A Serious Look at Changeable Silly Putty

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Abstract: Changeable Silly Putty is a thermochromic material. It changes color due to a change in temperature. This paper describes advanced experiments designed to find the mechanism of the color change, provides a discussion of proposed mechanisms, and describes three experiments using Changeable Silly Putty that are suitable for young children.

When we were kids, Silly Putty came in only one color—pinkish tan. Now, it comes in fluorescent colors, glow-in-the-dark colors, sparkle colors, and changeable colors. Changeable-color Silly Putty is produced in three colors and each changes to a different color when the product is heated above room temperature. It returns completely reversibly to its original color when cooled. Most people's hands are warm enough to effect this color change. Changeable Silly Putty caught our interest while we were preparing demonstrations for National Chemistry Week activities that had a polymer theme [1]. We became intrigued by Changeable Silly Putty as a chemical education tool for young people because everybody recognizes it, the product is nontoxic, and its color change occurs over a specific, low temperature range of 25–35 °C.

Silly Putty was first developed in 1943 by James Wright, an engineer with General Electric in New Haven, CT [2]. Wright was trying to develop a synthetic rubber using silicon instead of carbon. He used a base of silicone oil, a polymer that contains silicon–oxygen chains instead of the usual carbon–carbon chains of most polymers. When he heated the silicone oil with boric acid, the result was the bouncing putty whose properties are so familiar. Samples of the putty were sent for evaluation to General Electric engineers around the world, but none could find an industrial application for the "gupp" as Wright had begun calling it. The product languished on the shelf until Peter Hodgson, an out-of-work ad executive, encountered gupp at a party [2, 3] whose owner had obtained a sample from a friend at GE. Hodgson recognized its potential as a novelty toy. He renamed the product Silly Putty and became rich by marketing it creatively. Binney & Smith Inc., the makers of Crayola crayons, bought the rights to Silly Putty from Hodgson's estate and have marketed it since 1977 [3]. They began introducing colored Silly Putty types in 1990.

The toy industry is turning back to classic toys that invite hands-on discovery. Our student co-author [4] wanted to capitalize on the natural attractiveness of toys as entertaining teaching props. Toys can show chemistry as an integral part of a young student's everyday experiences. For example, in the book *Teaching Chemistry with Toys,* Sarquis, et al. discuss the applications of chemistry in the use of liquid crystals to make color-changing toy cars and the ink-absorbing and mechanical properties of plain Silly Putty [5]. We describe in this paper our advanced experiments with Changeable Silly Putty and the simpler classroom activities that we developed based on these experiments.

Advanced Experiments

Color-changing Silly Putty is an excellent example of a thermochromic material. Orange Changeable Silly Putty changes reversibly to yellow when its temperature increases as you handle it. While the color change can be observed with the naked eye, we wanted a more quantitative way to evaluate the color change. To begin our investigation we acquired visible spectra of orange Silly Putty using a CS-390 dual-wavelength TLC scanner (Shimadzu, Kyoto, Japan). The instrument was designed to analyze spots on thin layer chromatography plates and calculates the absorbance at different wavelengths based on the light reflected from the sample surface. A piece of the orange putty was placed on the glass stage of the TLC scanner and a spectrum acquired from 370 to 700 nm. The color change occurs at slightly above room temperature, and we noticed that the color of the sample changed from orange to yellow while it was in the instrument as a result of heat conveyed to the sample compartment from the tungsten light source. We also found that the thickness of the sample could affect the results of the spectral analysis and so selected one millimeter as the standard thickness for future analyses. To maintain the temperature of samples during spectral analysis we placed a 1-mm layer of Silly Putty on a chilled ceramic tile positioned on the instrument stage. After we obtained the spectrum, we warmed the ceramic tile and sample to effect the color change, repositioned the tile on the stage, and recorded the spectrum of the warmed Silly Putty. Thus, we were able to acquire visible spectra of orange color-changing Silly Putty at 20 °C (orange form, Figure 1A) and 35 °C (yellow form, Figure 1B).

Let us consider the spectrum of visible light and focus our attention on the region between 600 and 700 nm in the two spectra in Figure 1. The spectra of both the orange and yellow forms are almost identical. Both forms are reflecting rather than absorbing light of wavelengths of 600–700 nm (red and orange light). If that were all of the story, both the cool and the warm Silly Putty samples would look reddish orange. Now, study the spectral region between 500 and 600 nm. Here we see a difference between the two spectra. The warm sample (yellow form, Figure 1B) absorbs much less yellow light than the cool sample (orange form, Figure 1A). This is glaringly obvious at 535 nm, the wavelength of maximum absorbance, $\lambda_{max,}$ of the cool, orange sample. The wavelength 535 nm is in the yellow region. The warm, yellow form reflects yellow light in addition to red and orange. Our eyes are especially sensitive

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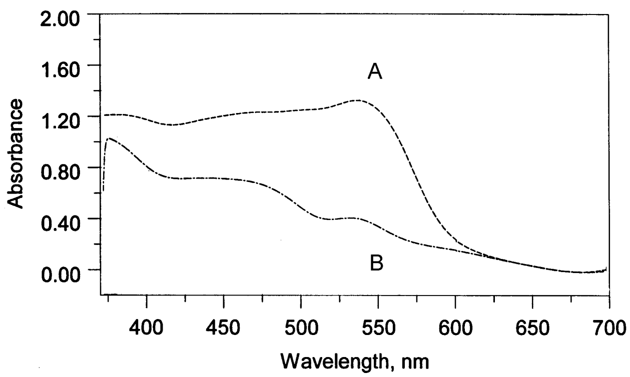

Figure 1. Absorbance versus wavelength for orange Changeable Silly Putty at (A) 20 °C and (B) 35 °C.

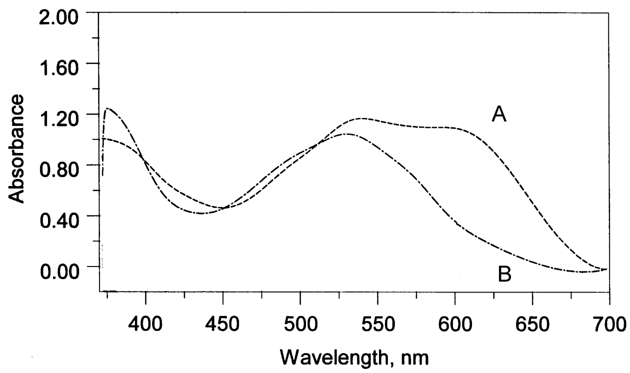

Figure 2. Absorbance versus wavelength for purple Changeable Silly Putty at (A) 20 °C and (B) 35 °C.

Table 1. Temperature and Color of Orange Changeable Silly Putty

Thermistor temperature, °C [a, b]	Silly Putty color
22.6	orange
25.7	orange
27.9	yellow-orange
29.5	orange-yellow
30.2	yellow
31.1	yellow

[a] The temperature calibration equation for the thermistor was $t = -3.2963R + 58.129$, where t is the Celsius temperature and R is the resistance in kΩ. The correlation coefficient squared was 0.9887. [b] Over a large temperature range thermistor calibration data are not a straight-line, but for small temperature changes a straight line approximation is sufficient.

Table 2. Temperature and Color of Purple Changeable Silly Putty

Thermistor temperature, °C [a]	Silly Putty color
24.7	purple
25.4	purple
26.4	light purple
27.1	light purple
27.9	light purple
29.1	pinkish purple
29.5	pinkish purple
29.8	purplish pink
30.9	hot pink
32.1	hot pink

[a] The temperature calibration equation for the thermistor was $t = -3.2963R + 58.129$, where t is the Celsius temperature and R is the resistance in kΩ. The correlation coefficient squared was 0.9887.

to yellow light [6]. So we see the overall color of the warm sample as yellow. The regions of the spectra in which the two samples display the greatest difference in light absorbance seem to have the most effect on the color we see.

Purple Changeable Silly Putty is purple at room temperature and changes to hot pink when you warm it in your hand. We used the temperature-control method described above to acquire the before and after spectra of purple Silly Putty (Figures 2A and 2B). Again, imagine the visible spectrum of white light from 400–700 nm (violet → blue → green → yellow → orange → red) and let the spectra mapped in Figure 2 tell us what colors result. From about 400 to 525 nm the two forms are quite similar in their light-absorbing properties. Both forms reflect purple light (400–450 nm) and absorb green light (475–525 nm); however, in the remaining spectral regions the samples absorb light differently. The cool sample (purple form, Figure 2A) absorbs orange and red light (600–675 nm). The cool sample subtracts these wavelengths from the light falling on it, and we can imagine that the cool sample will look purple because that is the color of light the sample reflects to our eyes. The warm sample (Figure 2B) does not absorb red light; it reflects it. When we look at the warm sample we see the result of the reflected red and purple wavelengths as hot pink.

To determine the temperature at which Silly Putty changes color, we devised the following method to monitor the temperature of the sample and to vary its temperature in controlled steps. Glass thermometers and digital temperature probes were too bulky and responded too slowly to effectively monitor the sample temperature. Instead, we inserted a calibrated thermistor (an electrical resistor that changes resistance with temperature) attached to an ohmmeter. The samples to be examined were placed on a piece of flattened, three-eighths-inch-diameter copper tubing, through which water could be circulated with a peristaltic pump. Nalgene tubing connected the short section of copper tubing to the pump and water reservoir. We used a constant temperature water bath as the water reservoir and a glass thermometer to measure the water temperature. Copper is an excellent heat conductor and the sample quickly approached the water temperature. While slowly changing the water temperature from approximately 22 °C to 36 °C, we recorded observations of the sample color using warmed and cooled pieces of the Changeable Silly Putty as reference colors (Table 1 and Table 2).

The λ_{max} of orange Changeable Silly Putty is 535 nm. This is also the wavelength at which the cool, orange and the warm, yellow forms exhibit the maximum difference in light absorbance. We were able to follow the change in absorbance at λ_{max} using the TLC scanner. We inserted the thermistor into a sample of the orange putty, mounted it on copper tubing inside the sample compartment of the scanner, and followed the color change at 535 nm while slowly raising the temperature of the sample with the water bath. Please see Figure 3.

Separation of the Color-Changing Component from the Silly Putty Matrix

Promotional information from Binney & Smith, Inc. recommends using “rubbing alcohol and patience” to remove Silly Putty from children’s clothes [3]. We placed 0.5-g

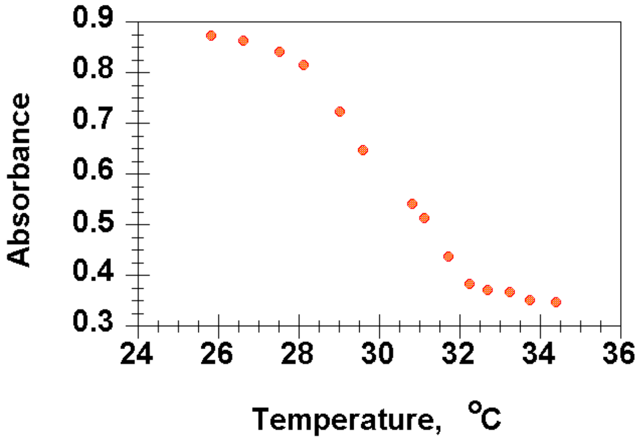

Figure 3. Absorbance versus temperature of orange Changeable Silly Putty at 535 nm.

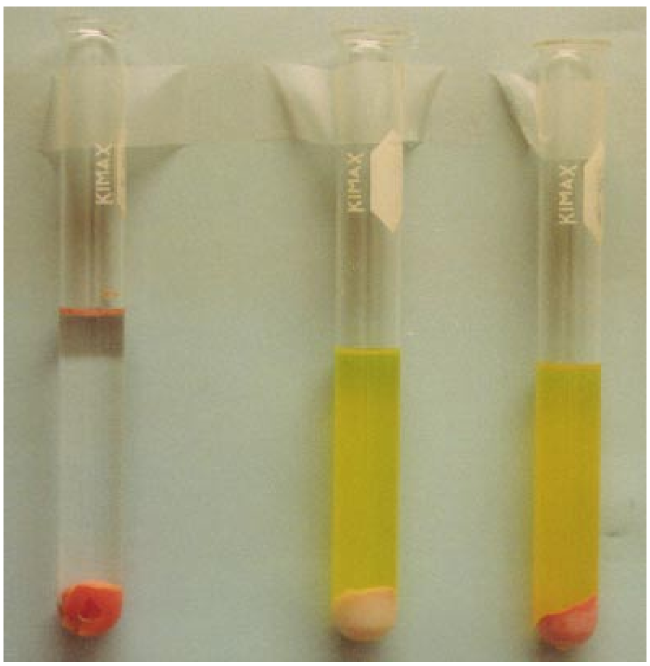

Figure 4. Separation of color changing component from orange Silly Putty using isopropyl alcohol: left tube, before mixing; right tube, after mixing; and center tube, after heating.

samples of color-changing Silly Puttys in separate test tubes and added 40 mL of rubbing alcohol (91% isopropyl alcohol) to each tube. The putty did not disperse readily when stirred (Figure 4, left tube) but eventually cloudy mixtures resulted. After the mixtures were centrifuged, a pink solid and a clear yellow liquid layer formed in the test tube with the orange putty (Figure 4, right tube). A pale blue solid and a clear pink liquid formed in the test tube with the purple putty mixture. Placing the test tubes in warm water caused both the pink solid (Figure 4, center tube) and the blue solid to turn white. The liquid layers did not change color with heat. After centrifuging to separate the color-changing solids from the alcohol, we used a pipette to remove the alcohol layer, then repeated the washing process on the solid until the alcohol layer was colorless.

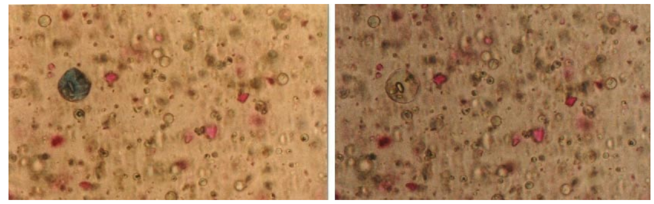

Figure 5. Micrographs of purple Changeable Silly Putty at 400×: left, at room temperature; right, after heating.

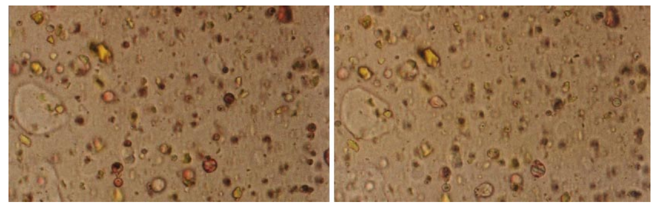

Figure 6. Micrographs of orange Changeable Silly Putty at 400×: left, at room temperature; right, after heating.

Microscopic Examination of Changeable Silly Putty

Several companies sell formulations to manufacturers of novelty products that change color at specific temperature ranges. Hallcrest, Inc., Glenview, IL, specializes in liquid crystals and Color Change Corporation, Addison, IL, makes leuco dyes. Both materials come in a microencapsulated form, that is, encased in a continuous, spherical polymer coating. We wondered if a similar product might be used in Changeable Silly Putty. From the description of the microcapsules, it seemed as if they might be visible with a microscope, so we placed a thin film of purple Changeable Silly Putty on a slide and used a compound light microscope to examine the sample at room temperature. At 400× magnification, irregular-shaped pink blobs and blue-colored spherical structures were visible against a gray background (Figure 5, left). When the slide was warmed enough to turn the sample to hot pink and then viewed with magnification, the formerly blue spherical structures were still visible but had become colorless (Figure 5, right). As the sample under the microscope cooled, we saw these spheres gradually regain their blue color. Without magnification the pink and blue colors reflected to our eyes from these little blobs and spheres blended so that the silly putty looked purple. A slide of the orange putty, when viewed at room temperature and 400× magnification, showed irregular-shaped yellow blobs and red spherical structures (Figure 6, left). The yellow blobs did not change color when the slide was warmed but the spherical structures changed from red to colorless (Figure 6, right).

We obtained from Hallcrest a sample of microencapsulated liquid crystals in a slurry that changed color in the same temperature range as the Changeable Silly Putty. A thin layer of the Hallcrest microcapsules, when air dried on a slide and examined under a microscope, showed different behavior from the color changing Silly Putty. The Hallcrest microcapsules changed from colorless through a range of colors and then back to colorless, as the temperature was raised from about 25 to 30 °C. Please see the micrographs in Figure 7.

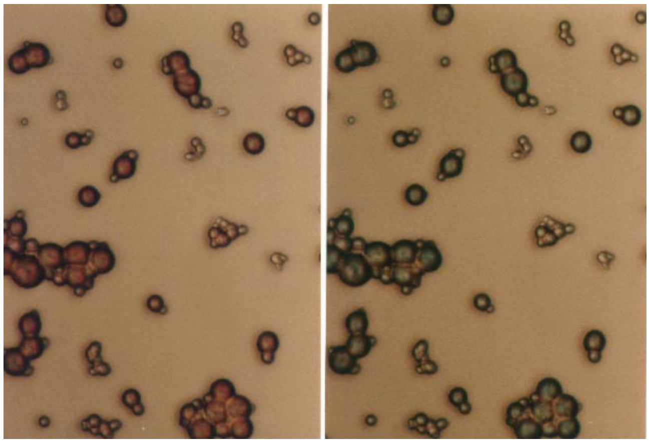

Figure 7. Micrographs of Hallcrest microencapsulated liquid crystals at 400×: left, at room temperature; right, after heating.

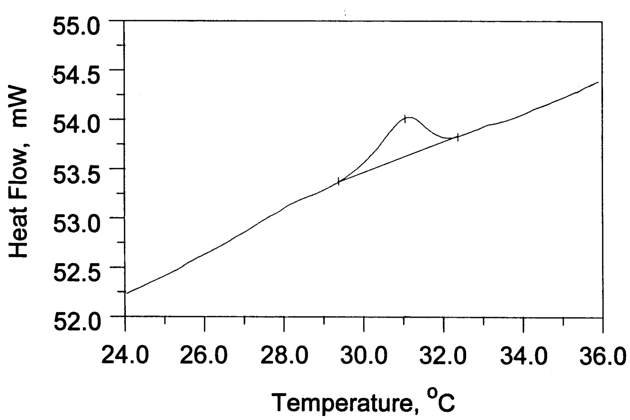

Figure 8. Differential scanning calorimetry plot for 0.07 g of orange Changeable Silly Putty.

Thermal Analysis of Orange Changeable Silly Putty

We wanted to determine if additional energy was absorbed in the color change process in excess of the energy required to heat the sample. Brown [7] recommends using differential scanning calorimetry (DSC) to detect and analyze phase changes in liquid crystals and other substances. DSC is a thermal technique in which differences in heat flow into a substance and a reference (usually sand) are measured as a function of sample temperature while the two are subjected to a controlled-temperature program [8]. We used a Perkin-Elmer DSC instrument to examine the color-change energy requirements of untreated orange Changeable Silly Putty samples weighing about 0.07 g. The baseline of the DSC curve in Figure 8 shows the heat flow required to heat the sample at a constant rate. The peak above this line represents the energy used by an additional endothermic process that is occurring in the sample; that is, some extra energy is required to heat the sample at a constant rate within the temperature range 29.5–31.5 °C. If you manually enter into the computer the beginning and end points of the peak, the DSC can connect the points generating a baseline for the peak and can then calculate the area of the peak and the corresponding energy change. The color change enthalpy for 0.07 g of the orange silly putty was about 0.4 J g^{-1}. Orange Changeable Silly Putty is only about 20% microcapsules, as determined by weighing; therefore, the enthalpies of transition for the color-changing part could be about five times higher than the number listed above or about 2.0 J g^{-1}, but the weight ratio of polymer to color component inside the microcapsules is unknown. The enthalpy of transition by DSC for the Hallcrest sample was 0.4 J g^{-1} for 0.04 g of microencapsulated liquid crystals changing color from 26.7–29.4 °C. The most interesting aspect of the DSC analyses for both samples was evidence of an endothermic process occurring within the same temperature range as the color change.

What Causes the Color Change in Changeable Silly Putty?

One can use several materials to bring about reversible color changes, but what would be best for making a color-changing putty? Liquid crystals give precise and sharp temperature ranges for the color change, but they require careful manufacturing and this is expensive. Liquid crystals typically go through a range of color changes as the temperature varies making them ideal for thermometers and other medical devices. Hallcrest does make a temperature-sensitive (called shear-sensitive) liquid-crystal formulation that is just a single color below a given transition temperature (called the clearing point) and changes to colorless above it. Besides liquid crystals, another kind of thermochromic material is a leuco dye. Leuco dyes are robust and less precise but cheap. Leuco dyes require about a 5–15 °F temperature range to undergo a color change [9]. The word *leuco* means colorless. Leuco dyes change from clear (no color) to a color upon heating. They are weak organic bases, and because it is their protonated form that is colored in solution, leuco dyes require a weak acid (a proton donor) as a color developer [10]. Leuco dyes are common in novelty applications such as toys. Color-changing toy cars, Hypercolor T-Shirts printed with a reversible photochromic (light sensitive) ink containing micro-encapsulated leuco dyes, and Star Trek color-changing coffee mugs are examples. Many authors have ascribed, perhaps mistakenly, the thermochromic behavior of novelty products to liquid crystals rather than to leuco dyes [5, 11]. One of us did this upon discovering both the Duracell Battery Test Strip [12] and the “liquid-crystal ready dot” on Clairol Style Setter heated hair rollers [13], which probably use leuco dyes instead.

Both leuco dyes and liquid crystals can be micro-encapsulated, and still a third alternative is to micro-encapsulate a mixture containing a permanent pigment in a solvent or to microencapsulate a leuco dye plus a color developer in a solvent [10]. Microencapsulation protects the pigment mixtures from air and UV radiation. Such pigment mixtures are usually microencapsulated in melamine formaldehyde—the same material as Formica—filled with a lipid (a fat) such as methyl stearate [14]. The microcapsules thus contain a pigment that is barely visible when the lipid is liquid but is vividly bright when the methyl stearate solidifies. This works because waxes and fats are opaque when solid and transparent when liquid, just like candle wax. When the wax melts, the dye and the color developer dissolve, protonation is disfavored, and the color is dispersed in the liquid. The pigment materials, however, are not as soluble in solid methyl stearate as in liquid methyl stearate. When the lipid solidifies, the leuco dye and color developer are frozen out, protonation is facilitated, and the color becomes easily visible. This gives us microcapsules that change from a color to colorless, rather

Figure 9. Isolation of color-changing component from orange Silly Putty using a coffee filter.

Figure 10. Determining the temperature range of the color change for orange Changeable Silly Putty.

than from colorless to a color as do most leuco dye mixtures. The color-change temperature is controlled by the melting point of the methyl stearate. We would expect a lowered melting point and broader melting range for a mixture of methyl stearate and several impurities. Pure methyl stearate melts at 39.1 °C. Other lipid–pigment mixtures can be used for a different temperature range over which the microcapsules change color. For example, ethyl stearate melts at 33.4 °C. We believe the color change technology used in Changeable Silly Putty is a combination of a microencapsulated wax–dye mixture in a silicone oil–boric acid matrix containing a second permanent pigment.

Still Silly After All These Years

The mechanism described above is complicated and not clearly understood even by us, but we enjoyed inventing it. It seems scientists get joy in curious places. Do you remember the joy you felt as a child discovering how simple objects work? As parents and science teachers of young children know, this delight in discovery need not end with adulthood. We hope we have conveyed our delight at investigating the color-change mechanism for Changeable Silly Putty. We encourage you to brighten the learning experience for students of any age by developing science activities using the colorful novelty toys of childhood, and by all means, be silly. We present here some of the activities we have adapted for younger students from our advanced experiments.

Hands-on Activities

We describe three hands-on activities designed to illustrate the properties of Changeable Silly Putty. The supplies listed are for one or two students. Scale them up for larger groups. Questions or comments are welcome [15].

Isolating Microencapsulated Pigments from Orange Changeable Silly Putty. *Supplies.* Two 5-oz paper cups, 12 mL of 91% isopropyl alcohol (rubbing alcohol), one popsicle stick, a pea-sized sample of orange Changeable Silly Putty, one disposable coffee filter.

Procedure. Place a pea-sized sample of orange Changeable Silly Putty into one of the paper cups. Add about 12 mL of alcohol to the cup. Use the Popsicle stick to break up the Silly Putty into smaller pieces. Stir the mixture for several minutes. A yellow liquid containing a solid pink residue results. Filter the mixture through a coffee filter into the other paper cup. The pink residue will remain on the filter paper. Spread out the filter paper and let dry. Please see Figure 9. When the pink residue has completely dried, breathe on it and watch what happens. The pink residue will turn white as it warms up and then back to pink as it cools down. Allow the yellow liquid in the cup to evaporate overnight. The isopropyl alcohol will evaporate from the yellow liquid leaving a yellow residue. More time may be required for complete evaporation depending on the temperature.

Note: Prolonged exposure to isopropyl alcohol destroys the color changing ability of Changeable Silly Putty.

Discussion. The pink residue contains microencapsulated pigment and fat. These microcapsules are responsible for the observed color change. The yellow residue functions as the background color. When the microcapsules are cool, the pink and yellow colors combine to make the Silly Putty appear orange. When warmed the microcapsules are colorless and the Silly Putty looks yellow.

Determining the Temperature Range for the Color Change in Changeable Silly Putty. *Supplies.* Two 10-oz clear plastic cups, one indoor/outdoor digital thermometer with temperature probe or one alcohol thermometer, hot and cold tap water.

Procedure. Half-fill one of the plastic cups with cold tap water. Place the temperature probe from the indoor/outdoor thermometer into the water. Measure the temperature of the water. Place the Changeable Silly Putty in the water. Observe the color of the Silly Putty. Slowly change the temperature of the water by adding a few milliliters at a time of hot water to the cold water with stirring. Note the temperature range over which the color of the Silly Putty changes from orange to yellow. Please see Figure 10. The experiment may be repeated in the opposite direction by starting with the hot water instead of cold water and slowly adding cold water to the hot water to

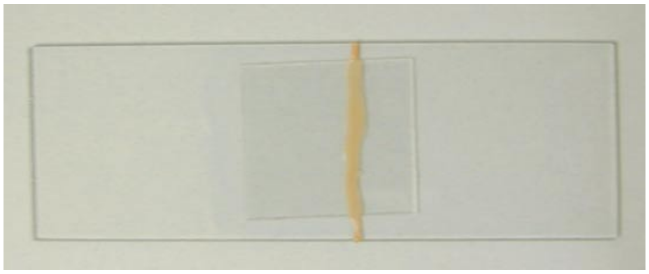

FIGURE 11. Strand of Silly Putty on a microscope slide.

decrease the temperature. Compare skin temperature to the temperature range of the color change of the Changeable Silly Putty.

Discussion. The color change is a reversible process. The temperature change occurs between 26 and 32 °C or between 79 and 90 °F. Please see Figure 10. Skin temperature is about 34 °C (94 °F). When two bodies are in contact with each other, heat flows from the hotter body to the colder one. The heat transferred from the skin causes the Silly Putty to change color.

Seeing the Microencapsulated Pigments in Changeable Silly Putty. *Supplies*. Microscope with 400× magnification, glass microscope slide, glass microscope cover slip, orange Changeable Silly Putty, blow dryer.

Procedure. Remove a small piece of Silly Putty, about the size of a pea, from the main sample. Stretch the sample slowly until you have a strand that is about the width of a pin. Lay the strand on a glass microscope slide so that it divides the slide into two halves as shown in Figure 11.

Lay the glass cover slip over the slide and press down on it so that it flattens out the Silly Putty. Place the slide on the microscope stage. Focus the objective lens of the microscope. You should see tiny red spherical structures dispersed among tiny irregular-shaped yellow structures. Remove the slide from the stage and gently warm it with a blow dryer. Quickly replace the slide on the stage and observe the differences.

Discussion. The spherical-shaped red structures in the cool putty are the microencapsulated dye mixture. The irregular-shaped structures provide the Silly Putty with yellow background color. When the sample is cool, the colors of the red spheres and the yellow structures visually blend together to appear orange. When heated, the red spheres turn clear while the yellow structures will remain yellow causing the Silly Putty to look yellow rather than orange.

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