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COVER PHOTOGRAPHY BY MIKE CIESIELSKI

Question From the Classroom

By Bob Becker

Q: My parents just bought new tires for their car, and the salesman told them they should inflate them with nitrogen gas instead of regular air. Is paying extra for nitrogen gas in car tires worth it?

A: This is a very intriguing question. My initial reaction is to assume that salespeople are just looking for one more way to squeeze a buck out of gullible customers. After all, air is 78% nitrogen. Why would inflating your car tires with pure nitrogen make that big of a difference? But this question is particularly tricky for me because it pertains to chemistry, which I have taught for the past 22 years. And cars, though I have driven for the past 29 years, I know next to nothing about. I do, however, know where to go for advice about cars: the famous Magliozzi Brothers, Tom and Ray, a.k.a. "Click and Clack, the Tappet Brothers"! (Their NPR radio show "Car Talk" is a weekend favorite.)

Their Car Talk website (http://www.cartalk.com) reveals that they have addressed the nitrogen question quite a few times, most recently in April 2005. Their advice: For the average driver, filling tires with nitrogen gas is not worth the added cost. Still, for a chemist, the "nitrogen in tires" question has an intriguing mix of silly and plausible claims swirling about it.

Race car drivers do it. Why? Air contains about 78% nitrogen, 20% oxygen and small quantities of other gases, including, most importantly, water vapor. On humid days, air contains considerably more water vapor than it does on dry days. What's more, because of the extensive hydrogen bonding, water vapor deviates quite dramatically from ideal gas behavior. Thus, as it heats up, an air-filled tire tends to show much more inconsistency in pressure changes than does a tire filled with pure nitrogen gas. In car racing, contact between the tire and the track is everything, and a fraction of a psi (pounds per square inch) in the tire can make the difference between winning, losing, or spinning out of control. NASCAR mechanics figured out years ago that the pressure in a nitrogen-filled tire was far more consistent and reliable than the pressure in air-filled tires. Does that necessarily mean that the average Joe or Jane on the street should swap out the air in their tires for nitrogen gas? Is it worth spending the extra money? Again, probably not.

A large number of web sites disagree. But, consider this: These sites tend to be the ones selling nitrogen. As such, the information they offer should be scrutinized and not merely accepted as factual.

One argument is that nitrogen is far less reactive than oxygen and thus does less damage to the inside of the tire. This all may be true, but it has been my experience that tire treads wear off long before any kind of deterioration from the inside could make a difference. Maybe nitrogen causes less oxidation of the wheel rims? But again, is this really even an issue?

They also contend that nitrogen-filled tires dissipate heat more quickly and thus run at a lower temperature. Unless this effect can be attributed to the water vapor, it makes very little sense, since nitrogen and oxygen have very similar thermal conductivities (0.02583 and 0.02658 W/mK respectively) and specific heat capacities (29.1 and 29.4 J/molK, respectively).

COREL

All the same, one of their more convincing arguments pertains to nitrogen's ability to maintain tire pressure. Nitrogen reportedly leaks out of tires more slowly than air. If you have discussed Graham's law in chemistry class this year, then you would probably expect the opposite to be true. Because nitrogen has a somewhat lower molecular weight than oxygen, its average molecular velocity should be greater and it should therefore escape or effuse through a small hole more readily. But effusion has to do with the passing of a gas through a small opening into a relative vacuum.

For the leaking out of a gas through a thick permeable layer of rubber, there is something else to consider. Molecular size and polarity play important roles too.

Gas permeability of rubber is believed to involve dissolution of the gas in the polymer, diffusion through the thickness of the rubber, and loss on the other side. The N-N bond is much shorter than the O-O bond, and the highest-energy electrons of O_2 are more polarizable than for N_2 (O_2 has a higher boiling point than N_2 for much the same reason). The greater polarizability of oxygen should make it slightly more soluble than nitrogen in rubbers. (For example, oxygen is more soluble in organic solvents than is nitrogen.)

This would mean that a nitrogen-filled tire should hold its pressure longer than one filled with air. How much longer? Here the websites disagreed, and it is important to note that not one of the commercial websites actually cited any scientific studies in their arguments.

An issue that far outweighs the nitrogen issue is this: An estimated 80% of the tires on the road today are not properly inflated; they're either underinflated or overinflated. Both conditions can shorten the lifetime of a tire. Underinflation lowers gas mileage and over inflation can dangerously lower the amount of traction your car has on the road. Drivers should check their tire pressure every month or so, and add or remove air as needed.

MIKE CIESIELSKI

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TEACHERS!

FIND YOUR COMPLETE TEACHER'S GUIDE FOR THIS ISSUE AT www.chemistry.org/education/chemmatters.html.

The Chemistry of Digital Photography and Printing

Once upon a time, people put stuff called film in the their cameras. First, they paid for it. Then they took photos, but couldn't preview them on a screen. No deleting, no computer editing—they paid strangers to develop every miserable photo, hoping that a few were OK! So primitive! So last-century!

By Brian Rohrig

Imagine needing eight hours to take a single photograph! That's how long it took French scientist and inventor Joseph Niepce to take the world's first photograph in 1826. And the end result didn't win any prizes—it was a grainy image of some buildings viewed from a third-floor window. We have come a long way since then! Today, any amateur photographer can produce a glossy full-color photo in a matter of minutes using a digital camera and computer. In just the past 10 years, digital photography has taken the world by storm, threatening to do to film what the DVD has done to video.

The world's first photograph!

Most of your family photos were probably taken the old-fashioned way, with film that had to be taken to a photo shop to be developed. There is a fascinating bunch of chemistry involved in this process. All photographic film is coated with a thin layer of a silver halide compound, such as silver bromide ($AgBr$). When light strikes this layer, an image is recorded on film, which is made visible during the developing process. If you have ever been inside a darkroom, you have probably seen all sorts of mysterious chemicals such as developers, fixers, and baths. Even if you don't quite know how it all works, you can still appreciate the fact that a lot of chemistry goes into developing pictures.

Does digital processing mark the end of chemistry in photography? There is actually plenty of fascinating chemistry going on—it's just on a much smaller scale.

Sensing light

All cameras work by focusing light through lenses to create an image. A conventional camera records this image on film. A digital camera records this image on a permanent part of the camera known as a sensor. A typical sensor in a digital camera measures only 4.4 mm × 6.6 mm. This is about the size of a fingernail.


GETTY IMAGES

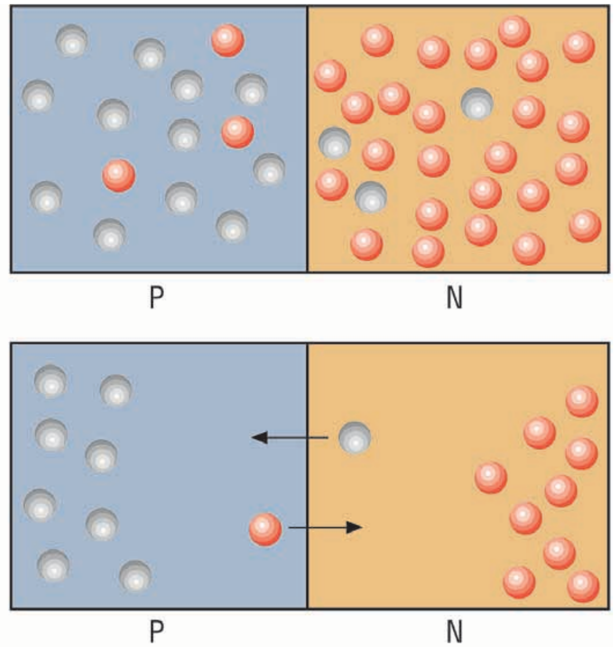
Sensor technology has enabled manufacturers to make digital cameras so small they can even be incorporated into cell phones. Similar sensor devices are used in fax machines, scanners, copy machines, and bar code readers at the grocery checkout.

The sensor is a semiconductor. Silicon is the material of choice for most semiconductors. This is ironic because silicon barely conducts electricity at all in its pure form. But if a small amount of impurity is added, through a process known as doping, then silicon becomes a fair conductor of electricity.

The sensor in a digital camera comprises many tiny semiconductors known as diodes. Diodes allow current to flow in one direction, but not another. Diodes are composed of two different types of doped silicon layers sandwiched together. One type of silicon is doped with phosphorus or arsenic. Both of these elements contain five valence electrons. Because silicon atoms only have four valence electrons, the doping agents provide the extra electrons that move throughout the material. With its excess of electrons, this type of silicon is known as *n*-type, with the "*n*" referring to the negative charge resulting from the free electrons.

Another type of silicon is doped with either boron or gallium, which only have three valence electrons. These doping agents create a deficiency of electrons in the structure, since silicon atoms have four valence electrons. This electron deficiency creates electron "holes" in the structure. Silicon doped with these deficient atoms is referred to as *p*-type silicon, with the "*p*" standing for the positive charge resulting from the deficiency of electrons.

When placed together, these two types of silicon form a diode, the one-directional conductor described above. Think of a diode as a one-way street for electrons. At the p-n junction, a positive charge builds on the n side, and a negative charge on the p side until the internal electric field counteracts the tendency of the electrons to fill the holes. The internal electric field then permits current to pass in one direction.

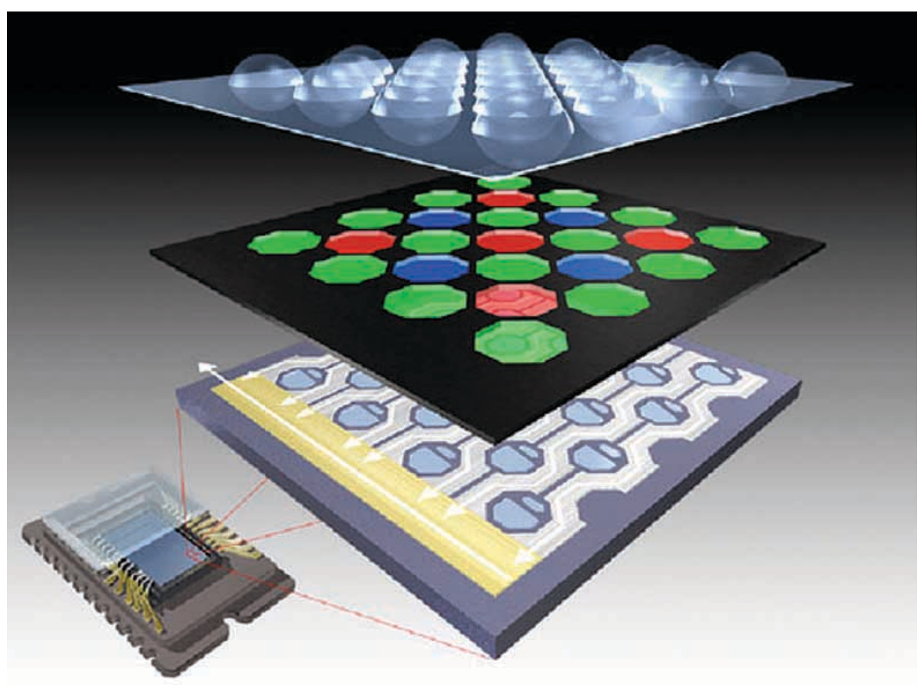


ACS STAFF

As more and more holes are filled with electrons, a region, neither P nor N, forms, called the depletion zone. Holes are shown as . Electrons are shown as .

Photosites

Each diode in a sensor is a *photosite*. Each photosite represents one picture element—better known as a pixel. The greater


FUGIFILM

SuperCCD SR structure diagram, one microlens, one color filter, two photodiodes per photosite.

the number of pixels, the greater the resolution and overall quality of the pictures you take. For example, a typical digital camera may have a resolution of 640 × 480 pixels, for a total resolution of 307,200 pixels. The best digital cameras on the market today have a resolution of more than 10 million pixels (10 megapixels). For comparison, you should take pride in your personal sensor. The human eye contains 120 million pixels!

The pixels of any photo can be clearly seen through the low power of a microscope. The larger the pixel size in a photo, the poorer the quality, as larger pixels mean fewer pixels within a certain area. If you compare a normal color photo with a newspaper photo, you can see a huge difference in pixel size. Newspaper photos will have larger pixels, representing poorer quality.

When you take a picture with a digital camera, each tiny photosite on the sensor is exposed to light. When a photon is absorbed by the semiconductor, it promotes an electron to a higher energy level. What this means is that the high-energy electron acts like an electron that was added by doping: It is free to move about the semiconductor. Normally, the electron would just relax back to its lower-energy state. However, if it is near the *p-n* junction, it is attracted to the positive side, and migrates there, where it is collected.

As more photons strike a photosite, more electrons are knocked free. The greater the intensity of the light that strikes a photosite, the more electrons accumulate. A useful analogy is to think of the photosite as a tree, the photons as balls that you throw into the tree, and the electrons as leaves on the tree. Suppose that every time you throw a ball into a tree, a leaf is knocked loose. The more balls that you throw into the tree, the more leaves will accumulate on the ground below. A photosite that has been exposed to very bright light will contain far more electrons than one that has been exposed to dimmer light. Generally, each image sensor can record 256 different shades of gray, ranging from pure white to pure black.

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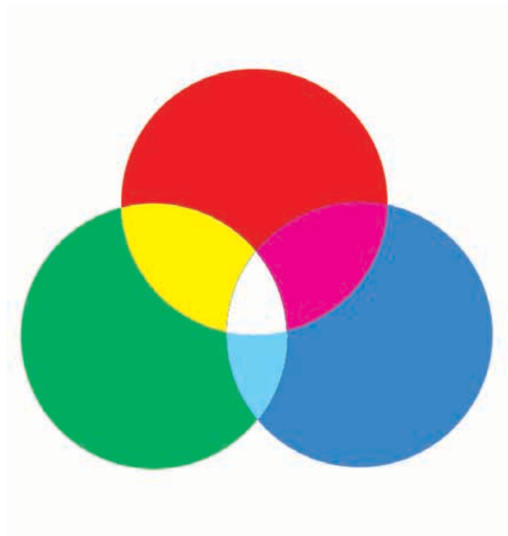
Information from photosites is converted to digital form and stored on memory cards for later retrieval.



Seeing in color

So then, how do digital cameras take color photos, if the sensors can only record shades of gray? The trick is to use filters, that combine to produce any color imaginable. Most cameras use the 3-color system to produce color. The three primary light colors are red, green, and blue. Together, these three colors make white. Any other color can be produced by mixing together various shades of these three colors. To accomplish this feat, either a red, blue, or green filter is placed over each photosite on the sensor of a camera. The most common pattern is known as the Bayer pattern, which alternates a row of red and green filters with a row of blue and green filters. This configuration gives you twice as many green filters as blue or red. Because the human eye is not sensitive to all three colors equally, extra green filters must be used to produce the best color for our eyes.

Next, the information at each of these photosites is converted to digital form. By themselves, electrons that accumulate at each photosite do not represent digital information that can be read by your computer. So every digital camera carries its own built-in computer that converts information to digital form and stores it on your memory card.

Printing

Once an image is recorded digitally by a camera and downloaded onto a computer, it can be printed. Or, it can be manipulated using software on a computer and then printed. The ability to choose, alter, and crop photos on screen before printing gives even a casual photographer unprecedented power to print only the images they want.

There are two basic types of printers that can print photos: laser and inkjet. The laser printer works by using static electricity. The underlying principle involves positively charged toner sticking to negatively charged paper, since opposite charges attract. A laser

beam projects a negatively charged image of whatever is to be printed onto the light-sensitive drum. The drum is then coated with positively charged toner, which is attracted to the negatively charged image on the drum. An analogy would be writing a message on the outside of a coffee can with glue, and then rolling it in flour. The flour will stick to the glue but not to the "unglued" parts of the can.

A piece of paper then passes over a charged roller, giving it an even stronger negative charge than the drum. The drum then rolls over the sheet of paper. The strongly negatively charged piece of paper pulls off the positive toner from the drum. Finally, the paper passes through a pair of heated rollers known as the *fuser*, which fuses the toner to the paper. After the paper attracts the toner from the drum, a discharge lamp bathes the drum in bright light, erasing the original electrical image.

Color printers work the same way, except the above process is repeated four times. Four types of toner are used: cyan (bluish), magenta (reddish), yellow, and black. By combining tiny dots of these four colors, nearly every other color can be created.

A photocopier works according to the same basic principle, except the electrostatic image that forms on the drum is formed by bright light that reflects off the paper to be copied. The drum is manufactured with a photoconductive material on its surface that makes it sensitive to light. White areas of the paper are reflected onto the drum. The black ink on the paper to be copied absorbs light, so parts of the drum do not receive an electrical charge. These uncharged parts of the drum will form the photocopy. Just like in a laser printer, the negatively charged toner is attracted to the positively charged image imprinted by light on the drum. A strongly positively charged piece of paper then attracts the toner from the drum. Your copy is complete once it passes through the heated rollers of the fuser.

Inkjet printers, as the name implies, work by spraying tiny droplets of ink onto the surface of the paper. Each drop is very tiny, being only about 50–60 micrometers in diameter. A micrometer (μm) is a thousandth of a millimeter. A human hair has a diameter of about 70 μm. There are two main types of inkjet printers on the market today. Bubble jet printers use heat to vaporize ink to form a bubble. This expanding bubble forces some of the ink onto the paper. When the bubble pops, a vacuum is created, causing more ink to flow from the cartridge into the print head. A piezoelectric printer works using piezo crystals (such as quartz). Piezoelectric crystals generate an electric field when distorted, but conversely, they can be distorted by an electric field. Thus, to get the nozzle to deform and eject the ink, an electric field is applied. This electric charge causes the nozzle to vibrate, forcing ink out on the paper.

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Inkjet printers work by spraying tiny droplets in ink on the surface of the paper and tend to produce better quality photos.

Digital photos can be printed using either laser or inkjet printers, but inkjet printers tend to produce better quality photos. An inkjet photo printer will generally use six colors as opposed to the four that are normally employed in a color printer. Other types of photo printers use a dye sublimation technique. Sublimation is the process of changing phase from a solid to a gas, skipping the liquid phase altogether. Heat is used to vaporize solid dyes, which permeate the paper before they return to the solid form. Thermal autochrome photo printers require the use of special paper that already contains the ink. A print head delivers various amounts of heat to the paper, causing various pigments to appear.

Amazingly, experts agree that digital photography is still in its infancy. We will no doubt see huge advances in digital quality and convenience in the near future. Will digital cameras completely replace conventional cameras? There are photographers who remain devoted to the artistic and visual effects of developed film and darkroom processing. For most of us, it's nice to know we have plenty of options available for recording lasting images of our big moments. And it's all due to—you guessed it—chemistry!

Brian Rohrig teaches chemistry at Jonathan Alder High School in Plain City, OH. His most recent *ChemMatters* article "There's Chemistry in Golf Balls" appeared in the October 2005 issue.

With a flash of light, nanotubes ignite!

Shine light on some materials and they will make an audible sound. This interesting phenomenon is known as a photoacoustic or optoacoustic effect.

The photoacoustic effect was first discovered by Alexander Graham Bell and reported to the world in 1880. While working on the photophone, he inadvertently discovered that if a beam of light was focused on a selenium cell and then rapidly interrupted by a rotating disk, the cell produced an audible sound. He further demonstrated that the strength of the photoacoustic effect is dependent on the strength of light absorbed by the material.

Shine light on some new nanoscale materials and they'll not only sound off, but they actually ignite under an ordinary camera flash. Enhanced photothermal properties are one of the many unexpected properties that researchers are discovering as they delve into the realm of nanoscale materials.

Single-walled carbon nanotubes

Last year, researchers at Rensselear Polytechnic Institute in Troy, NY, reported in *Science* that single-walled carbon nanotubes (SWNTs) of a dry, "fluffy" nature ignite when exposed to a conventional flash at close range.

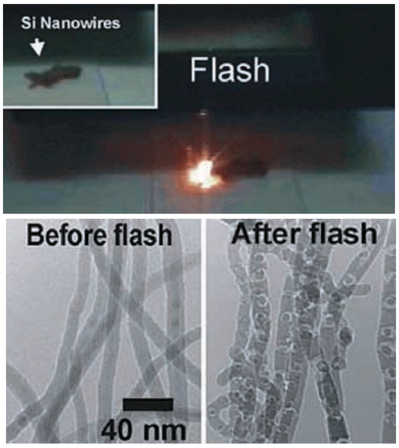
Similar materials such as C60, fluffy carbon soot, and multiwalled carbon nanotubes do not ignite.

The researchers believe the nanotubes must have an enhanced ability to absorb light and convert it to heat (a photothermal effect). In the "fluffy" bundles, the heat does not dissipate and reaches an estimated 1,500°C—more than enough to ignite the SWNTs. Other researchers have hypothesized that part of this effect might rely on metal impurities present from the manufacture of the SWNTs.

See SWNTs ignite and burn after exposure to an ordinary camera flash.
http://www.sciencemag.org/cgi/content/full/296/5568/705/DC1

Silicon nanowires

In an article in *Nano Letters*, researchers at the University of Science and Technology in Hong Kong have described a similar phenomenon involving enhanced photothermal effect in Silicon (Si) nanowires. When these nanowires are hit by a light, they make an audible pop. If the flash has sufficient power the Si nanowires ignite. Like SWNTs, the researchers see evidence that the Si nanowires experience temperatures of approximately 1500 °C during the flash.



The figures on the right show Si nanowires before and after a flash under an inert atmosphere. The nanowires don't ignite, but they get hot enough to melt Si. The authors believe that "the optical absorption in Si nanowires was enhanced by their special structure." The same effect is not observed in bulk silicon material, and yet the absorption spectrum of Si nanowires and pure Si single crystals is similar. The mechanism is unclear, but the Si nanowires must clearly "trap an incredible amount of energy from the flash." The ignition of the Si nanowires is distinct from carbon nanotubes because there is no metal impurity in Si nanowires.

Because of the unexpected ability to confine photoenergy, Si nanowires may find uses in "smart ignition systems, self-destructing systems for electronic devices, nanosensors, and nanostructural or nanophase reformation for nanotechnology."

See Si nanowires resist burning in gas flame, only to ignite after a flash of light at:
http://www.chemistry.org/portal/resources?id=3f136aba6e8711d7f03f6ed9fe800100

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