Matches— Striking Chemistry at Your Fingertips

By Brian Rohrig

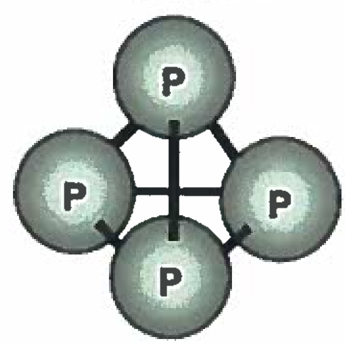
The simple match—so common, and yet so taken for granted. Billions are given away, simply to broadcast the advertising on their covers. But as Tom Hanks showed us in the movie "Cast Away", trying to start a fire without them can be a frustrating and exhausting experience.

At the tip of every match, you'll find the element phosphorus. So the fact that the story of matches bears a striking resemblance to the story of the element should come as no surprise. In 1669, a German alchemist named Hennig Brandt was pursuing the glorious and futile alchemist dream of converting common materials into gold. Regarding human urine to be a mysterious, magical, and not to mention yellow fluid, Brandt collected, and then evaporated a large quantity of it in a retort. Eventually, the mixture formed a solid lump. In what was probably an attempt to "fire" the lump into gold, he placed the retort in a furnace. Upon extensive heating, the solid began to glow. A shining liquid dripped out, igniting spontaneously when it contacted air. It wasn't gold, but he had to admit it was interesting!

PHOTOS BY MIKE CIESIELSKI

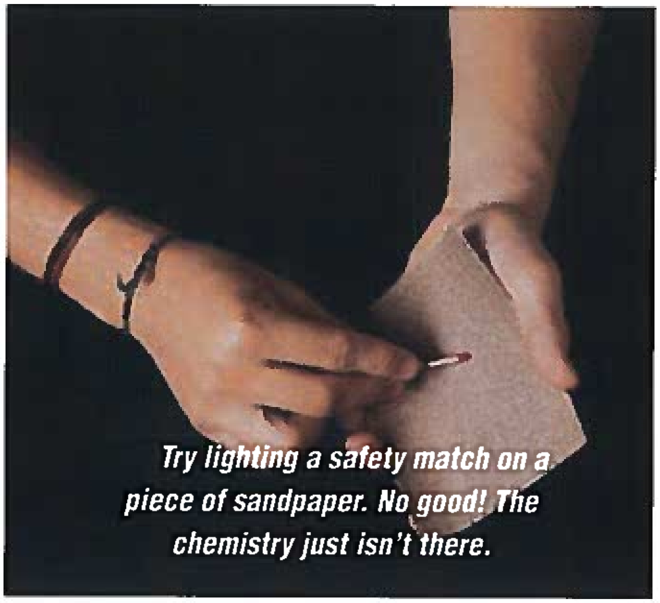
Today, we know that Brandt had succeeded in making highly reactive *white* phosphorus with the formula P_4—its four atoms arranged in a pyramid. In fact, white phosphorus is so reactive that it must be stored underwater. Its dramatic and spontaneous reaction with air remained a mystery well into the 18th century. Now we know that phosphorus reacts with the oxygen in the air at room temperature, but since oxygen hadn't been discovered in 1669, Brandt had no way of knowing what was actually occurring:

White phosphorus (P_4)



$$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s) + \text{heat}$$

Because of its dramatic combustion in air, phosphorus derives its name from two Greek roots: *phos* meaning light, and *phorus* meaning bearing. Ironically, the word phospho-



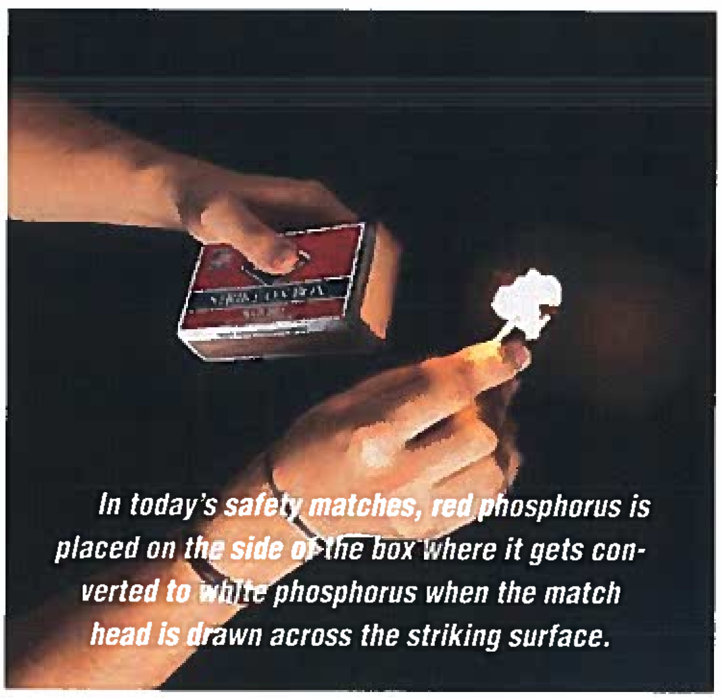
Try lighting a safety match on a piece of sandpaper. No good! The chemistry just isn't there.

rescence has come to describe the way certain elements glow when excited electrons release energy as they return to their lower-energy ground states. These elements glow with a cool light emitting no heat energy in the process. Phosphorus, on the other hand, truly combusts on exposure to air, giving off not only light but also significant heat in the process.

Go with the glow

After its discovery, there were reports of people painting their faces and hands with phosphorus in order to "glow" in the dark. But it's doubtful any person tried this more than once. Phosphorus produces painful burns on the skin. In the Sherlock Holmes mystery *The Hound of the Baskervilles,* a large dog is coated with phosphorus, making it appear as a ghostly apparition to frighten all who observed it.

Not long after phosphorus was discovered, the famous British chemist Robert Boyle began experimenting with it to create the earliest matches. Boyle coated a piece of paper with phosphorus and a small stick of wood with sulfur. When the stick was rubbed across the phosphorus its sulfur reacted, generating enough heat to produce fire. Impressive? Yes. But it proved impractical, because of the extreme instability of the white phosphorus. Nevertheless, Boyle's design represented the first example of a "safety" match—one that can only be lit if struck on a special type of surface.



In today's safety matches, red phosphorus is placed on the side of the box where it gets converted to white phosphorus when the match head is drawn across the striking surface.

Another early match invention involved coating the end of a stick with a paste of sugar and potassium chlorate ($KClO_3$). The end would then be dipped into a vial of concentrated sulfuric acid (H_2SO_4), causing the match to ignite. But the obvious hazards associated with handling concentrated acid soon halted the production of these matches.

The first strike-anywhere match was the invention of John Walker, an English pharmacist, in 1827. He mixed some potassium chlorate and antimony sulfide and applied it to a splint of wood. When the splint was drawn across a rough surface, enough heat was generated to start the following reaction:

$$Sb_2S_3(s) + 3KClO_3(s) \rightarrow Sb_2O_3(s) + 3KCl(s) + 3SO_2(g) + heat$$

The heat from this highly exothermic reaction in turn ignited the wood.

From the equation above, you see that sulfur dioxide (SO_2) is produced. SO_2 is a foul-smelling, poisonous gas. Warnings were included on the matchbox not to inhale the fumes after lighting. These bad-smelling matches, which made a loud bang when lit, became known as *lucifers*. This time, Latin was the source—*luc* meaning light and *fer* meaning to bear. The name was retained for nearly 100 years.

Eventually, a small amount of white phosphorus was added to each match tip during their manufacture. This addition made them easier to light and also eliminated the loud bang. The glue that held the match head together prevented the phosphorus from spontaneously combusting in air. However, due to the inherent instability of white phosphorus, these matches were somewhat dangerous. They often started accidental fires. In fact, they were so unstable they could ignite if a box of them were shaken. Or if exposed to direct sunlight, they would sometimes spontaneously combust.

A safer match

The world clearly needed a safer match, and such a match became a reality when another form of phosphorus was discovered in 1844. When white phosphorus is heated in a vessel devoid of oxygen, the unstable pyramidal P_4 molecules break apart and then relink to form a much more stable chain-like covalent structure called red phosphorus. Red phosphorus does not spontaneously combust when exposed to air. Now it was possible to remove phosphorus from the match head and put it on the side of the box, making accidental combustion less likely to occur.

People still demanded "strike anywhere" matches, so manufacturers still used white phosphorus despite all the health and safety problems associated with its use. Workers in match factories often contracted a disease known as necrosis or "phossy jaw". Inhaled vapors of white phosphorus corroded the teeth, finally working their way into the jaw, causing extreme pain. Workers mouths filled with open lesions that oozed pus.

Despite public demand, lucifers were outlawed in 1910. But soon the strike-anywhere match was reinvented in a new and safer form.

Match makers discovered that tetraphosphorus trisulfide (P_4S_3) could replace white phosphorus, with none of the health hazards associated with white phosphorus. This safer compound was made by heating phosphorus and sulfur in a 1:3 molar ratio:

$$P_4(s) + 3S(s) \rightarrow P_4S_3(g)$$

Next, the P_4S_3 was combined with potassium chlorate ($KClO_3$) and sulfur (S) to form a match head easily ignited by the heat of friction. Sometimes, powdered glass was added to the match head, producing more friction, and thus more heat when the match was struck. An added inert filler bound the ingredients together. The exothermic reaction went like this:

$$P_4S_3(s) + S(s) + 6KClO_3(s) \rightarrow P_4O_{10}(s) + 4SO2(g) + 6KCl(s) + heat$$

In today's safety matches, red phosphorus is placed on the side of the box, where it gets converted to white phosphorus when the match head is drawn across the striking surface. The white phosphorus then ignites spontaneously in the air. The generated heat initiates another chemical reaction with the sulfur and potassium chlorate to light the match. It works like this:

$$4P(red) + energy\ (friction) \rightarrow P_4(white)$$

$$P_4(s) + 5O_2(g) + 3S(s) + 2KClO_3(s) \rightarrow P_4O_{10}(s) + 3SO_2(g) + 2KCl(s) + heat$$

What happens when you blow out the match? Modern manufacturers have got that covered. Today, the wood of all matches is chemically treated to prevent accidental fire when a recently lit match is discarded. You've probably noticed that when an untreated wood splint is ignited and then blown out, a burning ember continues to glow. But when you blow out a wooden match, the match immediately ceases to glow. To accomplish this no-glow feature, wooden matches were once dipped in a solution of alum [$AlK(SO_4)_2$] or sodium silicate (Na_2SiO_3). Today, afterglow is prevented by dipping the wood for making matches in a solution of ammonium phosphate [$(NH_4)_2HPO_4$] and phosphoric acid (H_3PO_4).

About 100 years ago, 3 trillion matches were made each year. Today, with the availability of other fire-starting devices, half a trillion matches are manufactured annually. Modern box matches are still manufactured primarily from aspen and poplar woods, with few changes in the past century. Strike one, and you are looking at some fascinating chemistry—not to mention *chem-history*—right at your fingertips. ▲

They're a Blast!

Called "Hand Blasters", "Blaster Balls", or "Cracking Balls", this novelty toy item is a set of two ceramic balls about the size of ping pong balls. On the basis of chemistry similar to that of matches, they make a loud popping noise when struck together. Each ball is coated with a mixture of potassium chlorate ($KClO_3$), sulfur (S), powdered glass, and glue. $KClO_3$ is the oxidizer, and the sulfur is the fuel. The powdered glass increases friction, and thus the amount of heat generated, when the balls are struck together. The heat of impact produces enough energy to initiate a reaction between the potassium chlorate and the sulfur.

$$3S(s) + 2KClO_3(s) \rightarrow 3SO_2(g) + 2KCl(s) + heat$$

Because both balls are coated with the same substance, you'll get the noisy effect even if you drop a single ball on a hard surface. In this way, Blaster Balls are similar to a strike-anywhere match.

All the ingredients necessary to carry out the chemical reaction are contained on each surface. The only thing necessary to start the reaction is heat.

Before you rush out to buy these, here's our advice. Plan to use them outside. That's for the sake of safety, as well as the sanity of everyone in the area.

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