The Retrobright Mystery

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Source: VintageComputing

Prologue:

If you're involved in the retro gaming or retrocomputing community, you probably own vintage consumer electronics that have turned a nasty shade of yellow over the years. You've also probably heard of Retr0bright or watched the 8-Bit Guy videos on the subject. But the whole thing is shrouded in mystery: why does plastic turn yellow, and what does Retr0bright do? Is it safe to use it on collectible hardware? I have consulted with Dr. James E. Pickett (who has been kind enough to provide the chemical reaction diagrams), a polymer chemist who specializes in polymer degradation. To understand the Retr0bright process, we must first understand how plastic degrades, and why it turns yellow. ~~Skip to the conclusion if you really don't like chemistry.~~

Part I: The Bad Butadiene Boys

The most common plastic used in retro computer equipment is known ABS, which is notorious for yellowing over a period of a few years. Most plastics, including ABS, degrade when exposed to heat and light in combination with oxygen. This effect is called thermo-oxidation and photo-oxidation, respectively. Because of this, *it is best to store plastic in a cool, dark place* (There is a caveat, which we will talk about soon).

ABS plastic contains three main building blocks: acrylonitrile, butadiene, and styrene (shown in fig. 1). The two parts of ABS that are of interest are butadiene and styrene, as acrylonitrile does not contribute to the yellowing or Retr0bright process very much.

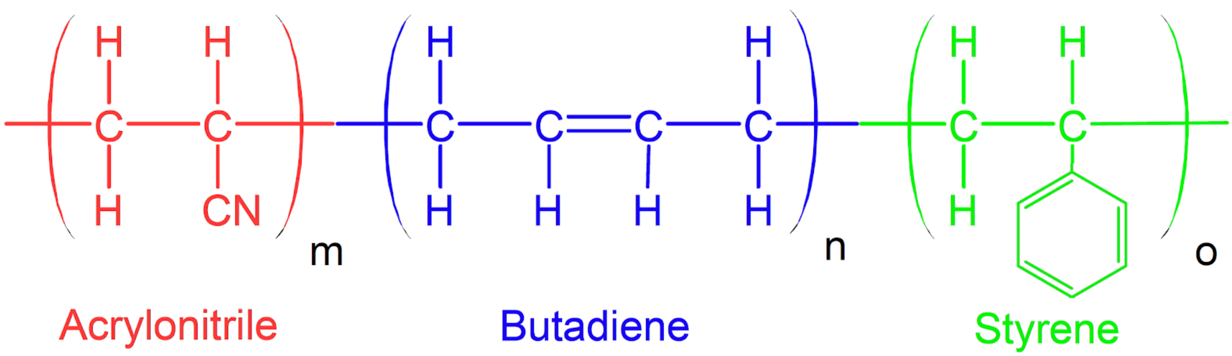


Fig 1. Basic ABS structure. The hexagon is a benzene molecule. Source: [1]

Oxygen molecules attack ABS plastic in the presence of heat or high energy light. Specifically, ABS plastic is attacked at the butadiene linkage. You can see this happening in the diagram below (fig. 2).

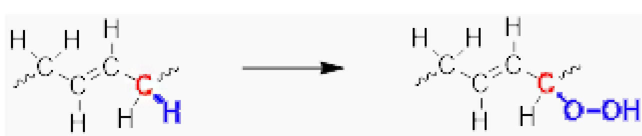


Fig.2 A butadiene molecule being oxidized. The squiggly lines are the rest of the chain. Source: James E. Pickett, PhD

Carbons that are near double-bonds have hydrogens are easier to remove, so this is where oxygen decides to squeeze in [8]. This forms a chemical called a hydroperoxide (shown in fig. 2 also), which is unstable. One of the oxygen atoms in this hydroperoxide decides that it feels too cramped, so it kicks out the other oxygen and hydrogen atom. This process is shown in fig. 3.

Fig.3 Source: James E. Pickett, PhD

The evicted -OH (oxygen and hydrogen) is also called a radical. Right now, it's homeless and just flapping in the breeze -- a free radical. So to find a home, it acts like a parasite in the styrene group [5,7]. This lengthy, nefarious process to infiltrate the poor styrene molecule happens over many steps, shown in figure 4.

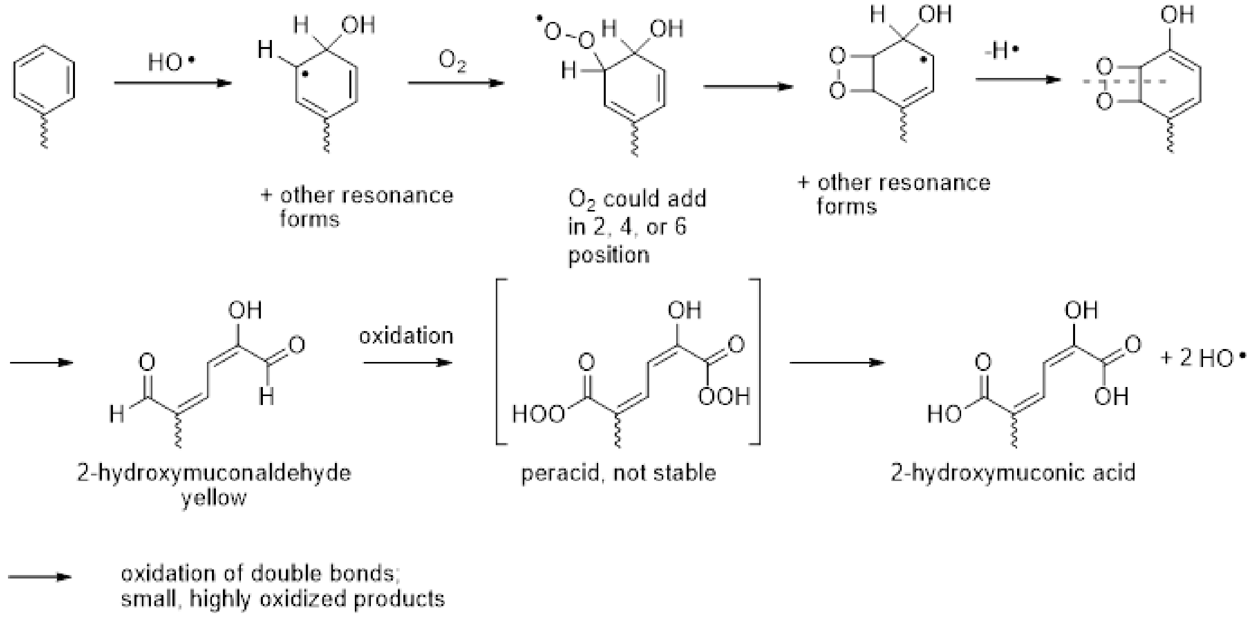


Fig.3 Source: James E. Pickett, PhD

Once parasitized by the radical, the styrene group unravels to form a nasty yellow colored compound called 2-hydroxymuconic acid, or muconic acid for short. The yellow color comes from something called conjugation. A conjugated system is any material that alternates in many single bonds and double bonds (shown in figure 4).

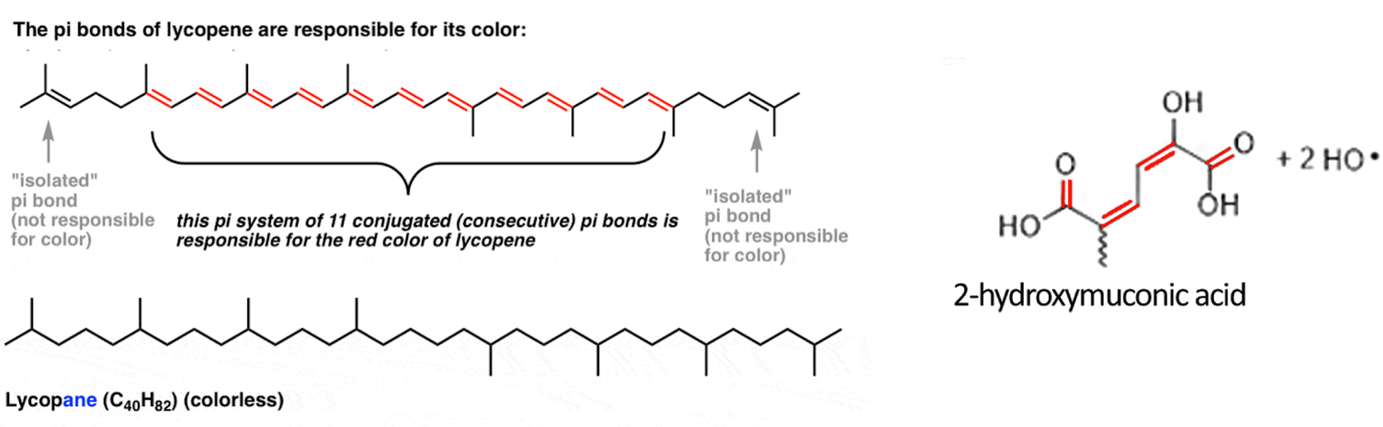


Fig.4 Examples of conjugation. Conjugated bonds are highlighted in red. Source: [3]

In fig. 3, you can see that muconic acid has many double bonds alternating with single bonds. Without conjugation, a chemical doesn't absorb visible light very well, so it appears to be white since all colors are reflected. When there is conjugation, a chemical absorbs many different colors of visible light. In this case, muconic acid absorbs blue and violet light; thus, yellow and red light gets reflected by the muconic acid, and that is the ugly color which we see. But it doesn't end there!.

Part II: The Shape Shifters

Muconic acid molecules are like insidious Decepticons that can change form. These molecules exist in many forms, but two forms, the *cis-cis* form, and the *trans-trans* form, are the most important to this process (shown in fig. 5).

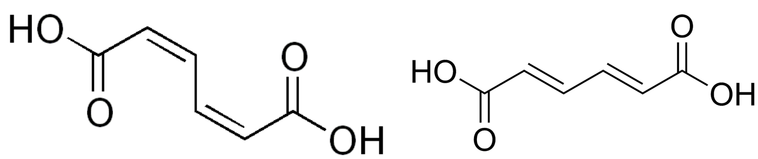


Fig. 5 Two forms of muconic acid. Left to right: *cis-cis* form*, trans-trans* form. Source: Wikipedia

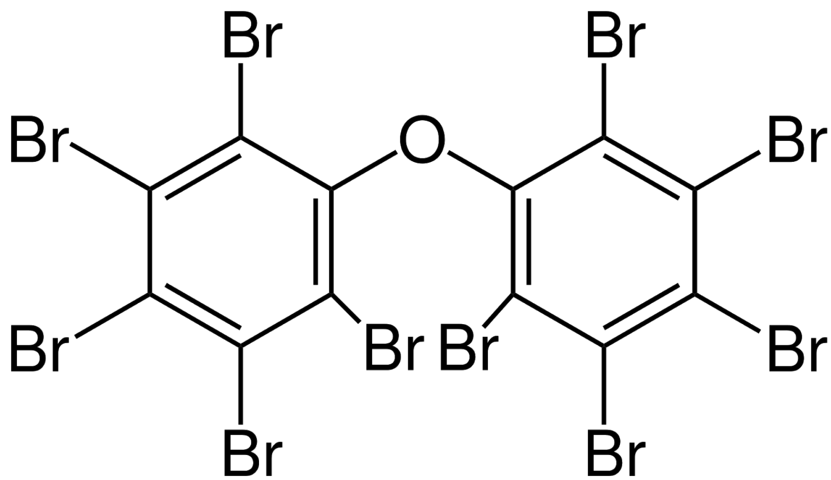
As you might have learned from high-school bio class, the *cis* forms and the *trans* forms are isomers of each other. This means that they have the same chemical formula but two different structures. Under certain conditions, the muconic acid isomers can shape shift between forms. This is very important since the *trans* forms, compared with the *cis* forms, are more thermally stable and contribute more to yellowing [4,7].

The shape shifting nature of muconic acid allows the plastic to become gradually more yellow in dark places, like the plastic bin under your bed or a storage unit. To reverse *this type* of yellowing, it is possible to just expose the plastic to the sun for a few hours (preferably behind glass to filter UVC rays that would cause further damage). This works because the sun can convert the *trans* form back to the *cis* form quicker than the other way around [6, 10].

Part III: Nintendo's story?

It's been debated in the retro computing community if flame retardants, specifically BFRs (Brominated Flame Retardants), cause yellowing. This belief supposedly originated with Nintendo, but I couldn't confirm that.

The answer in short is: yes, BFRs do cause yellowing. BFRs can be broken down to form double-bond conjugated chains that contribute to the yellow color. The quantity of BFRs, however, is small compared to --well -- the plastic itself, so this effect is tiny.



An example of a brominated flame retardant and its structure. Source: Wikipedia

But BFRs can cause yellowing through another mechanism. Similar to butadiene, BFRs can also be attacked by oxygen to form free radicals, and those free radicals can then attack the styrene chains, which contribute to the styrene's breakdown. This means that yes, BFRs do cause yellowing, but not in the way that most people think.

Part IV: Crispy Crackers

UV light causes plastics (like ABS) to become weaker, as demonstrated in numerous papers [5,8,9]. The oxidation and breakage of the butadiene groups causes the majority of the weakening, and the oxidation of the styrene causes even more weakening. The butadiene groups experience two mechanisms called crosslinking and scission [2]. Scission is a straight-up breakage of the butadiene linkage -- like a string being cut -- which is obviously no good for the plastic's strength. Cross linking (shown in fig.6) increases the molecular density and the rigidity of the plastic, as it bundles all the butadiene bits together. This, in turn, increases the brittleness of the plastic (which is done intentionally in some other plastics) [8]. Counterintuitively, this rigid plastic is also brittle and susceptible to breakage. (ABS is supposed to be slightly flexible; like a type of rubber, butadiene gives ABS its flexibility.)

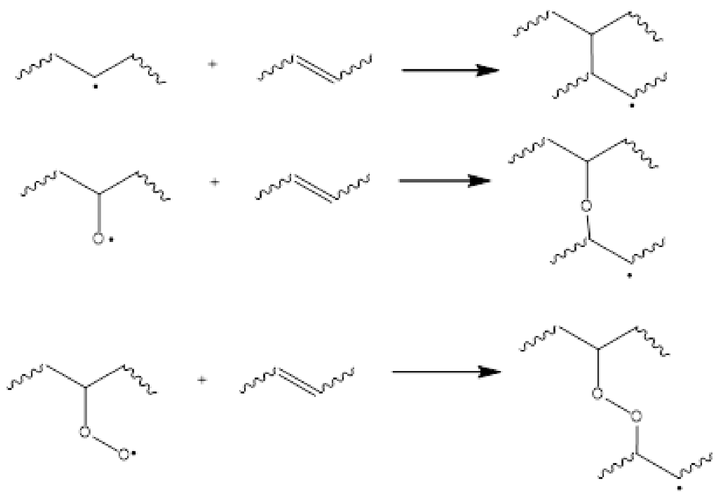


Fig. 6 Crosslinking of butadiene groups. Source: James E. Pickett, PhD

Figure 6 shows three series of different crosslinking reactions. All of them do the same thing: bundle the butadiene chains together.

The good news is that UV light degradation should only happen to the superficial layers of the plastic. The middle layers remain undamaged unless the plastic was improperly manufactured, in which case the oxidation can spread rampantly.

Part V: Retrobright

By this time you must be screaming at the screen: "Darn it! Just tell me how Retr0bright works!". Well, let's do it! Many people on the internet have demonstrated the use of hydrogen peroxide and heat or UV light, or even ozone, to whiten plastic.

If you know how oxidizers and peroxide work (hint: they add oxygen) you might be thinking, "Wait just a hot second! The chemistry of Retr0bright is eerily similar to the degradation of the process of the plastic! It oxidizes it!" You are totally correct, but read on though! The Retr0bright process is designed to take the oxidation a step further. Contrary to popular belief, The Retr0bright process does not actually fix the plastic; it just bleaches the plastic. In fact, there has even been a video where chlorine, a strong bleach, is used to whiten plastic. Please do not try that at home!

Most bleaches work by attacking double bonds and oxidizes them to single bonds [3]. Figure 6 shows how that is done. It takes double bonds and oxidizes them further.

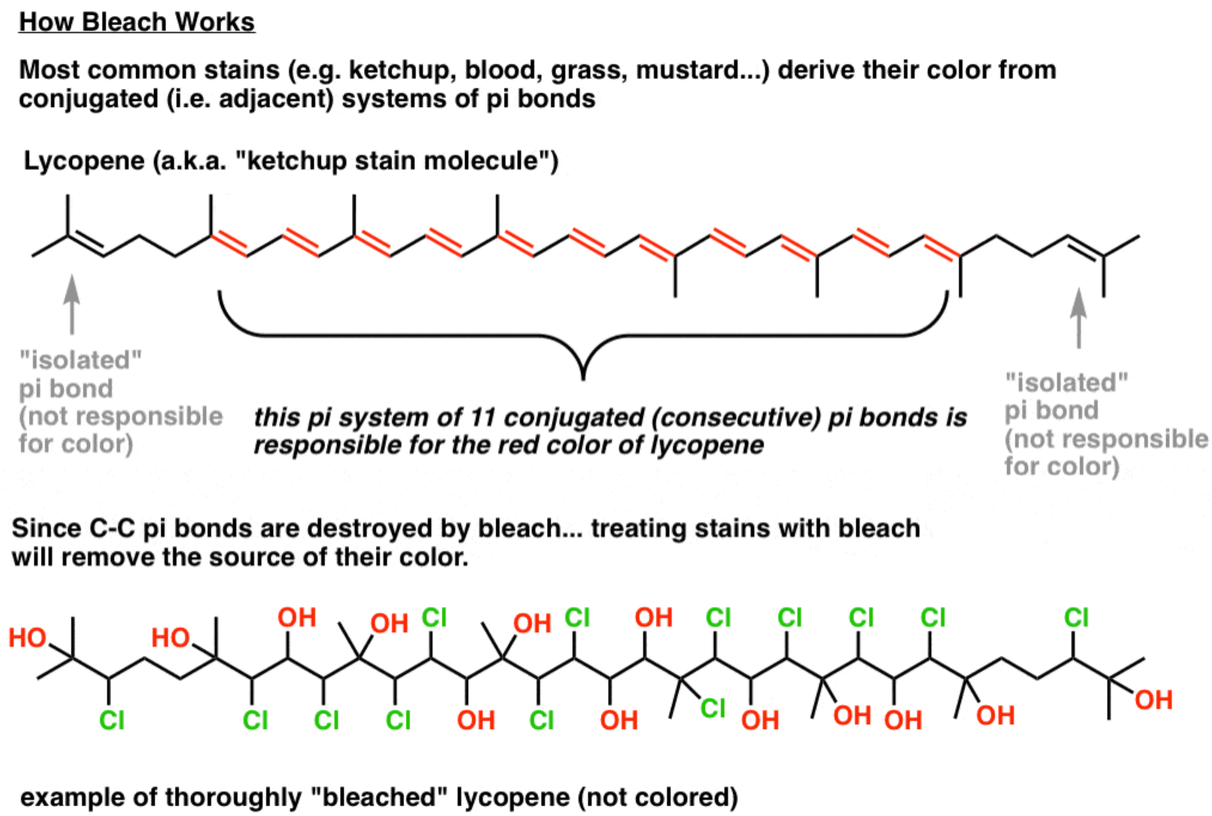


Figure 7. How bleach (chlorine bleach in this case) works, Source [3]

In figure 7, the double bonds are stolen by -OH (oxygen and hydrogen) groups and -Cl (chlorine) groups. We can apply this same principle to our culprit: muconic acid. From this, we can see how Retr0bright can whiten it: it removes the yellow-causing double bonds by oxidizing them and reducing them to single bonds. In the Retr0bright process however, only -OH groups are present because hydrogen peroxide contains no chlorine. The complete chemical reaction for Retr0bright is quite unclear though, as the peroxide can break the muconic acid into multiple smaller different chemicals.

Another question that causes great controversy is whether you should Retr0bright. The answer is more than just a simple yes or no, but it is good to know the pros and cons of Retr0brighting. As many people have previously noted across multiple forums, Retr0bright can cause embrittlement of the plastic. Retr0bright should only be attacking the superficial layer of the ABS plastic, which means little harm should be caused on uncracked plastic. Cracked plastic, on the other hand, can allow peroxide to seep into the cracks and cause internal damage to the plastic. This means that Retr0brighting cracked plastics will just make it worse.

Conclusion:

The process that causes plastic to yellow is attributed to heat, light and oxygen. The combination of the three forms yellow-colored compounds on the outer layer of the plastic. The Retr0bright process seeks to break down these yellow compounds, and should not cause further damage to the plastic, unless the plastic has cracks in it. If the plastic has cracks in it, the internal layer of plastic can be destroyed by the Retr0brighting compound.

The main takeaways:

- Oxygen+Heat/Light causes ABS plastic to turn yellow, so it is best to keep plastic in a cool, dark place. It will still turn yellow, but the process will be slower than if you left it out.
- Before you begin the Retr0bright process, try putting the plastic in the sun behind a glass window for a few hours and see if that helps. Avoid direct sunlight since the UVC will just cause further damage.
- Retrobright should only cause the plastic to become more damaged if the plastic is already cracked.
- Retrobright does not fix the plastic, rather it bleaches it.
- BFRs (Brominated Flame Retardants) contribute to yellowing but aren't the primary cause

Sources:

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(The Retr0bright process was a special pain in the rear, since no one really wrote anything about it, so please excuse my lack of citations there.)

(Most of the information came from Dr. Pickett as well)

Special thanks to:

Dr. James E. Pickett

Tube Time