



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.





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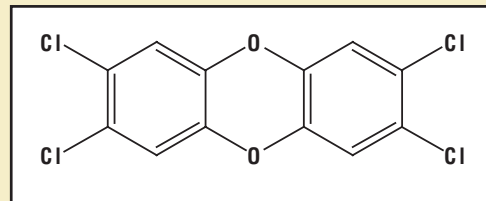
Oxidation of carbon: $C + O_2 \rightarrow CO_2$

Reduction of nitrogen: $N_2 + 3H_2 \rightarrow 2NH_3$

Back to stains. The color of the stain is a physical property caused by the chemical structure of its molecules. When an oxidizing agent removes electrons from a molecule, the chemical structure of the molecule is changed, and the physical properties (like color) are altered. Chlorine bleaches are oxidizing agents that work efficiently and cheaply in the laundry. Any excess is washed away in the rinse water. Problem solved? *Yes*, if you're only worried about those pink socks. *No*, if you're worried about the environment. Sometimes, oxidation with chlorine bleach involves addition of *chlorine* atoms to the colored stain molecules rather than just removal of electrons. The fact is that the addition of chlorine to an organic-rich waste stream leads to the formation of hazardous byproducts, such as dioxins.

A DIOXIN

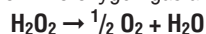
What are dioxins? They're a group of several hundred structurally similar compounds all sharing an uncanny ability to persist and accumulate in the food chain. People exposed to a large amount of dioxins can develop a condition called chloracne. Not your normal acne, chloracne is a severe skin disease 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 H_2O_2 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, H_2O_2 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



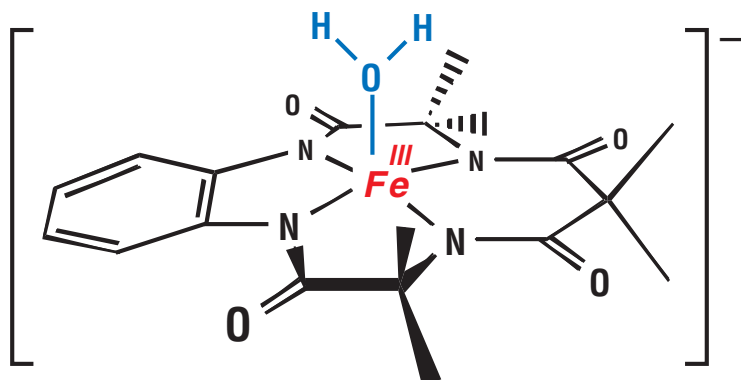
In the process of decomposing, H_2O_2 releases free radicals—highly reactive inter-

mediates that oxidize other molecules by removing electrons or hydrogen atoms from them. If these other molecules are colored stains or pigments, the chemical changes accompanying their oxidation may alter their physical properties, rendering them colorless—bleached.

Hydrogen peroxide sounds like our ideal bleaching agent! In addition to its everyday use as a household cleaner or hair dye, oxidative bleaching is now used in the pulp and paper, textile, and laundry industries. Hydrogen peroxide (H_2O_2) is a greener, or more environmentally friendly, alternative to chlorine (Cl_2), chlorine dioxide (ClO_2), and sodium hypochlorite ($NaOCl$) that are traditionally used for bleaching color from substances. And, best of all, hydrogen peroxide does not contain any chlorine atoms. It oxidizes by



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An example of a TAML oxidant activator

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 H_2O_2 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.



By using TAML activators, industrial processes like paper making and textile manufacturing that require bleaching, are becoming more energy efficient and less polluting.

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 H_2O_2 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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