TOTAL PROTECTION FOR HAIR DURING THE USE OF COLORING PRODUCTS*

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*This paper is being presented by Dr. Graham McKelvey on behalf of Dr. Marsh who was unable to attend.

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Background:

The use of permanent hair colorants products is widespread and allows the consumer to either change their natural hair color and/or cover gray. However, there are trade-offs that the consumer has to make if she is using these products on a regular basis. Typical trade-offs are the application time involved in the coloring event, typically 25-30 minutes to achieve the desired color, the unpleasant odor during application and the changes to the hair quality over multiple cycles. To try and reduce these trade-offs we have focused our research work to investigate alternative oxidants that can achieve the color result in a shorter time and ideally with an improved fiber damage and odor profile vs current products. The reason why our chosen focus was the oxidant system, i.e. ammonium hydroxide + hydrogen peroxide at pH 10, is because the long application time is controlled by the time it takes the oxidant to decolorize the melanin to achieve the required lightening. In addition, it is this same chemistry that causes the fiber damage and the poor odor profile.

Previous products have been formulated that can deliver lightening and color formation in shorter application time (10-15 mins) but this has been achieved by significantly increasing the hydrogen peroxide and ammonia levels. This leads to negatives in terms of skin irritation from the higher levels of hydrogen peroxide and also even worse odor from the higher ammonia levels.

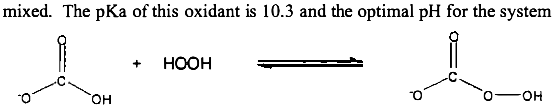
The oxidant system we have investigated is the combination of an ammonium carbonate salt with hydrogen peroxide at a pH of 9.0. We have demonstrated that with the addition of a radical scavenger such as glycine this system can achieve comparable lightening to current oxidants but at shorter application times and without significantly increased hydrogen peroxide levels. The lower pH also gives the system a lower ammonia odor and an improved fiber damage profile

Lightening:

The key species responsible for decolorizing the melanin in current colorants is the perhydroxyl anion (HOO^-) formed as the pH of hydrogen peroxide is increased with ammonia as the alkalizer. A minimum pH of 10.0 is required for sufficient levels of this anion to be present in the product and for good lightening to occur. Lightening is of course crucial for the achievement of blonde shades but also for good grey coverage for the light/medium brown shades and also to produce vibrant tonal shades such as reds.

$$H_2O_2 \Leftrightarrow HOO^- + H^+ \qquad (pKa = 11.6)$$

For the ammonium carbonate/hydrogen peroxide/glycine oxidant, the proposed key species responsible for the lightening of the melanin is the peroxymonocarbonate ion which is formed in-situ as the carbonate and hydrogen peroxide are mixed. The pKa of this oxidant is 10.3 and the optimal pH for the system to give lightening is pH 9.0.



Peroxymonocarbonate ion

Data will be shared that compares the lightening of selected ammonium hydroxide/hydrogen/pH 10 systems to ammonium carbonate/hydrogen peroxide/glycine systems at pH 9 at both 10 minutes and 30 minutes. The data illustrates that the ammonium carbonate/hydrogen peroxide/glycine system at 10 minutes can match current lightening levels at 30 mins.

Odor:

The optimum pH of the ammonium carbonate/hydrogen peroxide/glycine system is 9.0 vs 10.0 for the current ammonium hydroxide/hydrogen peroxide oxidant. As the pKa of ammonia is 9.3 a drop of one pH unit will significantly reduce the level of NH_3 in the system; NH_3 is the species responsible for the ammonia odor. Calculations have been done to predict the speciation of the different equilibria in two matched lightening oxidant systems and the relative concentration of the NH_3 formed (see table 1)

	Concentration of NH_3 (mol/l)
1.35% ammonium hydroxide/3% hydrogen peroxide	0.67
4.5% ammonium carbonate/3% hydrogen peroxide/1.9% glycine	0.27

Fiber Damage:

A key measure for a new oxidant is the change in fiber properties over multiple use cycles. It is also important to measure changes to the inside of the individual hair fibers (e.g. internal strength), to the outside of the hair (e.g. hydrophobicity/cuticle structure), and also to the how these changes affect the bulk properties of the hair. This is because the hair has a complex morphology and the reactivity of the different fiber components of the structure will be different for the different oxidants.

(1) Internal Strength Changes:

Tensile strength is a key method to assess the internal strength of hair. It was found that the internal strength of the hair treated with just the matched lightening ammonium carbonate/hydrogen peroxide oxidant at pH 9 was lower than the current oxidant system of ammonium hydroxide/hydrogen peroxide at pH 10. However, on addition of a radical scavenger such as a glycine both the wet and the dry tensile strength were significantly improved and were, depending on the level and oxidant system, equal or superior to the current oxidant system over multiple cycles.

Tensile strength measurements on wet fibers	**Plateau Load (Gmf/sq. micon x 10^3)**	**Break Load (Gmf/sq. micon x 10^3)**
Ammonium Hydroxide/Hydrogen Peroxide/pH 10	5.60 ± 0.81	18.4 ± 2.3
Ammonium Carbonate/Hydrogen Peroxide/Glycine/pH 10	6.08 ± 0.76	18.8 ± 1.7

The proposed mechanism for the role of the glycine is to act as a radical scavenger to protect against the formation of the hydroxyl radical and the carbonate radical inside the fiber. The hydroxyl radical is formed from the reaction of hydrogen peroxide with redox active metals. The carbonate radical is likely formed via the reaction of this hydroxyl radical with the carbonate anions present.

$$H_2O_2 + Cu^+ \longrightarrow Cu^{2+} + HO^- + HO*$$
$$HO* + CO_3^{2-} \longrightarrow CO_3^{-}* + HO^-$$

(2) Hydrophobicity Changes:

The surface of uncolored hair is hydrophobic due to the presence on the outer surface of each cuticle cell of the chemically bound lipid 18-MEA (18-methyl eicosanoic acid). During the use of current coloring products it has been demonstrated that this lipid is removed via a perhydrolysis mechanism (i.e. the key species responsible for its removal is the perhydroxyl anion, HOO^-). This removal dramatically increases the wet feel and wet combing forces and also the efficient deposition of conditioner actives such as silicones.

As the ammonium carbonate/hydrogen peroxide/glycine oxidant is formulated at a lower pH (9.0 vs 10.0) the concentration of the perhydroxyl anion is significantly reduced and as a consequence the F-Layer is less readily removed and the hydrophobicity of the fiber is retained. Data will be presented that measures the increased hydrophobicity of the ammonium carbonate/hydrogen peroxide/glycine oxidant by comparing the contact angle of a drop of water wetting the surface of the fiber for the two oxidant systems vs the starting untreated hair. In addition, supporting ToF SIMS data, that directly measures the presence of the 18-MEA lipid, will be presented.

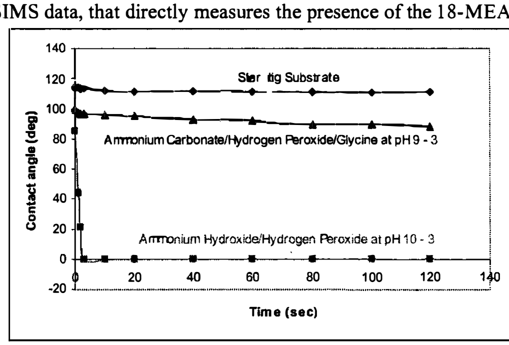


Chart 1: Cuticle Angle measurements as a function of time

(3) Cuticle Structure/Bulk Hair Property Changes:

The hypothesis was the improved retention of the F-Layer would also translate into improved cuticle quality over multiple coloring cycles with washing/combing/blow drying physical damage between cycles. This benefit is observed after treatment for five repeat coloring cycles in both the SEM (scanning electron microscope) and TEM (transmission electron microscope). In addition we have demonstrated how the changes in these single fiber properties have also improved bulk hair properties such as shine and manageability. Data will be presented that illustrates these benefits.

Conclusion:

The ammonium carbonate/hydrogen peroxide/glycine pH 9 oxidant system offers the possibility to formulate a hair colorant that has the ability to lighten and form color but in a shorter application time, at a lower pH giving an improved odor profile and also an improved fiber damage profile