

A new oxidant for hair coloring

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Synopsis

Coloring hair using a level 3 permanent colorant involves two processes, lightening the underlying melanin and formation of the colored chromophores inside the hair. In typical in-market products the oxidant used to achieve these changes is hydrogen peroxide buffered at pH 10 with an alkalizer such as ammonium hydroxide.

A new oxidant has been developed based on the combination of ammonium carbonate, hydrogen peroxide and glycine at pH 9 that can match the lightening and color performance of the current oxidant. It has the advantage that both the carbonate and hydrogen peroxide concentrations can be changed to alter the lightening performance making it a more flexible oxidant. This allows the capability to lighten the hair in a shorter time, or with lower hydrogen peroxide levels.

This paper discusses the key oxidizing species that are present in both systems and the mechanisms of melanin lightening. In addition, the lightening performance will be assessed as a function of time, pH, hydrogen peroxide concentration and carbonate concentration.

The importance of glycine to the oxidant is also described along with a proposal for its mechanism of action. It has been demonstrated that the addition of glycine can control the undesired formation of carbonate radicals that can be generated from the oxidant. The control of these radicals enables the oxidant to deliver excellent lightening with no negatives in fiber damage vs. conventional oxidants.

INTRODUCTION

Level-three permanent hair colorant products typically consist of three major components: the oxidant which is hydrogen peroxide, the alkalizer which is typically either ammonia or ethanolamine and the dye precursors (1,2). The final pH of the system is between pH 9.8 and 10.3. The role of the oxidant is three-fold. It must decolorize the melanin pigment to lighten the underlying color of the hair. It must also bleach previously deposited synthetic color in the hair and it must couple together the dye precursors to form the colored chromophores. It is this balance of melanin lightening vs. deposition of synthetic color inside the hair that gives the hair its final color. The lightening is very important to coloring products to enable the consumer to achieve the shade that she desires. This is critical for the blonde shades where very little dye is deposited and most of the final color is due to the melanin lightening. However, it is also very important for

achieving good gray coverage without the negative of the shade going too dark. In this case, the oxidant lightens the underlying pigment and previously deposited color thus allowing for the addition of dye to achieve good gray coverage with no decrease in the darkness of the shade and no build-up of dye and darkening over multiple usage occasions. The lighting is also important for the achievement of vibrant shades, for example the red shades.

However, the oxidant is also responsible for the fiber changes that can occur as the hair is colored for multiple treatments leading to consumer negatives such as poor shine, poor feel and reduced strength (3). The search for an alternative oxidant that can lighten hair but also have no negatives on fiber damage has long been one of interest to companies that develop hair coloring products. In this paper we explore the alternative oxidant of ammonium carbonate, hydrogen peroxide and glycine buffered at pH 9.0 and we describe its proposed mechanism of action.

This oxidant participates in the same color forming reactions as conventional oxidants and it can be used to match the typical range of shades. However, this color formation chemistry will not be discussed as part of this paper.

EXPERIMENTAL

Caucasian untreated mixed hair (medium brown), obtained from a commercial source (IHIP, New York), was formed into swatches (16 cm, 1.5 g) and used for all the testing.

A range of cream formulation products were made to test the lightening efficiency of the new oxidant as a function of pH, ammonium carbonate concentration and hydrogen peroxide concentration. A concentrated cream base was made using 5.0% of Crodafos CES® (a mix of cetearyl alcohol, dicetylphosphate and ceteth-10 phosphate) which was dissolved in hot DI water (85°C), neutralized with sodium hydroxide and then allowed to slowly cool. The ammonium carbonate, glycine and hydrogen peroxide were added to the remaining water and then mixed into the concentrated cream base until it was homogeneous. The pH was adjusted with sodium hydroxide.

The same concentrated cream base was used to make the formulations with the conventional oxidant. In this system the pH was adjusted with acetic acid.

The final cream formulation (4 g of product per g of hair) was thoroughly applied to the hair and then kept for 30 minutes at a controlled temperature of 30°C.

The color of the hair was measured with a bench top Minolta CM3600D spectrophotometer. Lab values were calculated under D65 illuminant, 10° observer, specular included. The lightening (dL) was calculated as the difference in L value between the final color and the starting color on the untreated hair.

¹³C NMR spectra were acquired on a Bruker Avance spectrometer operating at a ¹³C frequency of 100.6 MHz. All spectra were acquired with an inverse gated ¹³C experiment with a relaxation delay of 30 s, SW of 249 ppm and FID acquisition time of 1.3 s and 16 scans of spectral averaging were used. In the data presented later, in order to boost sensitivity, 10% of the quoted mass of ammonium carbonate solutions was replaced by 99% ¹³C atom percent enriched sodium carbonate (Sigma Aldrich).

The tensile properties of the fibers were measured using a Diastron Miniature tensile tester (MTT 675) equipped with laser micrometer in a water saturated environment. At least 100 fibers were run for each measurement point.

RESULTS

A series of cream formulations were made containing ammonium carbonate, hydrogen peroxide and glycine and compared to a conventional oxidant system of ammonium hydroxide and hydrogen peroxide at pH 10. This is the oxidant system used in the majority of retail and professional hair colorant products. The lightening of this new oxidant was investigated as a function of several important parameters:

- (i) Lightening as a function of pH
- (ii) Lightening as a function of hydrogen peroxide and carbonate concentration
- (iii) Lightening as a function of source of carbonate (i.e. ammonium carbonate vs. ammonium carbamate vs. potassium hydrogen carbonate)

(I) LIGHTENING AS A FUNCTION OF pH

A series of cream formulations were made with ammonium carbonate (4%), glycine (1.8%) and hydrogen peroxide (4.5%) at a pH range of 8.5 to 10.5. These cream products were applied to medium brown untreated human hair samples for a period of 30 minutes in a temperature controlled environment of 30°C. The lightening of the hair after these treatments was measured and Figure 1 demonstrates the pH dependence of this lightening.

The figure shows that the optimal pH is between pH 9 and 9.5 but significant lightening is still achieved at pH 8.7. This pH profile is very different from the profile found for the conventional oxidant system where the lightening maximum is found at approximately pH 10 and the lightening decreases sharply below pH 10.

Figure 2 shows the lightening for the two oxidant systems at pH 9 and pH 10. For the conventional oxidant system the cream formulations were made at a hydrogen peroxide concentration of 4.5% active with the pH adjusted with an ammonium hydroxide/acetic acid buffer (1.3% ammonia) to pH 9 and 10. The figure clearly shows that for the conventional oxidant the lightening at pH 9 is approximately 60% of the lightening at pH 10 but that

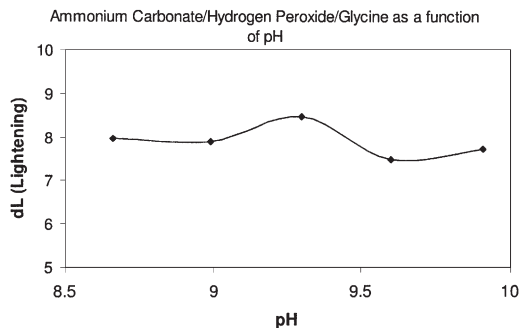


Figure 1. Ammonium carbonate + peroxide + glycine as a function of pH.

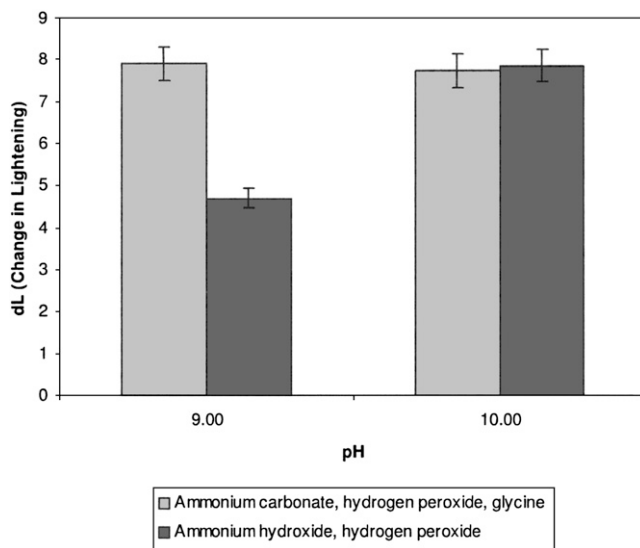
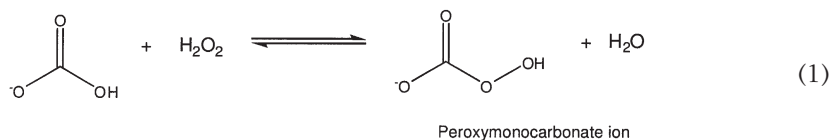


Figure 2. Lightening of oxidant systems at pH 9 and 10.

for the new oxidant system the lightening at pH 9 is very close to what is achieved at pH 10. These two charts also show that the new oxidant at pH 9 can achieve similar lightening to the conventional oxidant at pH 10 (~8–12 dL).

These results imply that a different oxidant is being formed with the addition of the ammonium carbonate. It is proposed that this new oxidant is the peroxymonocarbonate ion which is formed *in-situ* from the combination of hydrogen peroxide and hydrogen carbonate ions (see Equation 1). The formation of this species is documented in the literature (4,5), and the species has been shown to be an effective oxidant (6,7).



To study the formation of this species at the concentrations used in the oxidant system tested for lightening the hair we used ^{13}C NMR (8,9). This technique also allows us to track the formation of this species as a function of pH.

Figure 3 shows a typical ^{13}C NMR spectrum that was obtained for a solution containing ammonium carbonate, hydrogen peroxide and glycine at pH 9. The peroxymonocarbonate ion can be monitored and its relative concentration measured with these spectra. The spectrum clearly shows that the peroxymonocarbonate ion is formed at the concentrations used in the lightening experiment.

The above ^{13}C NMR spectrum was acquired from a solution of 4.5% w/w ammonium carbonate/0.5% w/w 99% ^{13}C atom enriched sodium carbonate, 2% w/w glycine and 6% H_2O_2 .

The spectrum also shows different species that are formed in the equilibria between the ammonia, the carbonate ions, the hydrogen carbonate ions, the hydrogen peroxide and the glycine (10). Equations 2–9 show these equilibria in more detail.

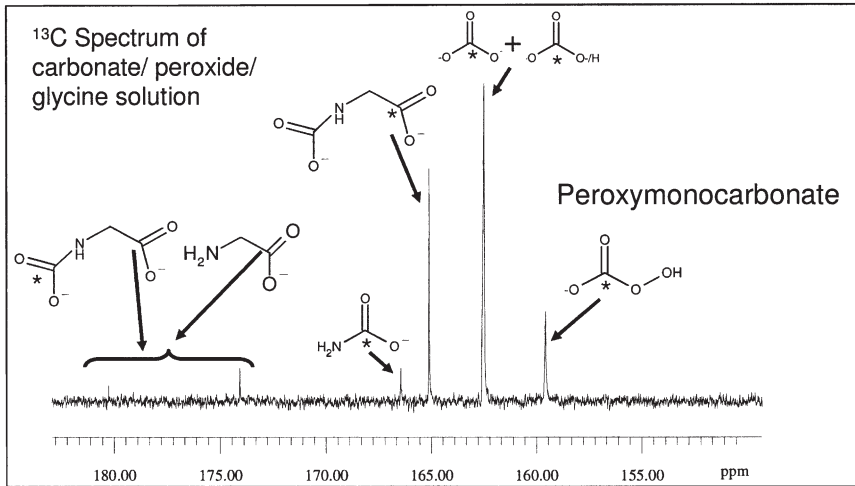
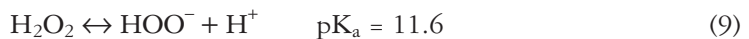
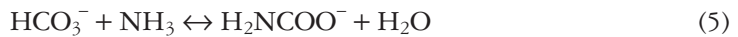


Figure 3. NMR of ammonium carbonate, hydrogen peroxide, and glycine solution at pH 9.0.



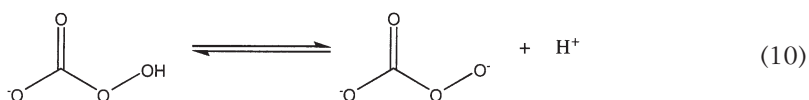
The ^{13}C NMR spectra can explain the pH dependence observed for the two oxidant systems. For the conventional oxidants the lightening species formed is the perhydroxyl anion (HOO^-) which is formed as the hydrogen peroxide is deprotonated at higher pHs (>10). For the new oxidant system there are two possible oxidants that are formed, the peroxydicarbonate ion and the perhydroxyl anion. Table I below shows the concentration of these two species as a function of pH. The concentrations used were 4.0% ammonium carbonate, 4.5% hydrogen peroxide, 1.8% glycine for the new oxidant and 1.3% ammonia, 4.5% hydrogen peroxide for the conventional oxidant. The concentration of the peroxydicarbonate ion is measured from the ^{13}C NMR spectra and the concentration of the perhydroxyl anion is calculated from the pK_a using the Henderson-Haselbach equation (11).

These data demonstrate that the peroxydicarbonate ion is present at pH 8.5 and 9 and it is proposed that this is the species that is responsible for the pH 9 lightening of the new oxidant. At pH 10 the peroxydicarbonate ion is not present but it is proposed that the

Table I
pH Dependence of the Peroxymonocarbonate Ion and Perhydroxyl Anion Concentrations

pH	Peroxymonocarbonate ion (mol ⁻¹)	Perhydroxyl anion (mol ⁻¹)
8.5	0.031	0.000
9.0	0.021	0.002
10.0	0.000	0.020

lightening for this new oxidant at pH 10 is being driven by the presence of the perhydroxyl anion. One reason why the concentration of the peroxymonocarbonate ion decreases at pH 10 is its deprotonation to the peroxymonocarbonate dianion (12) as shown in Equation 10.



(II) LIGHTENING AS A FUNCTION OF HYDROGEN PEROXIDE AND CARBONATE CONCENTRATION

A series of cream formulations were made at the optimal pH for the new oxidant system (pH 9.0–9.3). In the first set of formulations the ammonium carbonate concentration was varied from 2% to 5% with a fixed hydrogen peroxide concentration of 4.5% and glycine concentration of 1.8%. A second series of cream formulations were made with a hydrogen peroxide concentration that was varied from 3% to 9% and a fixed glycine (1.8%) and ammonium carbonate concentration (2%). All of these products were then applied to medium brown untreated human hair samples for a period of 30 minutes in a temperature controlled environment of 30°C. Figure 4 shows the lightening data as a function of the carbonate concentration and Figure 5 shows the lightening data as a function of hydrogen peroxide concentration. These data again clearly demonstrate that this combination of ammonium carbonate, hydrogen peroxide and glycine at pH 9 can give effective lightening. The lightening values are similar to these obtained for a conventional oxidant system of ammonium hydroxide and hydrogen peroxide at pH 10. It also shows that the lightening can be increased either by changing the carbonate concentration or the hydrogen peroxide concentration. As the carbonate concentration and the hydrogen peroxide concentration are increased, lightening also increases.

The reason for this lightening dependence on the hydrogen peroxide and carbonate concentrations can be explained by consideration of the equilibrium responsible for forming the peroxymonocarbonate ion (Equation 1). As either the hydrogen peroxide or ammonium carbonate concentrations are increased the equilibrium will be shifted to the right and form more of the peroxymonocarbonate ion. This relationship has been confirmed with the ¹³C NMR studies where the concentration of the peroxymonocarbonate ion was measured as a function of carbonate and hydrogen peroxide concentrations (see Table II).

Thus with this new oxidant we now have two 'levers' that can increase the lightening. This is different from the conventional ammonium hydroxide/hydrogen peroxide/pH 10 oxidant where the only lever to increase the concentration of the oxidant species is increasing the hydrogen peroxide concentration.

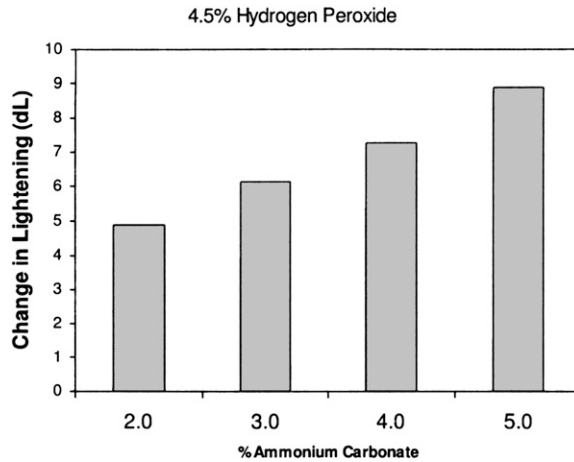


Figure 4. Lightening as a function of carbonate concentration.

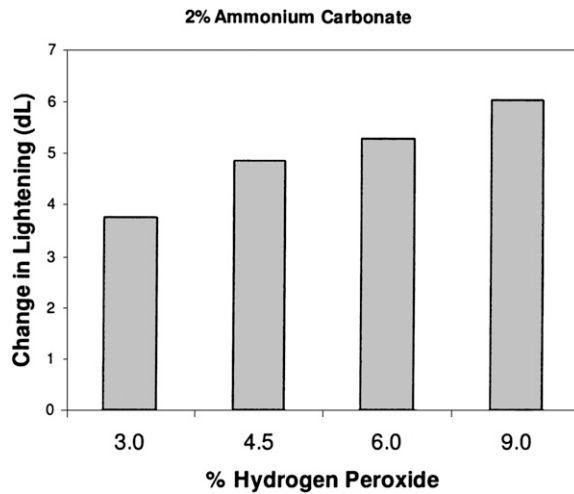


Figure 5. Lightening as a function of hydrogen peroxide concentration.

Table II
Concentration of Peroxymonocarbonate Ion as a Function of Ammonium Carbonate and Hydrogen Peroxide Concentration

% Ammonium carbonate	% Hydrogen peroxide	Peroxymonocarbonate ion (mM)
1.5	3.1	22.3
1.5	6.3	45.9
3.5	3.0	32.7
3.5	6.0	64.9
5.1	3.0	52.3
5.0	6.0	74.0

One benefit of this lightening system is its flexibility, i.e. the carbonate and hydrogen peroxide concentrations can be adjusted as two independent levers to alter the lightening. This can be used to match the current lightening performance of a conventional oxidant

either with a different hydrogen peroxide level or with a different time using the same hydrogen peroxide level. For example, Table III shows different options with the new oxidant to match the lightening of a medium blonde product. (i.e. 1.0% ammonia and 3% hydrogen peroxide. The same level of lightening can be achieved using the ammonium carbonate, hydrogen peroxide and glycine oxidant in three different ways:

- (i) Equal hydrogen peroxide level.
- (ii) Lower hydrogen peroxide level. This may be an advantage for formulating shades where increasing hydrogen peroxide is not desired (e.g. for a low skin irritation profile or where regulations prohibit certain hydrogen peroxide levels).
- (iii) Shorter time (for example, matches the lightening but in 10 minutes vs. 30 minutes)

An additional advantage of this lightening system is the ability to increase both the ammonium carbonate and hydrogen peroxide levels to increase the lightening beyond what can be achieved with the current oxidant. Table IV below shows the lightening for the two oxidants each with 4.5% hydrogen peroxide.

(III) LIGHTENING AS A FUNCTION OF SOURCE OF CARBONATE (I.E., AMMONIUM CARBONATE VS. POTASSIUM HYDROGEN CARBONATE)

The formation of the peroxy monocarbonate oxidant system does not depend on the presence of ammonia to form the oxidizing species. However, when a cream formulation was tested with potassium hydrogen carbonate instead of ammonium carbonate the level of lightening was significantly decreased. The importance of ammonia in the bleaching of melanin has been observed for the conventional oxidant systems and has been reported previously in the literature (13). It is proposed that ammonia plays the same role in the lightening mechanism for both systems. Figure 6 shows the lightening for both oxidant systems with and without ammonia. For the conventional systems 4.5% hydrogen peroxide was used with either 1.3% ammonia or sodium hydroxide adjusted to pH 10. The new oxidant was 4.5% hydrogen peroxide, 1.8% glycine and either 4.0% ammonium carbonate or 4.2% potassium hydrogen carbonate.

Table III
Lightening as a Function of Ammonium Carbonate and Hydrogen Peroxide Concentration

Oxidant system	Time	Change in lightening (dL)
4.5% hydrogen peroxide/1.3% ammonia, pH 10	30 min	7.84
4.5% hydrogen peroxide/2.5% ammonium carbonate, pH 9	30 min	8.20
3% hydrogen peroxide/4.5% ammonium carbonate, pH 9	30 min	7.82
3.0 hydrogen peroxide/6% ammonium carbonate, pH 9	10 min	7.90

Table IV
Lightening as a Function of Ammonium Carbonate and Hydrogen Peroxide Concentration

Oxidant system	Time	Change in lightening (dL)
4.5% hydrogen peroxide/1.3% ammonia, pH 10	30 min	7.84
4.5% hydrogen peroxide/7% ammonium carbonate, pH 9	30 min	13.41

(IV) ROLE OF GLYCINE

The use of ammonium carbonate with hydrogen peroxide at pH 9 to lighten hair was first reported in the patent literature in the 1960s (14) but it has only been commercialized in a very limited number of products. The issue found in early formulation work was that significant fiber damage occurred over multiple cycles. In particular for a system matched in lightening to a conventional oxidant system the tensile properties of the fibers after 3 cycles of treatment were significantly lower for the ammonium carbonate, hydrogen peroxide system. It has been found that this loss of tensile strength can be prevented by the addition of glycine with no detrimental impact on the lightening.

Figure 7 shows the tensile properties of the hair treated over multiple coloring cycles with the ammonium carbonate, hydrogen peroxide and glycine (pH 9) oxidant vs. the ammonium hydroxide, hydrogen peroxide (pH 10) oxidant. The systems were matched

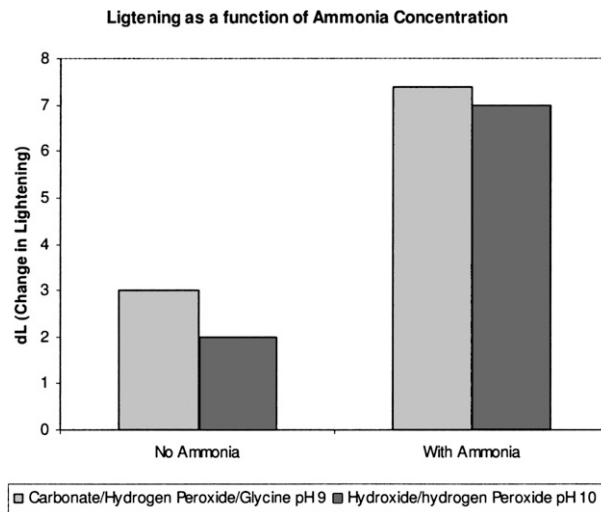


Figure 6. Role of ammonia in the lightening process.

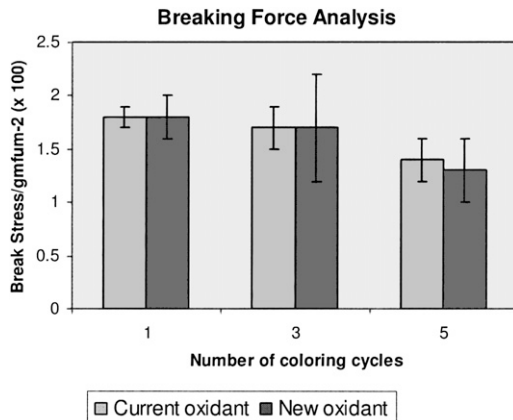
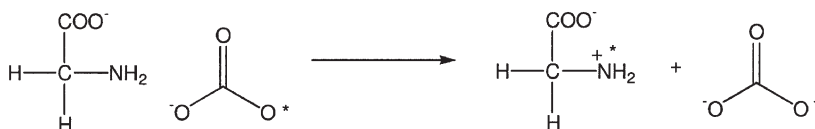


Figure 7. Tensile strength of oxidants over multiple coloring cycles.

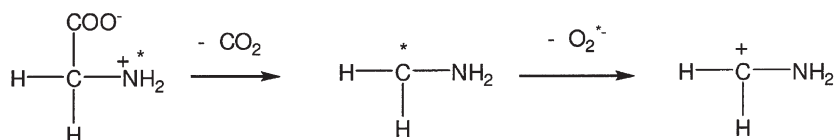
in terms of lightening ability. The data demonstrate that the tensile strength of the new oxidant is at least equal to the conventional oxidant.

The proposed mechanism for the action of glycine is its ability to control the concentration of the carbonate radical inside the hair. The carbonate radical is a highly oxidizing species and if formed could be responsible for the observed tensile loss (15,16). The glycine may act as a radical scavenger by enabling fast electron transfer from the nitrogen of the glycine to the carbonate radical. The reaction scheme below is only hypothesized; we have no direct evidence for the reactions, but it is supported by studies in the literature. (17,18).

Step 1:



Step 2:



CONCLUSIONS

The combination of ammonium carbonate, hydrogen peroxide and glycine at pH 9 provides a lightening system that delivers equal to superior lightening to the conventional oxidant of ammonium hydroxide and hydrogen peroxide at pH 10. It is proposed that the lightening at this reduced pH is due to the introduction of a new oxidizing species, the peroxyammonium carbonate ion, which is formed *in-situ* from the combination of hydrogen carbonate ions and hydrogen peroxide. This oxidant system has the advantage in that it has two levers, the hydrogen peroxide concentration and the ammonium carbonate concentration, to change either the level of lightening or the time of lightening. Both can be changed to achieve higher lightening, lightening with lower hydrogen peroxide concentrations or faster lightening. The introduction of glycine has allowed this system to deliver this lightening without the previously observed negatives of tensile strength loss. It is proposed that the glycine acts as a scavenger of the carbonate radical. The formation of the carbonate radical is an undesired side reaction that is separate from the chemistry involved in the lightening of the melanin. Thus with the combination of the ammonium carbonate, hydrogen peroxide and glycine formulated at the optimum pH of 9.0 the lightening can be optimized without fiber damage negatives.

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