so the reaction accelerates even more.

Another reaction can also occur. As the temperature increases, the iron can react with water to form iron oxide and the explosive gas hydrogen.

$$Fe + H_2O \rightarrow FeO + H_2$$

What starts as a hot spot spreads until it reaches the top of the pile where the hydrogen mixes with the oxygen in the air. Any spark or fire will then set off a hydrogen explosion. And that is what happened in the hold of the *MV B. Onal* on that cool winter day.

SAY WHAT ?

But how could the heat be trapped in the load of iron pellets? Aren't metals good conductors of heat? Indeed, solid metals are. However, because DRI pellets are extremely porous, only tiny areas of each pellet are in contact with neighboring pellets, and these contact points are full of holes. The heat must flow through thin, convoluted iron surfaces.

You can see the same principle at work in a coffee cup made of plastic foam. Very little heat flows through the walls of the cup because the foam consists of air bubbles covered with thin polystyrene. When you pick up the foam cup, you are actually touching thin ribbons of polystyrene that surround air bubbles. Neither the air nor the thin ribbons of polystyrene transports heat very fast. If, instead of a *foam* polystyrene cup, you picked up hot coffee in a *solid* polystyrene cup, you would burn your fingers.

BACK ON THE DOCK

But what of the burning cargo on the *MV B. Onal*? How did the Emergency Management Unit waiting on the dock

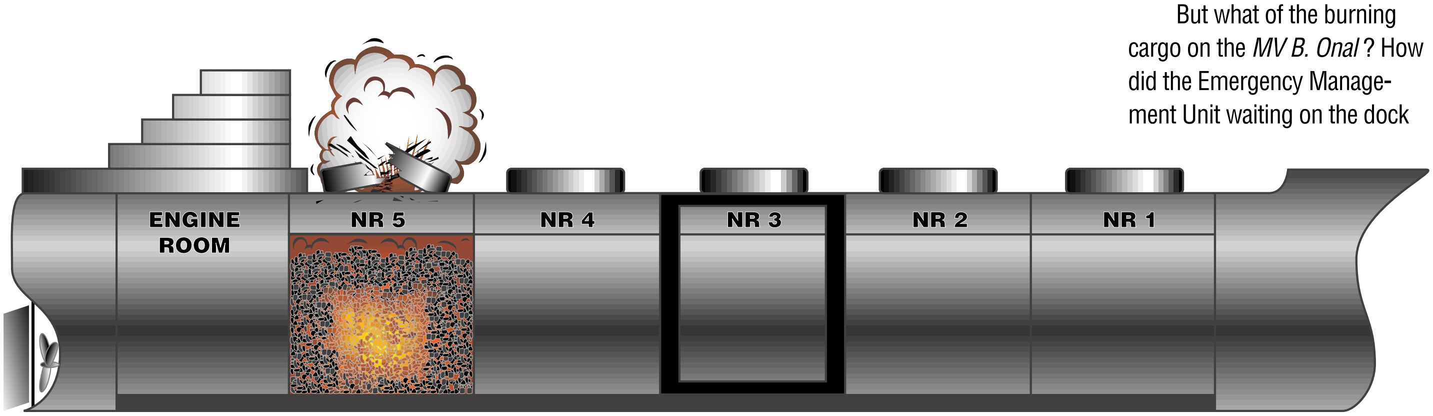


ILLUSTRATION BY CESAR CAMINERO

put it out? They were faced with a serious chemical dilemma.

If water were added, the red-hot pellets would react to form hydrogen gas, and an explosion could result. If the water could be added rapidly, the pellets might be cooled down before too much hydrogen was produced. But getting enough water in would be tricky. And adding water would ruin the value of the remaining unburned pellets.

The decision was made to add gaseous nitrogen to the cargo hold. A tanker truck of liquid nitrogen was standing by. The liquid nitrogen was evaporated, and the cargo hold flooded with gaseous nitrogen. This quickly suppressed the surface fire because the oxygen had now been removed from the space above the pellets. But, as expected, it did not stop the deeper burning. The pellets deep in the pile still had air and moisture in the countless tiny pores, and when the trapped heat from burning of adjacent pellets raised their temperature, they too reacted. A week later temperature probes showed hot spots moving deep inside the pile as they followed the moisture trails through the pellets.

Finally, a crane with a clamshell bucket was brought in, and the cargo was unloaded into piles less than 1 m deep. The heat escaped faster and the piles soon cooled to ambient temperature. The emergency was over but not the lawsuits.

PHOTO BY MIKE CIESIELSKI

Some hand warmers operate on the same principle that caused the fire on the *MV B Onal*. Inside the plastic package is a porous pouch that contains iron powder, water, salt, sawdust, and activated charcoal. When the pouch is removed from the airtight outer package, oxygen enters through pores of the pouch and oxidizes the iron, producing heat. (See "Hot and Cold Packs," *Chem Matters*, February 1987, p. 7.)

Robert Mentzer is an organic chemist who spent many years in research at a major industrial company. Currently he teaches chemistry and physics at William Penn High School, New Castle, DE. Dr. Mentzer edited the February 1997 issue of the *Chem Matters Classroom Guide.*

SPONTANEOUS COMBUSTION

This process of slow oxidation, along with trapping of the heat released until the temperature reaches a point where open flames occur, is called spontaneous combustion. By coincidence, while the *MV B. Onal* lay at anchor in Wilmington with the quiet fire in its hold, the results of spontaneous combustion were threatening a chicken farm just a few miles away.

Delaware has many poultry farms where chickens are raised by the tens of thousands. Naturally this generates large amounts of manure that must be disposed of in an environmentally safe way. After the manure is removed from the chicken houses, it is stored in a shed. Because manure is an organic product, it too can burn under the right conditions. As with DRI pellets, moisture can accelerate the reaction with oxygen. Water can also increase the rate of bacterial decomposition in the manure pile. With the right level of moisture in the manure pile, the heat generated by these reactions can be trapped, raising the temperature and leading to open flames when the expanding hot spot reaches the surface.

Safety recommendations for preventing manure fires sound like the methods for safeguarding DRI pellets. They talk of slow oxidation, trapping of heat, and temperature build up until open flames occur. Both recommend avoiding excess moisture and limiting pile depth if moisture is present.

Laundry Disks: Miracle or Money Down the Drain?

by Bruce Goldfarb

A product like Clean Power "activated ceramic laundry disks" sounds too good to be true. It promises to clean your clothes, save money, and be kinder to the environment.

The laundry disks are hollow plastic shells filled with small granules and surrounded by a ring of foam. They are sold in sets of three, priced at about $50, through stores and mail-order catalogs that specialize in environmentally sensitive products. The notion of an effective, less-polluting way to wash clothes appeals to millions of Americans who are concerned about natural resources. Companies that make laundry detergents took notice of the consumer interest in products with fewer additives and introduced detergents without fragrances or coloring agents. But the ceramic laundry disks go further, claiming to clean clothes without any detergent at all.

Toss three of these disks into your washing machine, and your laundry will come out as clean and fresh as ever. What's more, they're supposed to last for 500–700 wash loads, or about two years for most families.

How do they work?

Pacific International Group, the San Clemente, California, company that imports the laundry disks from Japan, provides some extraordinary scientific-sounding explanations. According to the company's product information:

- Metallic elements, including copper and silver, in the activated ceramic release electrons, which in turn, produce ionized oxygen. This form of oxygen is a totally natural cleanser that breaks up dirt and organic compounds.
- The activated ceramics also emit "far-infrared electromagnetic waves," which cause water molecule clusters to separate, allowing much smaller individual water molecules to penetrate into the innermost part of the fabric and remove dirt.
- When water contacts the activated ceramics, an abundance of OH^- ions is produced, reducing the surface tension of the water and greatly increasing its penetrating power. Ordinary detergents make use of this same principle, but do so by using harsh chemicals.

This all sounds impressive, but is it good science? Not according to Bob Allen, PhD, a chemist at Arkansas Tech University in Fayetteville. "Their explanation of the science behind it is nonsense," he says. "Absolutely nutty."

Allen contacted Real Goods of Ukiah, California, one of the companies selling the ceramic laundry disks. "I don't mind people hawking a product," he says, "but when they try to wrap it in scientific nonsense, that irritates me." Real Goods responded by giving Allen a set of disks so his chemistry students could perform tests under controlled conditions in a classroom laboratory.

Some of the claims about the laundry disks seem plausible, but others stretch scientific reasoning beyond its snapping point. For example, the "far-infrared electromagnetic radiation" referred to by the company sounds suspiciously like ordinary heat. Far infrared, the coolest part of the infrared spectrum, is emitted by most ordinary objects, including your body, the chair you're sitting in, and the rocks on the ground outside. If far infrared had any special cleaning power (which has never been observed), you could get the same effect by tossing three rocks into your washer.

PHOTO BY MIKE CIESIELSKI

It's quite possible that the laundry disks could produce a tiny amount of heat energy as they are agitated in water, says University of Colorado chemical physicist George Lawrence, who is a member of the Committee for the Scientific Investigation of Claims of the Paranormal.

"Agitating water with *anything* will increase its temperature," says Lawrence. But any heat that could be produced by the laundry disks would be insignificant compared with the energy of the warm water used to wash clothes and the far more powerful agitation of the washing machine itself, he adds.

And while it's true that water consists of polar molecules that tend to stick together—giving it surface tension—the laundry disks could not produce enough energy to separate water molecules to any meaningful degree, according to Lawrence. "It takes a lot more energy than far infrared" to dissociate water, he says.

Lawrence also doubts that the laundry disks produce an abundance of hydroxyl ions, OH^-. "The claim that it breaks water up into OH^- just isn't possible."

As founder of the firm EcoWorks, Albert Donnay was one of a growing number of environmental product marketers with serious doubts about the laundry disks. In a meeting with Pacific International president Takashi Shioya, Donnay asked questions about how the disks worked.

"Why three disks? I'm always looking to reduce, reuse, and recycle. I wanted to sell them one or two at a time," recalls Donnay. "Why do they need to float? Why do they stop working? What's in them that is depleted after a year or two? Are they affected by the pH or temperature of the water? [Shioya] couldn't answer any of our questions."

In the absence of concrete scientific information, Donnay decided not to sell the laundry disks through the EcoWorks catalog.

Shioya admits that many people have questions about his laundry disks, of which he has sold more than 120,000. "I'm not going to deny that the claim is weak," he says. "Of course it's weak. But we're making it better."

Shioya says that he is creating new product packaging that "does not claim to make an electromagnetic wave." He still insists that the laundry disks ionize water and separate water molecules from one another; "It's just how much that's being questioned."

Perhaps more important than the scientific theories behind the ceramic laundry disks is the question of whether they actually work. Although sales material promoting the laundry disks has plenty of testimonials from satisfied customers, good data from controlled scientific evaluations are not readily available. The proof will come out in the wash.

One such evaluation was done by chemist Paul Sosus, of Scientific Detergent Research Associates in Fair Lawn, New Jersey. Sosus, who has worked in laundry detergent research and development for 40 years, used standardized methods for a controlled, double-blind test of the laundry disks. "When we tested them, we didn't find them having any value at all," he says.

PHOTOS BY MIKE CIESIELSKI

One way to examine an advertising claim is to place a Clean Power disk in pure water overnight, then measure the pH (above). The vendor claims the disks produce an abundance of OH^- ions. The hollow disks are filled with dimpled beads of unknown composition (top right).

Similar findings were discovered in experiments done by a private laboratory hired by Seventh Generation, an environmental products company located in Colchester, Vermont. The lab found that the laundry disks were "no better than plain warm water," says Seventh Generation president, Jeffrey Hollender. "We discontinued the item, even though it was making more than $100,000 a year for the company. . . . It would have been unethical to sell something that didn't work."

The reason why the laundry disks rate such glowing testimonials is that "people don't appreciate how effective just washing clothes in warm water is," says Hollender. Clothing washed with the laundry disk appears clean because the fabrics contain residual detergent, says Albert Donnay. "Most of us wash clothes that have been washed before, and clothing contains soap residue."

Donnay did a test in which he stopped using detergent and washed his family's clothes in plain warm water. While the washing machine emptied into a utility sink, he observed the rinse water. "For weeks after we stopped using detergent, the water was still full of soap," he says. "People use too much detergent. That's the dirty little secret of the detergent industry . . . . Detergent is strong stuff, and it cleans clothes. Two tablespoons are all you need."

This is an interesting point. While the advertisements say that the laundry disks will clean clothes without detergent, the instructions that come with the disks tell a different story. First, the instructions recommend treating any stubborn stains with a stain remover. Second, for dirtier clothes, you are told to add a teaspoon of *detergent* to the washer along with the disks. Perhaps how they "work" is not such a mystery after all.

REFERENCES

"LAUNDRY DETERGENTS: DO GOOD THINGS COME IN SMALL PACKAGES?" *CONSUMER REPORTS* 1995, *60*(2), 92.

REAL GOODS HOME PAGE HAS INFORMATION ABOUT CLEAN POWER PLUS LAUNDRY DISKS. **HTTP://WWW.REALGOODS.COM**

Bruce Goldfarb is a science and medical writer in Baltimore, MD. His previous article, "Antifreeze Antidote," appeared in the October 1996 issue of *Chem Matters*.

Mezclas Químicas

by Alan Preston, Professor of Biochemistry, University of Puerto Rico School of Medicine

Here are five Mezclas Químicas riddles (Spanish: chemical mixtures). Use the clues next to each set of blanks to fill in the missing word. Then transfer the corresponding letters to the numbered blanks at the bottom to reveal the answer of the riddle.

(Anwers are on page3.)

1

_ _ _ _ _ (1 2 3 4 5) — Color of AgCl (s), $CaCO_3$ (limestone), NaCl (s)

_ _ _ _ _ (6 7 8 9 10) — Color of PbS, C (graphite), HgO

_ _ _ _ _ _ (11 12 13 14 15 16) — Transition metal, found in stainless steel and coins, Atomic no. 28

_ _ _ _ _ _ (17 18 19 20 21 22) — Two electrons in the same orbital spin but with opposite spins: _ _ _ _ _ _ electrons

What the physicist, turned pirate, made his captives do

1 18 7 10   4 2 21   17 16 8 11 9 14

2

_ _ _ _ _ (1 2 3 4 5) — Electrode at which oxidation occurs

_ _ _ _ _ (6 7 8 9 10) — cm, kg, °C are examples of _ _ _ _ _

_ _ _ _ _ _ (11 12 13 14 15 16) — Hemo_ _ _ _ _ _ is the oxygen-carrying protein in blood

_ _ _ _ _ _ (17 18 19 20 21 22) — √ is the symbol for _ _ _ _ _ _ root.

Best way to cross the Great Salt Lake

6 17 22   20   10 1 12 9   14 21 8 4 11 5

3

_ _ _ _ (1 2 3 4) — _ _ _ _ ash is the chemical name for Na_2CO_3

_ _ _ _ _ _ (5 6 7 8 9 10) — The "A" in AMU

_ _ _ _ _ _ (11 12 13 14 15 16) — "Vulcanized" form discovered by Charles Goodyear

_ _ _ _ _ _ _ (17 18 19 20 21 22 23) — Dilute acetic acid, used as condiment or preservative

What the student dialed to get mole-related information

22 17 2 21 5 3 16 7 1   19 12 8 13 20 23

4

_ _ _ _ _ (1 2 3 4 5) — Most plentiful of the noble gases, atomic no. 18

_ _ _ _ _ _ (6 7 8 9 10 11) — C=C represents a _ _ _ _ _ _ bond.

_ _ _ _ _ _ (12 13 14 15 16 17) — Type of ray from interstellar space

_ _ _ _ _ _ (18 19 20 21 22 23) — Law of partial pressures named for this English chemist

Why the electrolyte studied orchestration. To be

19   3 13 22 18   17 4 23 6 8 12 21 7 2

5

_ _ _ _ _ (1 2 3 4 5) — Defoliant used in Vietnam; _ _ _ _ _ Orange

_ _ _ _ _ _ (6 7 8 9 10 11) — Semiprecious stone ($ZrSiO_4$)

_ _ _ _ _ _ (12 13 14 15 16 17) — Alkaline metal used in white paints and rat poison, Atomic mass, 137

_ _ _ _ _ _ (18 19 20 21 22 23) — Alloy used to join metals (67% Pb, 33% Sn)

What Lord Kelvin was rated by the computer dating service

13 11   1 12 18 10 20 16 5 22   6 3 8 19