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Hair and amino acids: The interactions and the effects

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Synopsis

The interaction and the function of some amino acids in hair care applications are discussed. When amino acids are applied to hair in the form of simple aqueous solution, uptake of the amino acids is mainly controlled by ionic equilibrium. When amino acids were incorporated in a hair conditioner, the result was quite different, suggesting the importance of interaction between the amino acids and the cationic surfactants. Uptake of pyrrolidone carboxylic acid (PCA), a derivative of glutamic acid, is enhanced by combining with arginine, an amino with strong affinity towards hair.

Effects of some amino acids on bleached/dyed hair are described. A hair conditioner incorporated with alanine improves hair surface hydrophobicity of bleach-damaged hair. Histidine and phenylalanine improve tensile strength. PCA was proved to be effective to improve color-retention of dyed hair.

INTRODUCTION

Protein is the second major component of living organism, following water. All proteins, including skin and hair, are various compositions of amino acids.

Within the corneocytes, there is also a complex mixture of free amino acids and other low molecular weight, water-soluble compounds (Natural Moisturizing Factor or NMF)(1), and are known to contribute to maintenance of water balance in the stratum corneum. Amino acids, pyrrolidone carboxylic acid (PCA), lactate and urea, all components of NMF, are widely used in cosmetic fields and their usefulness is well established.

Unlike in the case of the skin, the presence and the role of naturally occurring free amino acids in hair shafts are not known yet. Although free amino acids are often detected in hair (2,3), they are more likely to be a product of protein degradation caused by UV or cosmetic treatment. But amino acids provided externally are known to interact with the hair to give various cosmetic effects, such as moisturizing, strengthening the hair (4), and retention of artificial color (5).

In hair care applications it has been a long-experienced strategy to share the idea of skin care and utilize materials which are established in skin care applications. Vitamins, hydrolyzed proteins, vegetable extracts are good examples. This strategy is often proved to be so efficient that understanding of their basic interaction with hair tends to be left behind. In this paper, interaction between hair and various amino acids are discussed as well as the benefits of amino acids treatment.

MATERIALS AND METHODS

MATERIALS

Natural hair of Japanese women, 18 cm in length from tip end, was obtained from private source and subjected to measurement of physical properties. The hair was treated with bleaching lotion for 30 minutes at 33°C, rinsed thoroughly in running tap water, and this process was repeated 4 times.

After the last bleaching, washing with 15% active sodium laureth sulfate solution, extensive rinsing and drying in a conditioned room (23°C, 40% RH.) followed.

METHODS

Uptake of amino acid. Japanese hair, treated with a waving lotion of thioglicolic acid and with a neutralizer of sodium bromate, was immersed in a solution of 11.5 mM amino acid. After 10 minutes the concentration of the amino acid solution was determined by HPLC method using an anion-exchange column and an electrochemical detector.

Uptake of PCA. Intensively bleached Asian hair swatches, weighing 0.8 g each, were purchased from Beaulax (Tokyo, Japan). Each swatch was washed with a 15 wt% solution of sodium laureth sulfate for one minute, rinsed extensively with running tap water for one minute and air dried.

A hair swatch was immersed in 6 ml of amino acid or PCA solution for 30 minutes. The swatch was rinsed in running tap water for 20 seconds and air dried overnight. For recovery of amino acid from the hair, the swatch was immersed in 15 ml of 10mM phosphoric acid buffer solution, pH 3.5. After 30 minutes, 10 ml of the buffer solution was removed for quantitative analysis. Concentration of the amino acid or PCA was determined by HPLC method.

Hair conditioner treatment and hydrophobicity measurement. Hair conditioner (cationic surfactant 0.6 wt% active, cetyl alcohol 3.0 wt%, 0.5 g per tress) was applied to wet hair and distributed manually for 30 seconds, then 30 seconds rinsing in running tap water (40°C) followed. The hair tresses were dried for more than four days in a conditioned room (23°C, 40% RH).

A hair fiber was fixed in a horizontal position and 1 μl of deionized water was mounted on the point 10 cm from the hair tip end. Twenty seconds later the contact angle which the water drop and the fiber surface form was measured microscopically.

Amino acid treatment and tensile strength measurement. A hair swatch was immersed in 100mL of 2 wt% amino acid solution at 35°C for three minutes. The swatch was then rinsed in 100 ml deionized water at 35°C for one minute, and air dried.

Tensile measurements were performed on single fibers in deionized water. Hair fibers, 40 mm in length, were immersed in deionized water for at least one hour before the measurement and then extended at a rate of 20mm per minute on a tensile tester KES-G1-SH (Kato Tech) to obtain force needed to extend the fiber by 20%.

Color-retention effect

Test I (Figure 1)

Extensively bleached Asian hair swatches, purchased from Beaulax, were dyed with

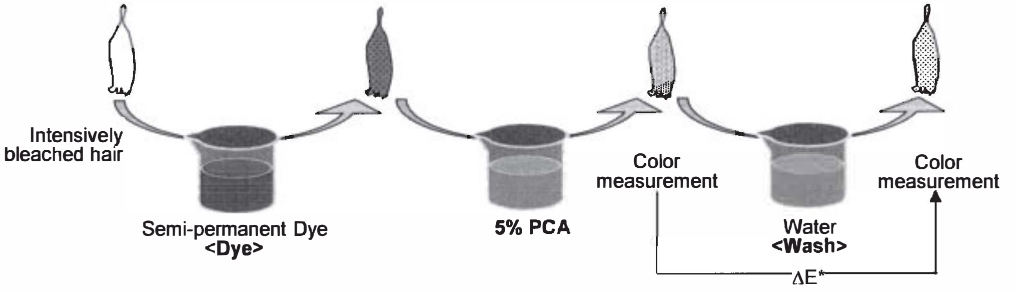

Figure 1. Experimental design of Test I.

4-amino-3-nitropheol by immersing in the 0.02 wt% solution for 30 minutes. After removal from the dye solution, the swatches were air dried.

Treatment with PCA solutions and color measurement: The pH of 5.0 wt% PCA or citric acid solution was adjusted with arginine. A hair swatch was immersed in 6 ml of the solution for 30 minutes. Treatment in deionized water was set as control. The swatch was rinsed in running tap water for 20 seconds and air dried overnight. The color value was measured by a colorimeter (initial value).

The swatch was immersed in 6 ml deionized water for 30 minutes, air dried overnight, and the color value was measured again (after wash).

$$\Delta E^* = \surd(L^*_{initial} - L^*_{after\ wash})^2 + (a^*_{initial} - a^*_{after\ wash})^2 + (b^*_{initial} - b^*_{after\ wash})^2$$

Relative δE* was determined as following in order to eliminate the variance among each experiment:

$$\text{Relative } \Delta E^* = \Delta E^*/\Delta E^*_{control}$$

Test II (Figure 2)

- Hair dye: Red shade. The dye component was the emulsion formula based on fatty alcohols and contained following dye precursors and direct dyes; Toluene-2,5-diamine sulfate, 2-Methylresorcinol, 4-amino-2-hydroxytoluene, 4-Amino-3-nitrophenol,

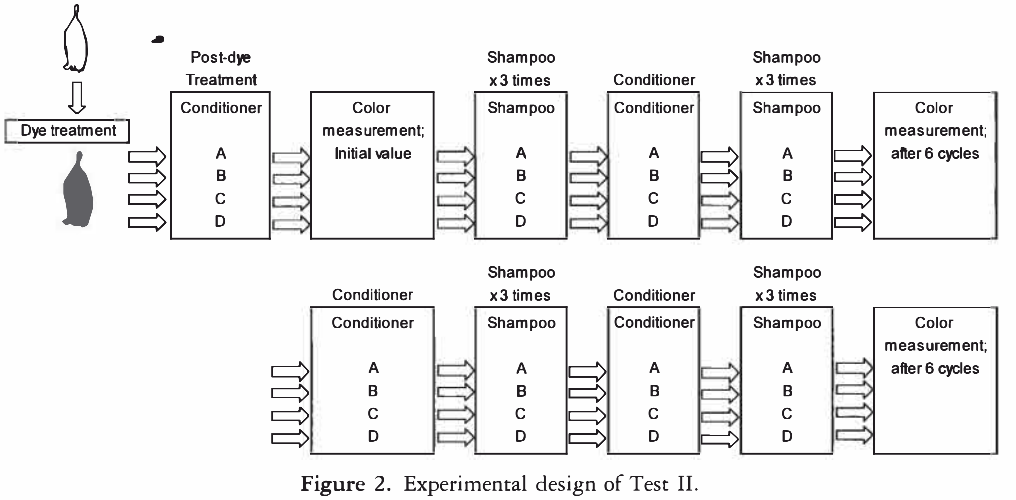

Figure 2. Experimental design of Test II.

Table Ib
Shampoos Used in Test II

	A	B	C	D
	Control	Sodium PCA	Sodium PCA + Arg	Silicone
Na Laureth sulfate (active)	7.56	7.56	7.56	7.56
Cocamidopropyl betaine (active)	1.20	1.20	1.20	1.20
Sodium PCA	—	2.00	1.00	—
Arginine	—	—	0.40	—
Amodimethicone, emulsion	—	—	—	2.00
Pearlizing agent	4.00	4.00	4.00	4.00
Preservatives	q.s	q.s	q.s	q.s
NaCl	2.00	2.00	2.00	2.00
Citric acid	pH 5.8	pH 5.8	pH 5.8	pH 5.8
Water	Balance	Balance	Balance	Balance

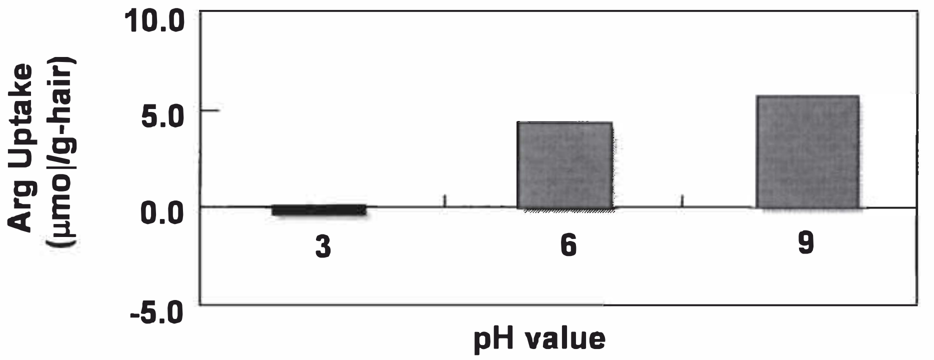

Figure 3. Arg uptake at various pH. Hair: Arg: 5.741 mM, 10 minutes immersion, 40°C.

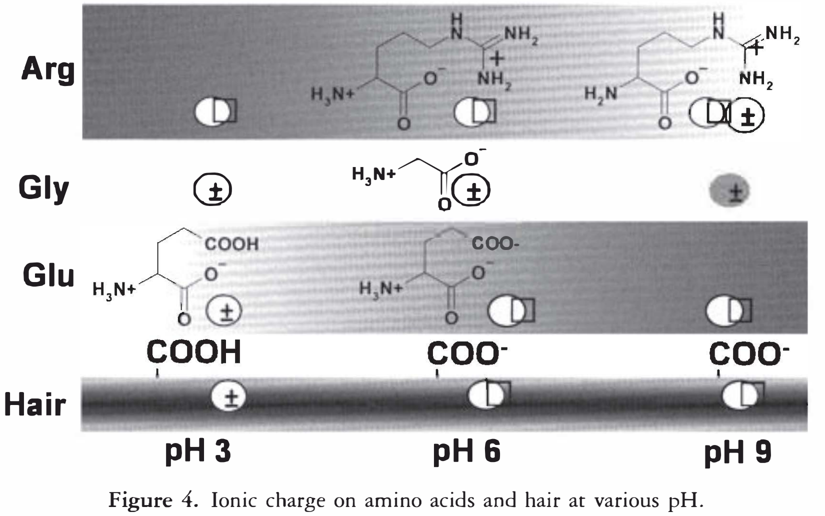

Figure 4. Ionic charge on amino acids and hair at various pH.

of the solution. It is also well known that the charges on hair also depend on the pH (Figure 4). The uptake of amino acids from the simple aqueous solutions is dominated by ionic interaction. Arginine, being a basic amino acid, bears cationic charge below $pK_2 = 9.04$, so has strong affinity for hair at pH over about 4, the isoelectric point of hair (6). Acidic or neutral amino acids having negative or neutral net charge at pH 3-7 are hardly taken up by hair.

UPTAKE OF AMINO ACIDS FROM HAIR CONDITIONERS

When we observe the uptake of amino acid from a cosmetic formulation, quite different phenomena occurs because cosmetic formulations are complex mixture of various chemicals. The example is shown in Figure 5. Although the interaction between glycine or glutamic acid and hair is very weak at pH 6, they are taken up by hair from conditioner formulations. This specific data was obtained from the material balance of the conditioner solution, so chemical interaction between the amino acids with the cationic surfactant probably makes the major contribution.

USE OF ARGININE AS AN "ANCHOR"

A guanidinium group is known to have quite high affinity for hair protein (7). Figure 6 shows the amount of arginine recovered from hair either by water or by acidic buffer solution (pH 3.5). The difference was greater at higher pH. This indicates the existence of strong interaction between acidic group on hair and arginine.

This implies potential use of arginine as an "anchor" for the deposition of other cosmetic material with weaker affinity for hair. One example is application in combination with PCA. PCA is derived from glutamic acid in the human skin. Salts of PCA are highly hygroscopic and thus they are useful as moisturizers and conditioners in cosmetics. However, being an acid with small molecular size, its affinity to hair is relatively low. Figure 7 shows the uptake of PCA at various pH. The uptake rises at pH below 4. At pH over the pKa of PCA and hair, the uptake decreases because of the ionic repulsion between both carboxylic acids. When PCA is applied to hair as arginine salt, the uptake was larger than that of sodium salt (Figure 8).

BENEFITS OF AMINO ACIDS FOR DYED HAIR

Because of different chemical structure, amino acids are can provide a variety of functions

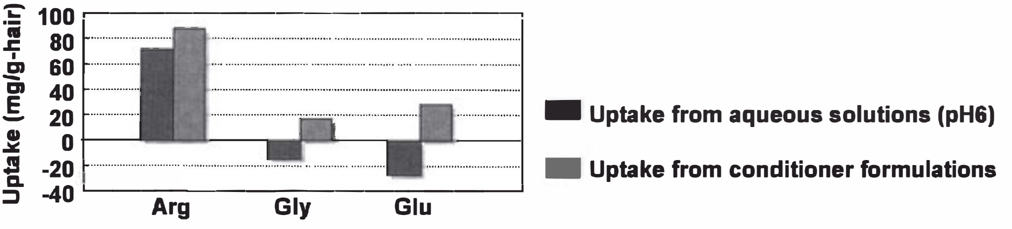

Figure 5. Uptake of amino acids. Amino acid: 11.5 mM, 30 minutes immersion, 25°C.

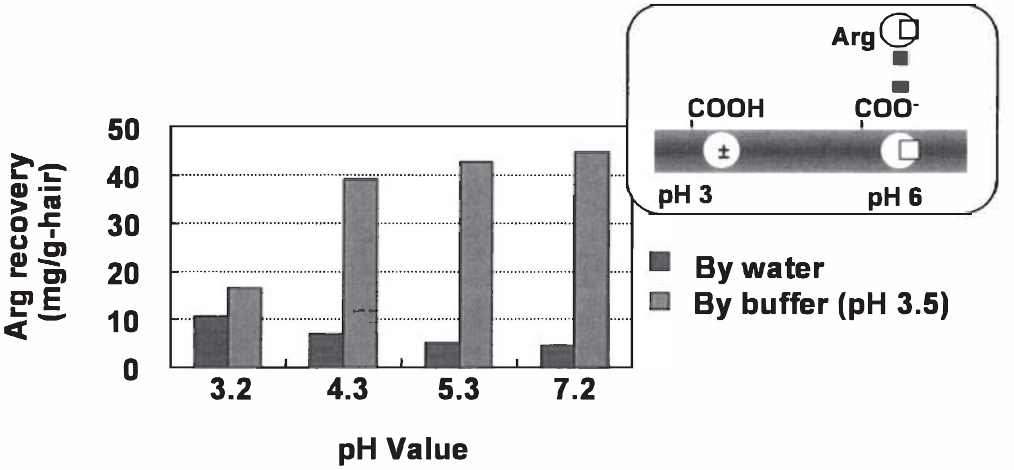

Figure 6. Recovery of Arg from hair. Arg treatment: 30 minutes immersion, 20 seconds rinse, 25°C. Recovery: 30 minutes immersion, 25°C.

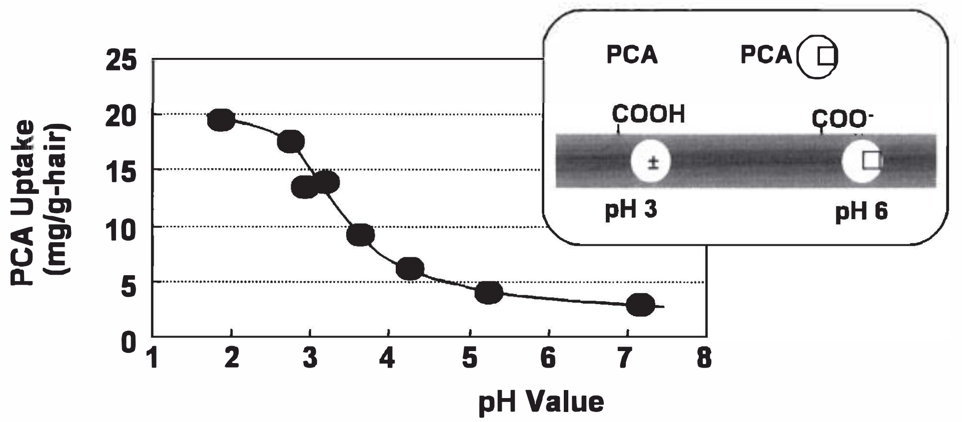

Figure 7. Uptake of PCA: pH dependence. PCA treatment: 5 wt%, 30 minutes immersion, 25°C. Recovery: 30 minutes immersion, 25°C.

in cosmetic preparations. Some beneficial effects found on bleached/dyed hair are described in this section.

Damage care by various amino acids. Bleaching hair decreases hydrophobicity of hair fiber (5). Figure 9 shows surface hydrophobicity of bleached hair treated with hair conditioners. The average contact angle for natural hair was 100° and four-time bleach treatment brought it down to 65°. By application of a simple model hair conditioner of monoalkyl trimmonium chloride, the contact angle increased slightly. With 1.5 wt% of L-alanine addition, the contact angle increased significantly to the similar value to that of dialykyl trimmonium.

Decrease in tensile strength of dyed hair fibers is not clear when it is measured in the dry state, but the effects of oxidization are clear when measurements are made in water (8,9). Figure 10 shows tensile strength of bleached hair measured in water. Tensile strength decreased by four-time bleach treatment, and significant increase was observed

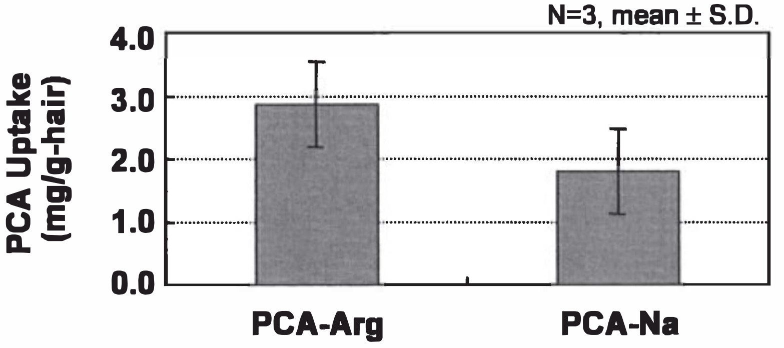

Figure 8. Uptake of PCA: the effect of counter ion. PCA treatment: 5 wt%, 30 minutes immersion, 25°C. Recovery: 30 minutes immersion, 25°C.

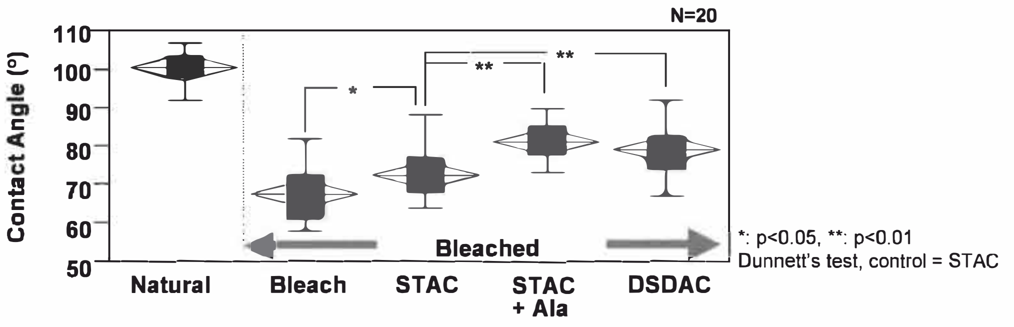

Figure 9. Improvement of surface hydrophobicity.

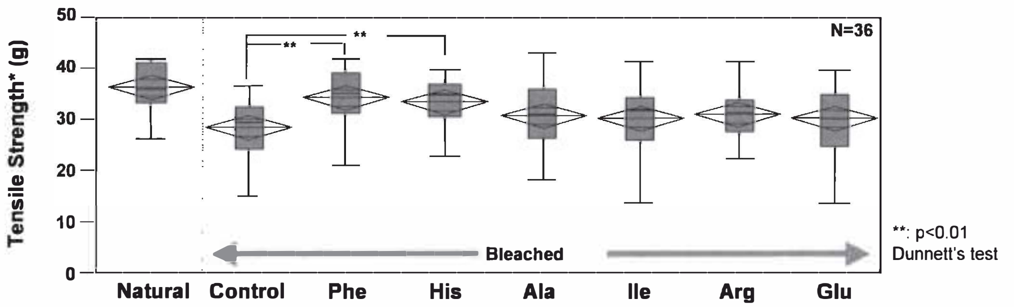

Figure 10. Improvement of tensile strength.

by application of phenylalanine or histidine. In fact, this increase is attributed to the increase of hair fiber diameter with the tensile strength per area being unchanged. These amino acids are probably diffused into hair fiber and interact with protein to influence the structure.

IMPROVEMENT OF COLOR RETENTION BY SODIUM PCA

Salts of PCA are highly hygroscopic. This property is expected to contribute to retention of not only water but also other water-soluble molecules in hair fibers, such as dye molecules.

Test I was designed to examine this idea. The result is shown in Figure 11. Basically the influence of pH is significant, but for all pH conditions better color retention was observed with PCA. The difference of color retention at pH 7.2 is impressive. Figure 12 shows the influence of counter ion on color retention effect: the combination of PCA and arginine exhibited the best. Taking the "anchor" effect of arginine into account (Figure 6), the amount of PCA in/on hair seems to be the key for the color retention effect.

Test II was designed to examine the color retention effect in more practical condition. Sodium PCA was employed instead of PCA in consideration of material availability and cost aspect. Color development was significantly improved by Sodium PCA or Sodium PCA/arginine combination (Figure 13). After 6 or 12 wash cycles Yak hair treated with the PCA containing products showed a distinct brighter, more vibrant shade (Figure 14).

CONCLUSION

A variety of methods were applied to evaluate the interactions and effects of amino acids on bleach- or dye-treated hair. The findings obtained in this study were summarized as follows:

- When amino acids are applied to hair as the state of simple aqueous solution, uptake of the amino acids is mainly controlled by ionic equilibrium. When amino acids were incorporated in hair care formulations, interaction between the amino acids and other ingredients.
- Uptake of pyrrolidone carboxylic acid (PCA), a derivative of glutamic acid, is enhanced by combining with arginine, an amino with strong affinity towards hair.
- A hair conditioner incorporated with alanine improves hair surface hydrophobicity of bleach-damaged hair.
- Histidine and phenylalanine improve tensile strength.
- PCA was proved to be effective to improve color-retention of dyed hair.

In conclusion, we emphasize the potential of amino acids as hair care material. While more than twenty specific naturally occurring amino acids are found in various proteins, only a few of them are outlined in this study. Further investigation will be required.

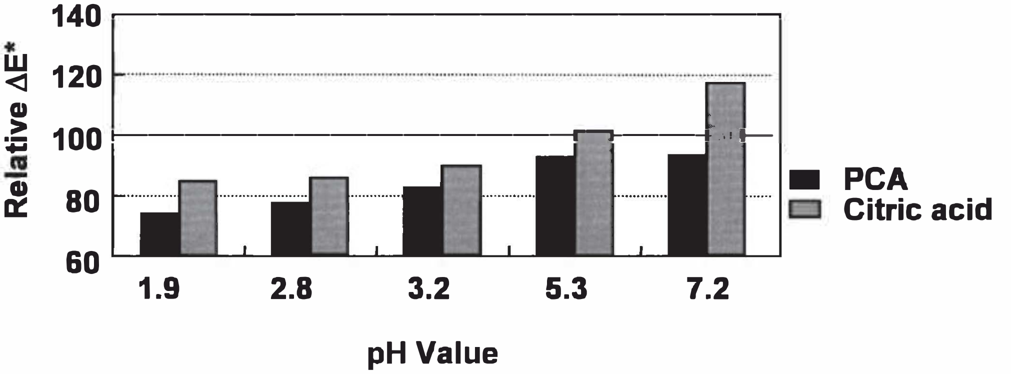

Figure 11. Color retention of semi-permanent hair dye.

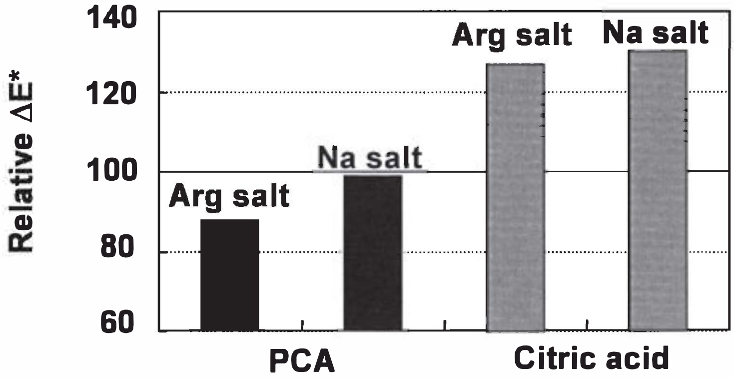

Figure 12. Color retention of semi-permanent hair dye: influence of counter ion.

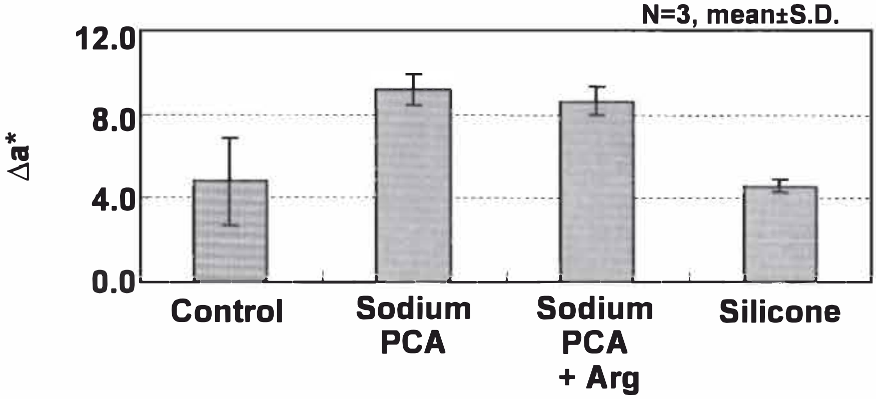

Figure 13. The effect of PCA on color development of permanent hair dye.

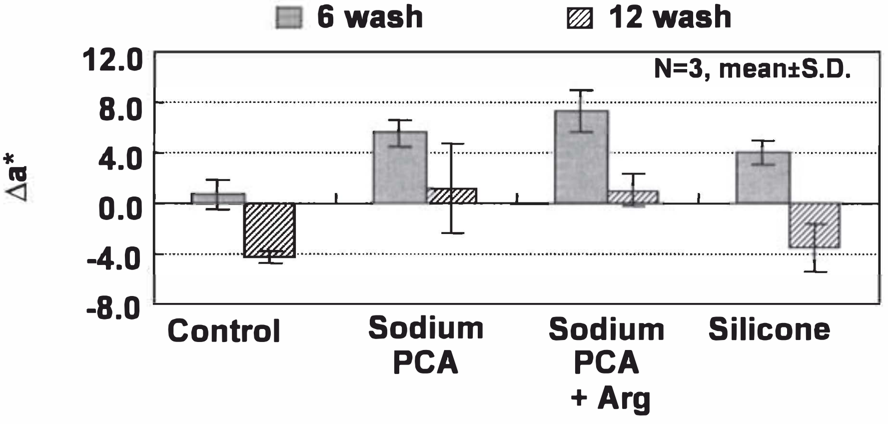

Figure 14. The effect of PCA on wash-fastness of permanent hair dye.

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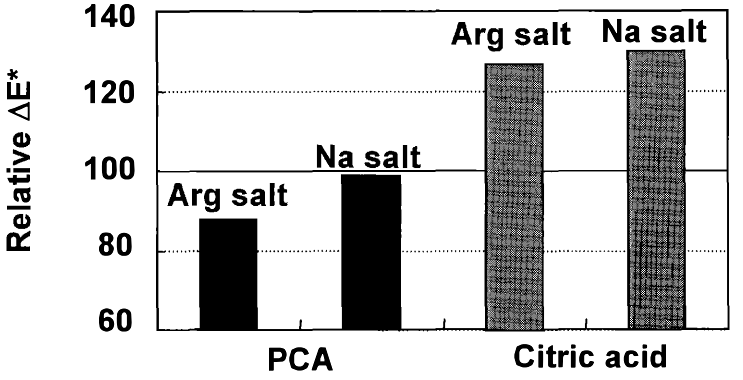

Figure 12. Color retention of semi-permanent hair dye: influence of counter ion.

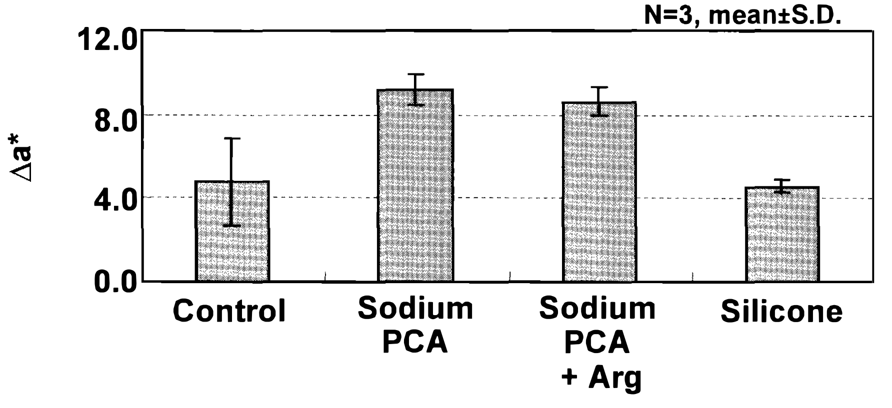

Figure 13. The effect of PCA on color development of permanent hair dye.

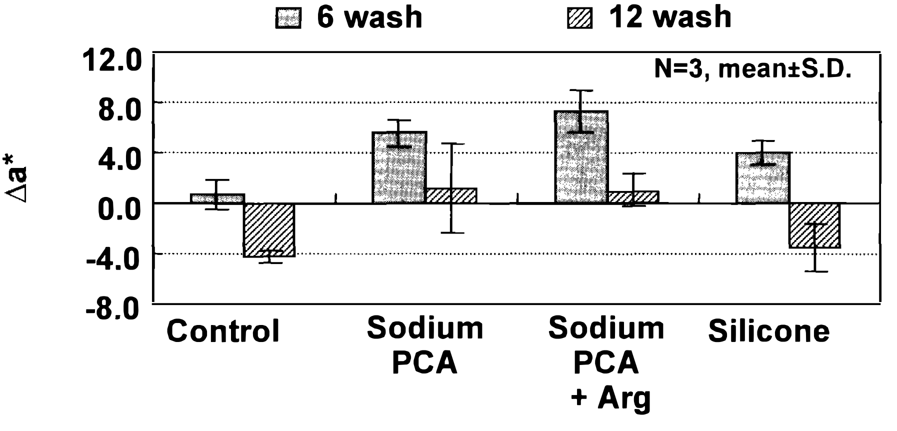

Figure 14. The effect of PCA on wash-fastness of permanent hair dye.

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