PAINTBALL

Chemistry Hits Its Mark

PHOTOS BY MIGUEL CRUZ

Your heart is pounding as your adrenalin skyrockets. Projectiles whiz past your head as you dive for cover behind a makeshift plywood barrier. You return fire, but you know you are outnumbered. The enemy is closing in. Suddenly, you're hit. You reach for the wound. Your fingers are covered in a sticky red liquid. You have become another casualty. Fortunately, the red liquid is not blood, and the battle you have bravely fought is not actual combat—it is the exhilarating sport of paintball!

The first paintballs were fired by foresters and ranchers to mark trees and cattle. Then someone got the bright idea that it would be more fun to fire paintballs at people than at trees and cows. Thus the sport of paintball was born. From its inception in the 1980s, the sport has grown by leaps and bounds. Today, over 10 million people participate annually in paintball games. Over 1 billion paintballs are produced each year!

Although there are numerous variations, players typically attempt to capture an opponent's flag without being shot by a paintball. The first team to capture the opponent's flag and return it safely to their territory is the winner. The action is fast and furious, with a typical game lasting anywhere from 5 to 30 minutes. Sound dangerous? Other than a little bruising, it's actually safer than golf because of the protective face gear that all players are required to wear. And the game itself would not be possible without—you guessed it—chemistry!

By Brian Rohrig

Paintballs

Paintballs are a marvel of both engineering and chemistry. They must be strong enough to be fired at an initial velocity of up to 91 m/s (200 mph) without breaking, yet burst open when they hit someone without causing any tissue damage beyond mild bruising. The deformation of the paintball on contact greatly increases its stopping time, thus lessening the force (and the sting) of its impact. To accomplish this task, paintballs are made with a tough but elastic outer coating of gelatin, with a liquid center. The process by which liquids are manufactured within a gelatin shell is known as encapsulation.

Encapsulation technology originated with the pharmaceutical industry. The process involves enclosing a substance—either liquid or solid—within a thin transparent gelatin membrane. These capsules are commonly called soft gels, since they are somewhat elastic and give a little when squeezed. Soft gels are commonly used for medicine, vitamins, bath oil beads, and a variety of other applications.

Gelatin is made from denatured collagen fibers, which are derived from the skin, bones, and connective tissue of animals. The gelatin for paintballs is usually made from pig skins, which tend to make the best paintball. A plasticizer is also added to increase stability and make the gelatin more moldable. The gelatin-plasticizer ratio is formulated so as to establish the optimal balance between elasticity and brittleness, enabling the paintball to break open on impact yet not break when initially fired.

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Though technically not water soluble, gelatin does break down in water to form a colloidal gel. That is why it is so important to keep paintballs dry. Gelatin is used in a variety of foods. Jell-O, marshmallows, gummy bears, ice cream, yogurt, cream cheese, and margarine all contain gelatin. Its unique constitution helps to give foods thickness and texture. And it provides the perfect medium to keep the paintball intact—until it hits you!

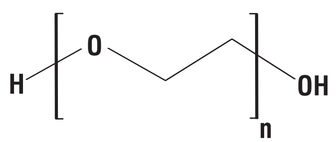
A typical paintball is 68 caliber, meaning its diameter is 0.68 inches (1.7 cm). They are also available in other sizes as well. Paintballs come in a variety of colors; some glow in the dark, others fluoresce under black light.

The first paintballs were not water soluble, since they were similar to the original formulation which was used to mark trees and cattle. When a forester marks a tree, it is important that rain not wash off the mark. The first paintball contests resulted in a lot of stained and ruined clothing, to the chagrin of many parents.

In the mid-1980s, the paintball manufacturers decided to make a water-soluble paintball. This was a daunting task, since the "paint" for the paintballs could not contain any water or else they would break down the gelatin shell. This feat was accomplished by using water-soluble compounds, but not water itself. And once paintballs became water soluble, the popularity of the sport skyrocketed.

After much research, it was determined that polyethylene glycol (PEG) would be an excellent substance for the liquid inside of a paintball.

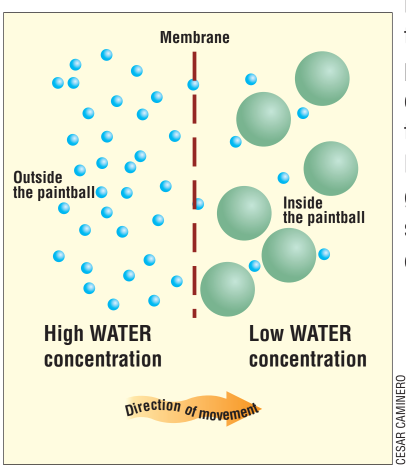
Polyethylene glycol is a tasteless, colorless, and nearly odorless compound that dissolves in water but has no effect on the gelatin shell. PEG is very viscous, meaning it flows slowly. Its thick syrupy consistency makes it perfect for use in paintballs; they have a consistency somewhat like blood when they break open.



polyethylene glycol, PEG

That's swell

If a paintball is dropped into a beaker of water, it will expand to an impressive size. Through osmosis, water will pass through the gelatin membrane and hydrogen bond with the polyethylene glycol within. Since the concentration of water is much greater outside of the paintball than inside, water will diffuse inward in an attempt to equalize the concentration of water. Water will continue to travel through the gelatin membrane until the concentration of water inside the paintball is equal to the concentration of the water on the outside of the paintball. However, as it swells the gelatin shell will break down, spilling the contents before equilibrium is reached.

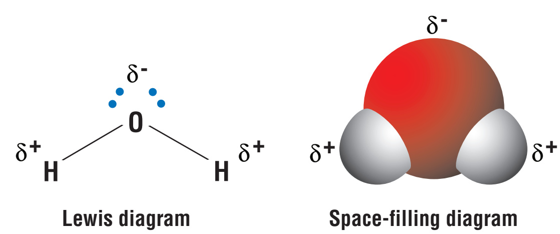


Osmosis: a paintball swells up when placed in water.

As you can see, paintballs are not really made from paint, but rather from a mixture of nontoxic food grade ingredients. The exact combination of ingredients is a trade secret but we do know that in addition to polyethylene glycol, they also contain colored food dyes, preservatives, and a thickener such as starch or wax. The ingredients within the paintball are also biodegradable, so they pose no threat to wildlife or the environment.

Bonding with your paintballs

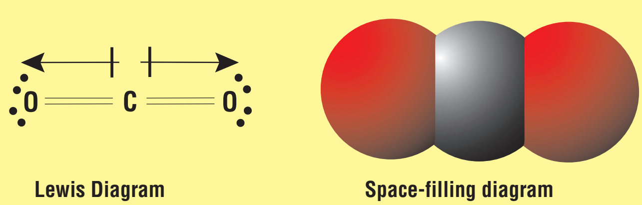
What makes paintballs water soluble? The answer lies in polarity and hydrogen bonding. Water is a polar substance that has distinct regions of positive and negative charge. Water's polarity is due to the differences in electronegativity between oxygen and hydrogen. Electronegativity, as defined by the late American chemist Linus Pauling, is "the power of an atom in a molecule to attract electrons to itself." Oxy-



Two representations of water, showing regions of partial charges.

Are all molecules with polar bonds polar?

The answer is no; in some cases, the polarity of the bonds is effectively cancelled. Consider a CO_2 molecule. Oxygen is more electronegative than carbon, so the covalent bond between the two atoms is polar. This is called a polar covalent bond; the O-H bond in a water molecule is also polar covalent. The polar nature of this bond is indicated by the arrow ($+\!\!\longrightarrow$) in the figure below. But the linear nature of the CO_2 molecule dictates that, overall, the molecule is nonpolar. That's because while one oxygen atom is drawing bonding electrons toward itself, the oxygen atom on the other side of the molecule is doing the same thing; the net effect is that they cancel each other out. That makes CO_2 a nonpolar molecule.



Two representations of CO_2, showing an overall nonpolar molecule.

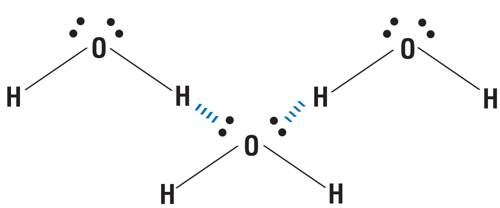
So when predicting the polarity of a molecule, the shape must be considered. Often, molecules that are symmetrical will be nonpolar even if polar bonds are present.

gen is more electronegative than hydrogen, so it attracts electrons to itself more strongly than does hydrogen. For a water molecule, this creates a region of partial negative charge (δ^-) on the side of the oxygen atom, and a region of partial positive charge (δ^+) on the side of the hydrogen atoms.

Because of the shape of the water molecule, these polar bonds make the molecule polar overall.

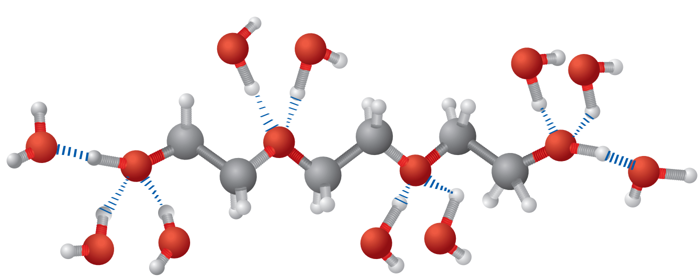
Polar molecules are attracted to other polar molecules. This attraction is due to the positive side of a polar molecule being attracted to the negative side of another polar molecule. This attraction is the basis of the intermolecular bonding that may occur when one substance dissolves into another. This tendency is summed up nicely in the principle "like dissolves like," meaning that polar substances dissolve in other polar substances.

We can take a closer look at the interaction between water and polyethylene glycol molecules. The oxygen atoms in the polyethylene glycol chain each have two nonbonding electron pairs. The partial positive charges around the hydrogen atoms in water are attracted by these



Hydrogen bonding between water molecules.

nonbonding electrons. This particular type of intermolecular attraction is called a hydrogen bond. Hydrogen bonds occur when a hydrogen atom attached to a small, highly electronegative atom (typically F, N, or O) is in the vicinity of an atom with nonbonding electron pairs. Although not as strong as covalent or ionic bonds, hydrogen bonds are the strongest of the intermolecular forces. The hydrogen bonds between water molecules are responsible for its unusually high boiling point.



Hydrogen bonding (blue lines) between polyethylene glycol and water. Hydrogen bonds are about 1/15th the strength of a covalent bond. Red = oxygen atoms, grey = carbon atoms, and white = hydrogen atoms.

The dyes used in paintballs are also polar and water soluble. The polar nature of the polyethylene glycol enables these water-soluble dyes to be dissolved within the paintball. We can't show you the structures of the dyes because they are proprietary—that means a closely guarded secret. But the colored dyes and the polyethylene glycol are water soluble, so today, when a paintball combatant returns from the field of battle and her clothes are splattered with paint, they simply need to be thrown into the wash and they will generally come out clean—though it may take more than one washing!

Magic markers

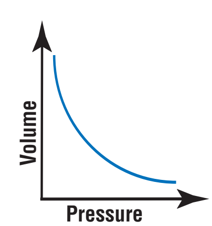
The firing instruments used to shoot the paintballs have come a long way since the game began. Known as markers rather than guns, they have evolved from hand-cocked, single-shot pistols into rapid-firing, high-precision instruments. The "marker" term arose from the first use of paintballs, which was to mark trees and cattle. The term also gives the sport of paintball a less violent image.

The markers come in a variety of makes and models—from pistols to semiautomatic rifles. Some models can fire 100 paintballs at 30 per second using a single 12-gram CO_2 cartridge. Extra large hoppers (the storage chamber that holds the paintballs before they are fired) can hold up to 250 paintballs. Fully automatic models are available, but these are prohibited on most playing fields. There are even paintball "landmines" that will spray paint all over whoever is unfortunate enough to step on one.

Markers all operate on the same basic principle—using compressed gas to launch a paintball. Gases can be readily compressed because there is so much space between the molecules. When the marker is cocked, a paintball falls from the hopper into the barrel. When the trigger is pulled, a quick blast of compressed gas is released directly behind the paintball, propelling it forward at an initial velocity up to 91 m/s.

It's a gas

The most common gas used in paintball markers is compressed CO_2. The CO_2 within a gas canister is at an extremely high pressure—around 800–850 psi (pounds per square inch). At this pressure, however, CO_2 will actually liquefy. So, within the high-pressure confines of a gas cartridge, much of the CO_2 will typically exist as a liquid. The liquid is actually responsible for controlling the pressure of the CO_2. As long as there is



Boyle's Law

some liquid present, the pressure of the gas in contact with the liquid will remain constant. The pressure of the gas will equal the vapor pressure of the liquid. Thus, the pressure of the CO_2 will stay constant for each shot; if there were no liquid present, releasing the gas would decrease the pressure of the remaining gas. However, if the marker is fired many times in succession, the pressure will temporarily drop since it takes some time for the liquid CO_2 to vaporize and restore the pressure.

The vapor pressure of CO_2 at room temperature is about 60 times atmospheric pressure. To prevent a canister from exploding under high pressure, CO_2 tanks are fitted with a copper burst disk that is made to pop off if the pressure exceeds a safe level. This varies between 2200 psi and 2800 psi, depending on the manufacturer.

When a small amount of this gas is released, it expands greatly, since it is now under much less pressure. Boyle's law states that the volume of a gas is inversely proportional to its pressure, so long as the temperature is held constant. Inversely proportional means that when one factor decreases, the other increases. When the volume of a gas goes down, its pressure goes up. Likewise, when the pressure decreases, the volume increases.

The paintball is propelled forward by the increase in the volume of the CO_2, which is due to the decrease in pressure the gas experiences as it leaves the cartridge and enters the firing chamber. The only thing standing in the way of the expanding gas is the paintball, which is launched effortlessly through the air.

Just do it.

The sport of paintball is highly addictive. Serious players can spend hundreds, or even thousands, of dollars on high-tech gear. There are numerous organized leagues and tournaments in nearly every state and in countries around the world.

Even the U.S. Army is getting into the game; they have made an arrangement to sponsor the Long Island Big Game, to be held May 19–20, 2007, in New York. Organizers expect over 2000 players, and the game will feature tanks, a helicopter, missions, and prizes.

A few bruises are a small price to pay for a sport that not only is immensely entertaining, but also teaches strategy, builds teamwork, and provides great exercise. And if that upcoming chemistry test is stressing you out, there is no better way to relieve that stress than by heading to the woods with some friends and blasting each other with spheres of brightly colored gelatin-encapsulated solutions of pigment used polyethylene glycol!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Can you find the density of a paintball?

Paintballs come in various sizes, but a typical paintball will have a diameter of 1.7 cm and a mass of 3.1 grams. Can you determine the density of a paintball? The formula for the volume of a sphere is $4/3\ \pi\ r^3$. The formula for density is m/v.

You can find the answer on page 20.

Ten tips from tourney players

Get in shape: It's a physical sport. Eat well, stay active, and cut bad habits such as smoking.

Protect yourself: Cover up with appropriate gear to prevent bruises or a blood clot.

Know the rules and abide by the do's and don'ts. Be a good sport.

Learn to shoot with either hand. This increases your mobility.

Be unpredictable: Make yourself a harder target for the competition.

Prepare: Study the game and walk the field. Pack your gear the night before.

Communicate with team members. Tournament players yell at each other constantly.

Practice: Simple drills can improve your aim.

Be safe: Always wear your mask, listen to the ref, and follow the rules of the field.

Always treat a marker as if it is loaded.

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