

Serendipitous Chemistry



Writing up a lab report? If so, you know the drill—introduction, hypothesis, method, observation, analysis, conclusion—done! But did you ever wonder whether this is the way scientific discoveries are always made?

By Brian Rohrig

Ask scientists what their day jobs entail, and they will probably tell you that “doing science” involves a lot of putting, some trial and error, and, often, just plain luck. As for luck, there’s a word for it: *serendipity*—the fortunate discovery of something by accident. And the history of science is full of wonderful accidents that have proven to be *serendipitous*.

When Archimedes, the Greek mathematician and scientist, eased himself into his bathtub and saw the water rise, the idea of determining volume by water displacement dawned on him. George DeMestral, the Swiss inventor, got the idea for Velcro when he noticed cockleburs sticking to his clothing after a walk through the countryside. Chemistry is no exception—many important and fortunate discoveries were made solely by accident.

Vaseline: The wonder jelly

In 1859, chemist Robert Chesebrough found that his fortune was in jeopardy at the early age of 22.

His business relied heavily on obtaining sperm whale oil for use as a fuel. When petroleum, a far cheaper fuel, became widely available, the popularity of whale oil declined significantly—good news for the whales, but bad news for Chesebrough! Deciding to go with the flow, he visited the booming oil fields of Pennsylvania in search of new business opportunities.

While in Pennsylvania, Chesebrough noticed that the oil workers often suspended operations to remove a viscous greasy substance that adhered to the drilling equipment. The substance, called rod wax, clogged up the machinery and needed to be frequently removed. According to the oil workers, the only upside to this gooey material was that it worked wonders on cuts and burns, soothing the pain and speeding the healing process significantly.

Seeing opportunity where others saw a problem, Chesebrough took a load of this greasy gunk to his lab in Brooklyn, NY. After much trial and error, he turned the rod wax into an odorless, tasteless, and colorless translucent

substance. Chesebrough called his creation *Vaseline*, purportedly from the Greek word for oil “elain” and the German word for water “wasser.” Others called it petroleum jelly or petrolatum.

Chesebrough’s testing methods went well beyond even those seen on “Mythbusters”! He deliberately injured himself—cutting, stabbing and burning his skin—and subsequently applied Vaseline to the wounds. Chesebrough then traveled the country by wagon, giving away free samples, and inviting onlookers to observe the healing of his wounds as proof that the product fulfilled its claims.

Satisfied that Vaseline worked as advertised, people began requesting it from pharmacies, soon establishing it as a staple in every drug store and medicine cabinet. As an effective water barrier, Vaseline works by sealing off a wound and preventing bacteria from entering, thus speeding up the healing process. It also serves to hold in the skin’s moisture, preventing it from drying out.

Today, petroleum jelly is used for a variety of purposes. As a hydrocarbon, it is a flammable fuel source. Campers take note: it makes an excellent fire starter when applied



to cotton balls. The list goes on—trout bait, makeup remover, remover of chewing gum from hair, and remover of gummed labels from glass. You've probably used it as a lubricant to loosen a tight ring from your finger. Robert Peary even took it to the North Pole to prevent his lips from chapping and to keep his machinery running smoothly.

Chesebrough died a very wealthy man at age 96. He attributed his longevity to eating a spoonful of Vaseline every day! (Don't try this at home!)

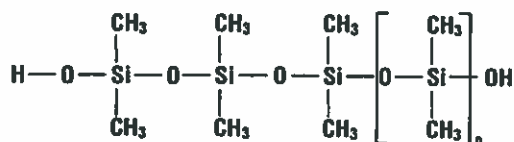
Silly Putty: Serious fun

In 1943, during World War II, many products that we take for granted today were scarce or unavailable. Nylon, needed for parachutes, made stockings a rationed luxury.

As a measure to conserve copper, pennies were made from steel for the first and only time in our nation's history. Rubber was also in short supply. General Electric was one company contracted by the U.S. government to formulate a rubber substitute.

Because the main ingredient in rubber is carbon, elements chemically similar to carbon were the first to be considered. Silicon, in the same group on the Periodic Table of the Elements as carbon, was viewed with particular interest. Elements in the same group contain the same number of valence electrons, and as a result, typically have similar properties. Silicon and carbon both tend to form four bonds, making them geometrically suited to form long chains. Each carbon (or silicon) links to the preceding atom and the following atom in the chain to form two of its bonds. The remaining two bonds form to connect groups that protrude away from the chain.

Substances like natural and artificial rubbers that are made from such long-chain molecules are called *polymers*. Carbon-based polymers are characterized by strong, chemically inert carbon-carbon bonds. Silicon-silicon bonds, however, are much weaker and more reactive, making them less suitable for forming long chains. But silicon-oxygen bonds are very strong indeed. As a result, *silicones*, polymers made of chains with alternat-



Polydimethyl silicone

ing silicon and oxygen atoms, are quite stable. The silicon atoms use their two remaining valence electrons to form bonds with a variety of organic groups, thus giving chemists many options in their search for a rubber substitute.

In his New Haven, CT, laboratory, engineer James Wright was fully immersed in the silicone project. In the spirit of trial and error, he added boric acid, H_3BO_3 , to a test tube of silicone oil. Not knowing what would happen, he hoped it would be an important step toward synthesizing hard rubber.

The boric acid reacted with hydroxyl groups in the silicone oil to form molecular bridges, or *cross-links*, between the silicone polymer chains. Cross-linking was a well-known requirement for giving rubber its stiffness. The harder the rubber, the less



The images above represent polymers. Individual subunits (monomers) comprise each polymer chain. The graphic on the right shows polymer chains that are cross-linked (represented by the red lines between chains). Cross-linking gives polymers stiffness and causes them to snap back when stretched.

the chains can stretch. And when they do stretch, cross-links cause them to snap back afterward.

But with boron as the cross-linking agent, the new substance failed to live up to its expectations as a rubber substitute. Silicon-boron bonds break (and reform) rather readily. Striking the substance suddenly caused it to act like regular rubber. But pulling it slowly allowed the bonds to reform, and the material continued to stretch without snapping back.

Thus, the newly created material bounced like rubber but did not retain its shape like typical rubber compounds do. Instead, it slowly assumed the shape of its container. Unlike rubber, Wright's creation was not even a solid, but rather a viscous liquid.

Samples of this strange new substance were sent to scientists and engineers around the world. No one could come up with a practical use for it, but everyone had fun stretching, squeezing, and bouncing it.

Several years later, a toy store owner stumbled across a sample of this substance, gave it the name Silly Putty, and the rest is history. Since its introduction in 1950, over 300 million plastic eggs of Silly Putty have been sold. In 1968, it was even taken to the moon by the Apollo 8 astronauts! Silly Putty may not have changed the world, but it has proven to be a great toy and a nice example of *serendipity*.

Artificial sweeteners: Sweet accidents

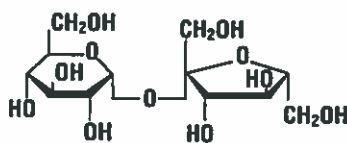
Diet sodas are big business. Many people prefer the taste of artificially sweetened

beverages and appreciate their low caloric count.

Artificial sweeteners are especially important to diabetics who are unable to tolerate ordinary table sugar. The discoveries of these sweet substitutes represent an interesting chapter in serendipitous chemistry.

The discovery of aspartame (aka Nutra-Sweet or Equal) was a classic accident. In 1965, Dr. James Schlatter, a chemist at the G. D. Searle Laboratories, a pharmaceutical manufacturer, was researching antiulcer drugs. While heating a flask of an experimental drug, he accidentally bumped it, spilling some its contents down the sides of the flask and onto his hand. Later, while licking his finger to pick up a piece of paper, he noticed a very sweet taste. (Check your chem lab rules.





Sucrose

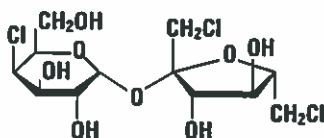
Any problem so far?)

Remembering his earlier accident, he tasted a little of the substance from the flask—a clear violation of proper lab protocol! Dr. Schlatter's chemistry knowledge made him *reasonably* confident that the substance in the flask was not toxic, as it was a small peptide that he expected would break down rapidly in the stomach to a few dietary amino acids. It did indeed taste sweet, much sweeter than sugar. Thus, aspartame ($C_{14}H_{18}N_2O_5$), the king of artificial sweeteners, was discovered—totally by accident.

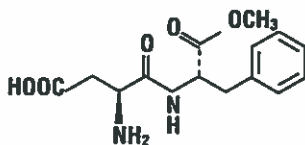
It took another 30 years for aspartame to gain full approval for use in the United States. Today, it represents a multibillion dollar industry. However, aspartame falls short of being an ideal sugar substitute. One drawback to aspartame is that it breaks down upon heating, so it cannot be used in cooking. Furthermore, it decomposes under conditions of high pH. One byproduct of aspartame breakdown is methanol (CH_3OH), which is further metabolized to produce formaldehyde (CH_2O), a toxic substance, thereby raising questions about its safety.

Proponents of aspartame counter that although methanol is hazardous in large doses, it occurs naturally in the body in small quantities, and the human body has well-developed pathways for methanol detoxification. Exhaustive and rigorous controlled testing has shown aspartame to be safe when used in reasonable quantities.

Astonishingly, the discoveries of all the other major artificial sweeteners were also the result of serendipity. Ira Remsen, a professor at Johns Hopkins University, and Constantine Fahlgberg, a postdoctoral fellow working in Remsen's lab, were eating when they noticed a very sweet taste. Realizing that they had not



Sucralose



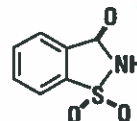
Aspartame

Aspartame, saccharin, and sucralose are artificial sweeteners that serve as substitutes for sucrose (aka table sugar). Note the differences and similarities between each of these artificial sweeteners and sucrose.



washed their hands (sound familiar?) since working in the lab, they deduced it was from some chemical with which they had been working. The resulting substance became the first widely used artificial sweetener—saccharin ($C_7H_4NNaO_3S \cdot 2H_2O$), most widely marketed as Sweet 'N Low.

A recent arrival on the sweetener shelf is sucralose ($C_{12}H_{19}Cl_3O_8$), more commonly marketed as Splenda. Its discovery could have been tragic. A graduate student by the name of Shashikant Phadnis was working in a lab at King's College in London in 1976. With



Saccharin

a limited grasp of English, he did not understand when his instructor told him to test a substance. Phadnis thought the instructor said "taste," and he did just that! Fortunately for him, he survived to describe a very sweet-tasting substance—approximately 650 times sweeter than sugar. Unlike aspartame, sucralose is stable when heated and does not break down when subjected to extremes of pH. As a result, it is useful in baking and in the preparation of acidic foods.

While these artificial sweeteners have made life sweeter for diabetics and others wishing to limit their intake of table sugar, the rule still stands: NEVER taste anything in the laboratory, even in the name of serendipitous science!

It has often been said that chance favors the prepared mind. All of these serendipitous moments in chemistry might easily have been cast aside by less curious and less adventurous observers. Also true is the fact that many of these moments could have ended in tragedy. Certainly, no reasonable chemist recommends tasting or self-mutilation in the name of science. But chemistry, like any other field, has its memorable legends of accidents and adventures. ▲

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Brian Rohrig teaches at Jonathan Alder High School in Plain City, OH. His most recent *ChemMatters* article, "Paintball! Chemistry Hits Its Mark," appeared in the April 2007 issue.