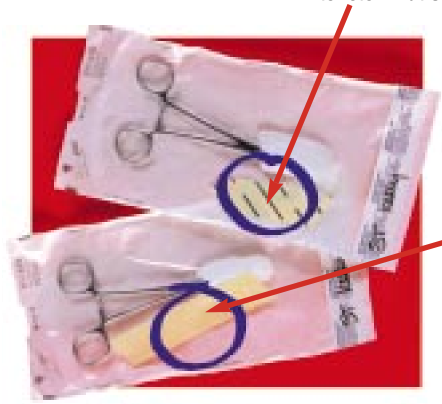
Color in a Capsule

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.

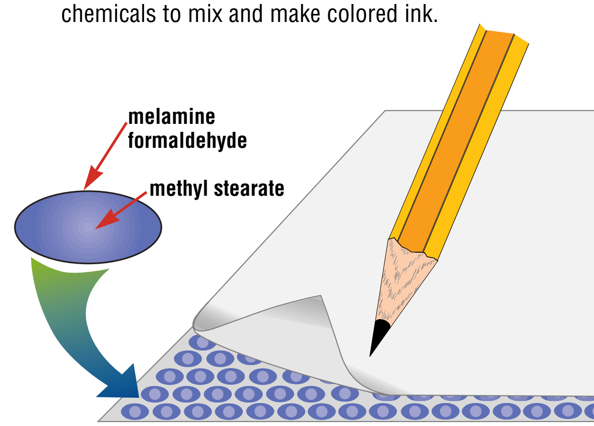


Hospitals use color-changing indicator strips on equipment and supplies so that they can tell whether the item has been sterilized or not.

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.

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).

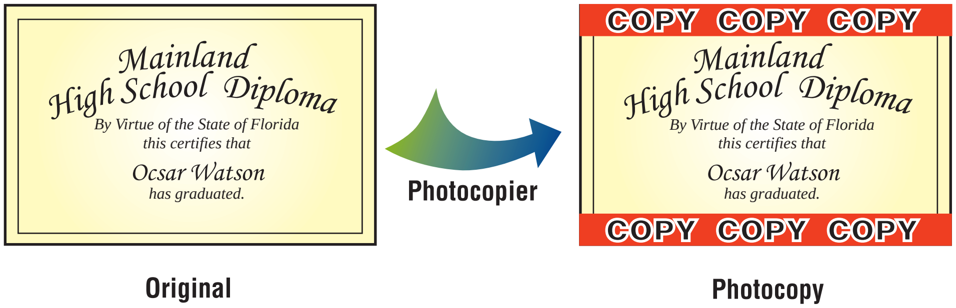
The microcapsule contains a dye that is barely visible when the lipid is liquid but is vividly bright when the methyl stearate solidifies. A jar of pure microcapsules has a pale color. When the pigment is diluted in an ink or paint medium and spread in a thin layer during printing, it becomes essentially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

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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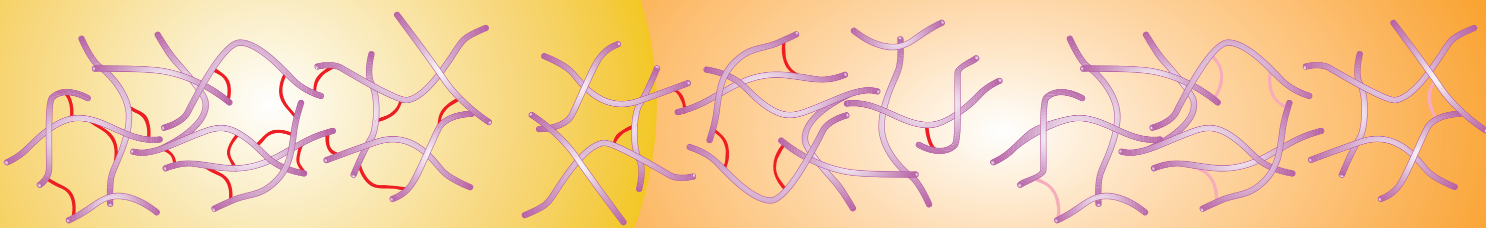
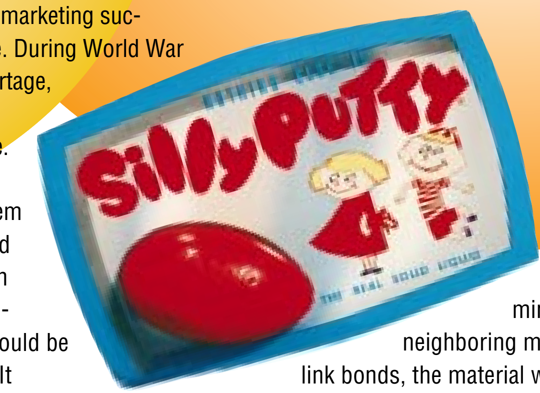
A Successful Failure



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.

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.



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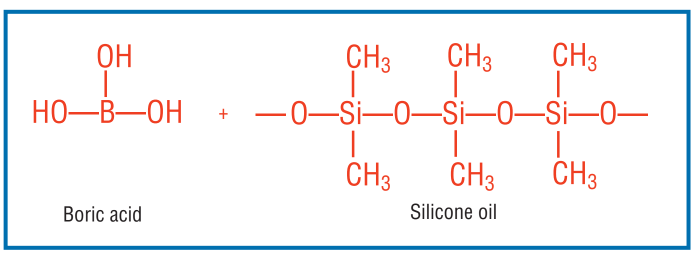
GE sent samples to engineers and scientists, hoping that somebody might think of a use for this material—and perhaps make a profit for the company. Dozens of the most creative scientific minds could not think of a single practical use for Wright's plastic.



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.