Building a Better Bleach: A Green Chemistry Challenge

**Problem 1:** You need to wear your new dark red T-shirt, and there it sits in the dirty clothes hamper. Wait! The washer is loaded and filling with water. Problem solved! You just add the shirt to the rest of the load—the load that happens to be filled with everyone’s white shirts, socks, and underwear. You, my friend, are headed for trouble! (See Problem 2.)

**Problem 2:** You need to find a place to hide when everyone starts screaming about pink underwear and socks!

**Problem 3:** You need to turn pink back into white.

*By Kathryn Parent*

A stain is a color where you don’t want it. It might surprise you that stain removal is actually not removal at all. The secret behind getting rid of the unwanted color is not a matter of removing the offending molecules, like detergents acting to remove soil. Instead, the stain molecules are altered chemically so that they no longer reflect light in just the same way as before. We’ll call it *decolorizing*, or *bleaching*—words that imply the chemistry going on in the process.

Fine then! Let’s get back to the problem at hand. What chemical is going to solve the problem? Let’s start with ordinary household bleach. The active ingredient in bleach, sodium hypochlorite (NaOCl), keeps white clothing white and your bathtub sparkling. But handle with care. If you’ve ever spilled bleach, you know it can also add white blotches to a favorite pair of blue jeans.

How does bleach act on stain molecules? Bleaching is an example of the basic chemical processes—oxidation and reduction—at work. Oxidation is generally defined as “losing” electrons, and reduction as “gaining” them. The two processes occur together, so one compound is reduced in the process of oxidizing another compound. Another common definition of oxidation is the gain of oxygen atoms or the loss of hydrogen atoms. Reduction is then the loss of oxygen atoms or the gain of hydrogen atoms. Here are two ordinary examples.
A DIOXIN

What are dioxins? They’re a group of several hundred structurally similar compounds all sharing an uncanny ability to persist and accumulate in the food chain. People exposed to a large amount of dioxins can develop a condition called chloracne. Not your normal acne, chloracne is a severe skin disease causing lesions to appear on the face and upper body. High dioxin exposure has also been linked to an increased cancer risk in adults. The main sources of dioxins are waste incineration and forest fires. But dioxins can also be produced by industrial processes that use chlorine, like textile and paper manufacturing. Although the exact health risk posed by dioxins is controversial, the tendency for the compounds to linger in the environment prompts the U.S. Environmental Protection Agency to work with industry to find ways to limit their production.

Nonchlorine bleaches to the rescue

If the release of chlorine—especially on a large scale—is bad for the environment, what else can we use to get rid of stains? Alternative “nonchlorine” bleaches are also available. They contain hydrogen peroxide or other peroxide compounds instead of sodium hypochlorite. Because H₂O₂ is a liquid, it is not actually present in solid nonchlorine laundry bleaching products. These solid bleaches contain ingredients like perborate or percarbonate—compounds that react in water to release hydrogen peroxide. Thus, H₂O₂ is the nonchlorine bleaching agent common to almost all of these products. Hydrogen peroxide is also the bleaching agent in many hair dyes. Alone, peroxide alters hair pigments to bestow the “peroxide blonde” effect, but most permanent dyes rely on peroxide as a key ingredient, either to alter natural pigment in the hair or to activate the new dye.

Dilute hydrogen peroxide (3%) is also commonly found in medicine cabinets. Used as an antiseptic for minor cuts and scrapes, it’s also effective at removing bloodstains from clothing. The bubbling that occurs when the peroxide encounters blood is due to its decomposition into oxygen gas and water

H₂O₂ → ½ O₂ + H₂O

In the process of decomposing, H₂O₂ releases free radicals—highly reactive inter-
Either adding oxygen or removing hydrogen atoms. As a result, the oxidized compounds do not include organochlorine-type pollutants, and the problem of hazardous pollution is prevented at the source.

So, what are we waiting for? Why not stop using chlorine bleach altogether and replace it with hydrogen peroxide alternatives? The challenge of replacing traditional chlorine bleaches with hydrogen peroxide is twofold. First, the peroxide oxidation process can be unselective. Because any molecules in the vicinity that are exposed to decomposing hydrogen peroxide get exposed to reactive free radicals, some unwanted chemistry might accompany the desired oxidation. Second, successful bleaching with H₂O₂ requires higher temperatures and pressures and longer reaction time than those required for chlorine bleach. On an industrial scale, this means higher costs for energy, equipment, and labor for the bleaching process.

A research group led by Professor Terry Collins at the Institute for Green Oxidation Chemistry (we’ll get to the Green part in a minute) at Carnegie Mellon University may have solved our bleaching problems by developing some heroic molecules with names to match. Collectively, they are called tetraamido macrocyclic ligands or TAML for short. These versatile molecules (picture above) function as catalysts in the hydrogen peroxide bleaching process. Their presence allows hydrogen peroxide oxidation to proceed at much lower temperatures and pressures. And like all catalysts, they are not consumed in the process.

That’s the kind of good news the Environmental Protection Agency rewards with the annual Presidential Green Chemistry Challenge Awards, a program that recognized Prof. Collins’s research team for their innovative research in 1999. Green chemistry is the design of chemical products and processes that are environmentally benign by design. That means that the products can be made from renewable resources, that they consume minimal energy resources in their manufacture, and that they don’t release polluting end-products into the environment that must be cleaned up later. It’s easy to see how bleaching with TAML-activated H₂O₂ would be an ideal example of green chemistry in action. Made from naturally occurring biochemicals, TAML catalysts reduce energy costs and not only prevent pollution, but are also useful in cleaning up pollutants that other processes have left behind.

Let’s get back to the pink underwear problem. You’ll be happy to know that TAML technology has been applied to laundry. Commercial laundries, as well as homeowners in drought-stricken areas are looking for ways to reduce water usage. But using less water leads to problems with dye transfer. The highly selective TAML activators use the peroxide present in some detergents to hunt and destroy free dye molecules, while leaving fabric-bound dye molecules unchanged.

All of which might be too late for your current crisis. But TAML may protect you and your pink-outfitted family from suffering similar laundry mishaps in the future. Check the product labels.

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