Abstract

Typical whitening systems are designed to provide what dentists and patients want, however these “wants” typically fly in the face of what is physically and chemically possible. For whitening success, tooth color molecules must be broken down by radicals produced by peroxide, however, there are a myriad of stumbling blocks to achieving this goal.

With most current whitening systems, peroxide gels may already be degraded when received because of inadequate handling and lack of refrigeration by whitening product companies; gels may be chemically altered to lengthen shelf life, leading to acidic pH, higher osmolarity, higher sensitivity and less effectiveness of the products; and they typically have inadequate continuous activity to accomplish thorough cleansing and whitening of tooth structure.

In-office whitening lacks the time necessary to thoroughly degrade color molecules, and antioxidants found in saliva and sulcular fluid rapidly seep under and into whitening trays, destroying peroxide on contact.

Educational Objectives

Most dentists currently understand very little about teeth whitening, how it works and why it often does not work. After reading this article, dental professionals will understand:

1. Why teeth have differing color
2. What is responsible for tooth color
3. How and why teeth darken over time
4. How peroxide causes teeth to lighten
5. Requirements for routinely successful teeth whitening
6. Reasons for unsuccessful whitening
7. Physics of why whitening lights and lasers are of no benefit to whitening
8. The laws of physics that determine effectiveness of whitening
9. The laws of chemistry that determine effectiveness of whitening

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Introduction

It is well recognized that whiter teeth is the most commonly desired cosmetic enhancement of any type.\(^1\) One study published in JADA showed that 81.8 percent of the population stated they would like to have whiter teeth.\(^7\) Fifty-seven percent even stated that they have significant dissatisfaction with their smile, specifically due to tooth color.\(^7\) So the market for teeth whitening procedures would seem to be very strong.

Given this high demand for whiter teeth, we would assume teeth whitening procedures would be a beneficial addition to the perceived success of dental treatment and the financial bottom line for virtually all dental practices. But this has not necessarily been the case for the majority of dental practices.

Dentists have found wide-spread poor, unpredictable whitening results; sensitivity; rapid rebound; embarrassed dental staff; and patients who are less than impressed or downright dissatisfied with whitening results.\(^2,3\)

Whitening companies have promised dentists that teeth whitening will build dental practices by encouraging referrals, and that teeth whitening is the gateway to additional cosmetic treatment – stating that patients will become excited about their whiter teeth, leading to more desire for additional cosmetic treatments. But most dentists have not found this to be the case.\(^2,4\)

Many dentists have even found teeth whitening to be detrimental to their practices.\(^4\) When dentists are unable to impress patients with whitening results, patients become less confident in the dentist, leading to less acceptance of other necessary and elective treatments; fewer referrals; and even loss of dental patients.\(^4\)

Conversely, dentists who achieve truly impressive whitening results do find that many patients become infatuated with their newly white teeth. They can’t seem to stop looking at their teeth in the mirror. This often leads to various orthodontic treatments, replacement of restorations, cosmetic procedures requiring porcelain or composite resins, and even cosmetic periodontal surgery. Dentists also notice these patients seem to have more confidence in the dentist, leading to a higher acceptance rate of necessary and discretionary treatment, and especially more referrals of new patients.\(^4\)

Teeth whitening systems seem to have been developed based on what patients and dentists want, rather than what the laws of physics and laws of chemistry will allow. It is certainly an admirable goal of product companies to give their customers what they want; however, when what they want is not physically or chemically possible, this approach results in problems. Unlike Scotty in Star Trek who said, “Ya can-nah change the laws of physics, Captain! I’ve got to have thirty minutes,” the rest of us cannot ever change the laws of physics or the laws of chemistry.\(^5\)

These scientific laws do, however, allow for the potential of predictable effective whitening, even in severe cases of teeth discoloration, when the physics and chemistry of whitening are strictly adhered to.\(^6-13\) For routinely successful whitening, the science dictates:

1. High potency, highly active (chemically unstable) whitening gels at the time of use.\(^6-15\)
2. Step-by-step protocol and chemistry resulting in driving high concentrations of peroxide breakdown products deeply into the microstructure of teeth for extended periods of time.\(^6-13,18,19\)

What is Responsible for Tooth Color?

What accounts for tooth color/darkness?

1. Organic pigment color molecules trapped in tooth structure during formation.\(^6,10,20,21\)
2. Extrinsic stain molecules that become intrinsic.\(^6,10,20,21\)

These two types of molecules are similar, act the same and can be treated the same – therefore we will simply refer to them as “color molecules.”

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Properties of Color Molecules

a. Color molecules have chromophores (Fig. 1)

Molecules are clusters of specific atoms held together by an array of magnetic bonds between negative electrons and positive protons. A chromophore bond is any bond within a molecule that creates a magnetic field which absorbs and reflects various wavelengths of visible light. By absorbing light, chromophore bonds make things look darker, and by reflecting certain wavelengths of light, they create the appearance of color. Look around you; everything you see is due to chromophores within molecules, absorbing and reflecting light.

Given that these fields are created by the interaction of various negatively charged electrons and positively charged protons, we can think of chromophore bonds like magnets. Just like with magnets, some chromophore bonds are stronger and more difficult to pull apart than others. This is one of the factors that make some whitening cases easier and some more difficult.

b. Color molecules tend to join together

Color molecules join together, forming larger and larger color molecules. As these color molecules join, the percentage of the chromophore bonds within them increases, causing them to appear darker and darker as they become larger.

How Teeth Darken over Time

1. Color molecules collect on the surface of teeth (extrinsic stain) and slowly penetrate into the microstructure of teeth (intrinsic stain).
2. Original pigment molecules and accumulated intrinsic stain molecules join together forming larger, darker molecules.

How Does Whitening Work?

All forms of peroxide gels work by forming hydrogen peroxide as their end active product. In school we were told that $2H_2O_2$ breaks down to form $2H_2O$ [water] + $O_2$ [oxygen], but this is the over simplified kindergarten explanation of what is really happening when peroxide breaks down. Yes, peroxide can and does break down to water and oxygen, but it also breaks down to various radicals (also called “free radicals”) including perhydroxyl radicals, hydroxyl radicals, superoxide radicals, as well as oxygen ions and hydrogen ions (Fig. 2).

Fig. 1: Chromophore bonds between certain atoms within a molecule create fields, which absorb and reflect various wavelengths of visible light. By absorbing light, chromophore bonds make things look darker, and by reflecting certain wavelengths of light, they create the appearance of color.

Fig. 2: Upper left: After years of compaction of intrinsic stains, and joining of these molecules throughout the microstructure of the teeth, the result is a densely packed, tightly woven matrix throughout the microstructure of the teeth, effectively preventing the penetration of bleaching factors into the teeth. Upper right: Bleaching factors can easily penetrate tooth structure in young teeth that have not yet been densely packed with debris, and in older teeth that have been cleansed by hours of continuous oxygenation by peroxide bleaching factors. Lower: Hydrogen peroxide ($H_2O_2$) is the active end product of all peroxide whitening systems. $H_2O_2$, depending on the whitening gel storage temperature, whitening tray environment and whitening gel chemistry, may break down to ineffective oxygen and water, or it may break down to effective bleaching factors including free radicals. When radicals are produced, hydrogen ions (acid) are also produced.
Keep in mind that hydrogen ions are acid. For example, remember that the H in “pH” represents Hydrogen. pH measures the hydrogen ion concentration based on a negative logarithmic calculation, therefore the more hydrogen ions (acid), the lower the pH number.

The goal of whitening is to get rid of chromophores in teeth so that light will be reflected to our eyes (and therefore appear whiter) instead of being absorbed by chromophores, causing teeth to appear darker.6,7,23

**Peroxide Whitening Removes Chromophores in Two Phases, Which Occur Simultaneously**22,26

1. **Oxygenation**

   Oxygenation refers to the very aggressive microscopic activity of radicals and oxygen. The aggressive agitation of these “bleaching factors” breaks up some of the large, long-chain color molecules into smaller chunks, and because of the vigorous activity, removes these chunks of color molecules from the tooth via diffusion. The result is a cleansing of the built-up intrinsic color molecule debris, resulting in the removal of these color molecules (and the chromophores they contain) from the tooth.13,22,23

2. **Conversion**

   Conversion is a term I have used meaning the attack of chromophore bonds by bleaching factor radicals (most prominently perhydroxyl radicals). The bleaching factor radicals produced by the breakdown reaction of peroxide diffuse into the tooth, attacking and breaking apart color molecules at their chromophore bonds. As the chromophore bonds of these huge color molecules are broken apart, the molecules become smaller and smaller, with fewer and fewer chromophore bonds, and therefore the teeth become lighter and lighter in appearance. The desired end result is millions of molecules that each are so small they do not contain any chromophore bonds (Fig. 3).11,13,16,22,25,24,28,29,31

   For the two phases of peroxide whitening to be successful, the following features are required:

   1. The peroxide gels must be fresh (highly potent).5,6,8,10,13,31
   2. The peroxide gels must be very unstable so that peroxide is able to break down, releasing high concentrations of bleaching factors.10
   3. Peroxide gels must break down releasing high concentration of radicals instead of only releasing oxygen and water.10,13,26,27
   4. Peroxide gels must be in contact with tooth structure continuously for long periods of time5,6,7,10,13 to allow for effective 1) deeper and deeper oxygenation cleansing of tooth structure and removal of color molecules,6,7,10,13 and 2) deep, thorough penetration of bleaching factors into the microstructure of teeth4,10 to break apart (conversion) chromophore bonds.7,10,11,13,22-24,26,28,29,31

As the vast majority of dentists have found, there are problems with whitening systems, preventing them from accomplishing these requirements.24 We will now discuss the reasons that each of the requirements may not be met by typical whitening systems.

**Reasons for Unsuccessful Whitening**

1. Peroxide gels may not be fresh (highly potent).

   Although most manufacturers recommend that dentists refrigerate whitening products once received, they do not refrigerate all carbamide peroxide and hydrogen peroxide whitening products themselves during the weeks and months during storage or shipping.14

   All forms of peroxide whitening products are unstable chemicals.14-16,30,32 They’re supposed to be — this is a desired feature. This is why they can break down quickly and release bleaching factors when placed in the mouth. The problem is that, without constant refrigeration, these unstable whitening gels start to break down immediately upon manufacture.5,8,14-16,30,32 At room temperature, whitening gels start to break down at a relatively slow rate. The warmer the temperature, the more rapid is the breakdown.5,14

   The most common storage scenario for whitening products is to store these products in warehouses, which are typically warm or even hot. When whitening gels are then transported from the manufacturing facility to the whitening company, they are typically shipped via freight truck, which most commonly

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has temperatures ranging from 125 to 165 degree Fahrenheit in the freight bay of the truck for up to three days or more.

The peroxide products are then usually stored in the warm or hot warehouse of the whitening company, and ultimately shipped to dentists via UPS or FedEx in trucks also typically exceeding 125 degrees Fahrenheit. It is therefore no surprise that most dentists find that each batch of whitening gel they receive works differently than previous batches, and some batches seem to not work at all.3

Though refrigeration virtually stops the degradation process of carbamide peroxide and low concentrations of hydrogen peroxide, and greatly slows the degradation of high concentration hydrogen peroxides,14 constant refrigeration of whitening gels throughout all phases of storage and shipping is quite costly for whitening product companies. The overhead costs, refrigeration-proof packaging and burdensome handling required by constant refrigeration discourage whitening companies from constantly keeping these gels under refrigeration. Instead, whitening companies tend to prefer adding chemical stabilizers to whitening gels to lengthen shelf life;14,16 however, the use of chemical stabilizers adds even more to the problems of whitening.15,17

2. Adding chemical stabilizers to peroxide gels reduce effectiveness of whitening and increase sensitivity.

The addition of these chemical stabilizers can reduce effectiveness of whitening and cause significant sensitivity.14-17

Common methods to chemically stabilize whitening gels are the use of anhydrous bases and the addition of acid (“acidifiers”) such as phosphoric acid.10,14,16,17 Not only do these chemical stabilizers greatly increase osmolarity,16,17 resulting in much stronger “pull” on dentinal tubular fluid and much higher levels of tooth sensitivity,16,17,59-56 but when whitening gels are made more stable, they are not as un-stable as desired when placed in the mouth and are not as effective.14 In other words, a more stable peroxide formulation will not break down as readily when placed in the mouth. It is also well known that the acids in whitening gels cause detrimental changes to tooth structure.35,56

Acidified whitening gel also causes more liberation of molecular oxygen (which is relatively ineffective in whitening) and less liberation of peroxide radicals such as perhydroxyl radicals (which are the most effective in whitening).14

3. Peroxide gels may not produce enough radicals, resulting in poor whitening effectiveness.

Without proper chemical influence, peroxide breaks down to higher concentrations of less effective oxygen, and fewer of the effective whitening radicals.7,20,37

When acidifier stabilizers are added to whitening gels, not only does this slow the speed of the whitening process, but it causes peroxide to break down to more water and oxygen, and fewer radicals, leading to less effectiveness of whitening.14,37

Hydrogen ions (acid) are produced as peroxides break down, resulting in more and more acidic pH. As gels become more acidic, this too slows the reaction and shifts the reaction to producing more water and oxygen, and less of the effective radicals.7,14,37

4. Peroxide gels may not be continuously active for long enough periods of time to be truly effective.

Remember that highly active whitening gels must be in contact with tooth structure for continuous extended periods of time to effectively oxygenate (cleanse) the microstructure of teeth deeply.14 If you have whitened the teeth of a 14-16-year-old patient, you have seen the teeth become extremely white, extremely fast. On the other hand, if you have whitened the teeth of a patient 80+ years old, you have likely found whitening to be extremely difficult.

Remember that teeth darken via years of extrinsic stain penetrating into tooth structure becoming intrinsic stain.6,10,20,21 Also remember that these molecules tend to join together forming larger and larger molecules.7,16,20-25 After years of compaction of intrinsic stains, and joining of these molecules throughout the microstructure of the teeth, the result is a densely packed, tightly woven matrix throughout the microstructure of the teeth, effectively preventing the penetration of bleaching factors into the teeth (Fig. 2).

Young teeth have not accumulated this debris, so absorb bleaching factors and whiten quickly. Old teeth are so densely packed with debris that they cannot absorb bleaching factors. If bleaching factors are unable to penetrate teeth, even very effective whitening gel formulations cannot have much of an impact.7,10,13

Extended periods of contact of tooth structure with highly effective whitening gels allows prolonged oxygenation of the


teeth, breaking up and removal of this built-up stain debris.\textsuperscript{13,22} somewhat rejuvenating adult teeth back to their youthful ability to absorb bleaching factors, allowing extremely white results. 

Problems

\textbf{a. Short period of in-office whitening} – provides only short periods of time (one hour or less) of active whitening. This provides inadequate time to effectively oxidize (cleanse) tooth structure.\textsuperscript{7,10,15}

\textbf{b. Short duration of action of whitening gel in at-home whitening trays} – has been shown that typical whitening gels in typical custom made whitening trays commonly lose 60-95 percent potency in only 25-35 minutes, and are nearly ineffective shortly thereafter.\textsuperscript{4,5,6}

Saliva and sulcular fluid both have high concentrations of peroxidase, a natural antioxidant enzyme.\textsuperscript{13,14,39-43} The job of antioxidant enzymes is to instantly destroy peroxide by causing it to break down 	extit{only} to ineffective oxygen and water, and preventing it from breaking down to effective radicals.\textsuperscript{44}

Not only do typical custom-made whitening trays not adequately seal in whitening gel, but more importantly, they allow seepage of damaging saliva and sulcular fluid peroxidase under and into the whitening trays, destroying saliva on contact.\textsuperscript{45} In fact, peroxidase in saliva alone is so damaging to peroxide that it is capable of destroying 29mg of peroxide every minute.\textsuperscript{45} When you consider that the average set of upper and lower whitening trays, even with reservoirs, contain a total of only about 6.5mg of peroxide,\textsuperscript{46} this means that theoretically, if your saliva was able to penetrate under the whitening tray immediately, the saliva alone is capable of destroying all of the peroxide in these trays in only 14 seconds!

This is the reason that the time of effectiveness in typical whitening trays, with typical whitening gels is found to be so short – saliva and sulcular fluid peroxidase quickly seeps under the whitening tray, quickly destroying peroxide.

Dentists have found that whitening seems to be less effective in the cervical areas of teeth.\textsuperscript{46} Obviously, saliva and sulcular fluid enter under the whitening tray first in the cervical area, destroying the gel in this area first.

Whitening tray designs that cover the marginal gingiva might help to exclude saliva from the whitening tray; however, this design specifically directs the equally damaging sulcular fluid immediately into the whitening tray, followed by rapid destruction of the whitening gel by sulcular fluid peroxidase.

\textbf{What About Bleaching Lights?}

The use of bleaching lights and lasers add flair to the in-office whitening procedure.\textsuperscript{3,16} However, the consensus of research studies (not funded by bleaching light or laser manufacturers) agree that lights and lasers are of no benefit to whitening teeth, yet add to the discomfort felt by patients.\textsuperscript{3,16,17,47-62}

What is it that lights or lasers are supposedly adding to the effectiveness of the whitening procedure? The claims are that lights and lasers add photon energy to speed up the breakdown reaction of peroxide. Think back to chemistry lab classes when you would place reactants in a dish and place the dish over a Bunsen burner. The addition of energy (heat) caused the chemical reaction to proceed.

But, remember that there are two general classifications of chemical reactions – endothermic and exothermic. Endothermic reactions require the input or absorption of energy (heat, light, electricity, etc.) for the reaction to proceed. On the other hand,
exothermic reactions must get rid of energy to proceed. An example of an exothermic reaction is the setting of dental stone or plaster, which gives off heat while setting.

Can you guess which type of chemical reaction the breakdown of all types of peroxide is? Yes, it is an exothermic reaction. According to Le Chatelier’s Principle of Chemical Equilibrium, adding energy (heat or light) to an exothermic reaction (such as the breakdown of peroxide) will inhibit (slow) the reaction. Therefore, the addition of lights or lasers to the whitening process could actually slow down the process, not speed it up.

The chemical breakdown reaction of hydrogen peroxide is best directed via appropriate pH with additional true chemical catalysts added when rapid reaction time is critical, such as during in-office whitening.

In fact, it is true that even in-office whitening gels intended for use with lights and lasers still utilize chemical acceleration (dual-barrel). One would assume if bleaching lights and lasers were genuinely effective, the addition of chemical accelerators would be unnecessary.

**Summary**

The technique and chemistry of typical whitening systems seem to be at odds with the laws of physics and chemistry, and the majority of dentists often find frustration and disappointment with whitening results. Routine impressive whitening success requires diligent knowledge of the laws of physics and chemistry, and a whitening technique designed to work with these scientific laws instead of against them.

[Editor’s Note: If you have questions or would like to learn more, please contact Dr. Kurthy at rod@evolvedental.com or call 866-763-7753]
Post-test

1. The laws of physics and chemistry:
   a. Do not always apply to the teeth whitening process.
   b. Are strictly adhered to by whitening companies when designing whitening products and protocol.
   c. Apply to any tooth whitening and can never be changed.
   d. Have no bearing on teeth whitening results.

2. The following are responsible for color we see in teeth:
   a. Organic pigment molecules trapped within tooth structure during tooth development.
   b. The position of enamel rods causing reflection of various wavelengths of light.
   c. Extrinsic stain molecules that absorb into tooth structure and become intrinsic.
   d. a and c

3. Chromophores are:
   a. Individual atoms within mineral components of enamel and dentin.
   b. Very specific magnetic fields between certain atoms within molecules.
   c. Clusters of color molecules.
   d. Dense fields of orbiting electrons within certain types of molecules.

4. Chromophores are responsible for color seen in:
   a. Teeth only.
   b. Organic substances.
   c. Inorganic substances.
   d. Any substance showing color of any type.

5. Chromophores are responsible for color because:
   a. They reflect all light wavelengths.
   b. They absorb all light wavelengths in the visible spectrum.
   c. They absorb some light wavelengths and reflect other light wavelengths.
   d. They allow light to pass directly through without reflection of light.

6. Teeth darken over time due to:
   a. Color molecules within tooth structure joining together, forming larger and darker molecules.
   b. Enamel becoming more translucent, allowing the darker dentin to show through more.
   c. Extrinsic stain slowly penetrating into tooth structure, becoming intrinsic stain.
   d. a and c

7. Select the true statement:
   a. The chemical reaction of the breakdown of hydrogen peroxide is endothermic and breakdown of carbamide peroxide is exothermic.
   b. The chemical reaction of the breakdown of hydrogen peroxide is exothermic and breakdown of carbamide peroxide is endothermic.
   c. The chemical reactions of the breakdown of hydrogen peroxide and carbamide peroxide are both exothermic.
   d. The chemical reactions of the breakdown of hydrogen peroxide and carbamide peroxide are both endothermic.

8. The goal of whitening is to:
   a. Create more chromophores in teeth.
   b. Remove only dark chromophores and stabilize light chromophores.
   c. Remove all chromophores.
   d. Create more opacity in teeth.

9. Adding chemical stabilizers to peroxide gels is:
   a. Beneficial because stabilizers prolong shelf life and do not alter the effectiveness of whitening gels.
   b. Beneficial because stabilizers prolong shelf life and also enhance the effectiveness of whitening gels.
   c. Detrimental because stabilizers are ineffective and do not lengthen shelf life.
   d. Detrimental because stabilizers raise osmolarity, increase sensitivity, causing more production of oxygen and less production of radicals and reducing the effectiveness of whitening gels.

10. Whitening gels are seen to become inactive very quickly in at-home whitening trays because:
    a. Gel is sucked out of whitening gels quickly.
    b. Saliva seeps under and into whitening trays, diluting whitening gel.
    c. Saliva seeps under and into whitening trays and peroxidase in saliva and sulcular fluid quickly destroys peroxide.
    d. a and b

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Why We See Problems with Teeth Whitening:
The Science of Whitening, Part 1 by Rod Kurthy, DMD

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