

The green hair problem: a preliminary investigation

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Synopsis

The phenomenon of blond hair acquiring a green tint when exposed to swimming pool water containing copper is examined. The GREEN coloration is attributable to absorption of copper by HAIR which occurs when the former is present in the water in the form of a weak complex such as copper sulfate. Oxidation of the hair enhances copper absorption and pretreatment with a formulated quaternary ammonium compound inhibits the process. The green color cannot be stripped by subsequent shampooing.

INTRODUCTION

Many people with natural or dyed blond hair encounter the problem of having their hair acquire a green tint after frequent exposure to swimming pool water (1-8). This problem is usually speculatively attributed to the sorption on to the hair of copper, present in swimming pool water either from corrosion of copper plumbing or from copper salts added to the pool as algacides. It is commonly thought that the green color can be removed by shampooing. The scientific literature, however, has few references to investigation of hair-copper interactions directed toward the speculations mentioned above. The most informative work in this respect is that of Edman and Marti (9). The authors have shown that hair treated in a solution of copper sulfate acquires a green color and that the copper uptake, which they have calculated from the extent of depletion in solution, provides a method for indicating small oxidation damage to hair fibers.

The work reported has three parts: to investigate discoloration of hair by interaction with copper in a simulated swimming pool; to determine the effects of mild oxidation of hair on such interaction; and to examine the effects of a formulation containing a quaternary ammonium compound as a pretreatment.

While this investigation is confined to discoloration of hair due to copper, it is realized that other elements such as chromium, nickel and cobalt may be present in the swimming pool water and may cause similar effects. Copper, however, is certainly a more likely candidate since copper-based algacides are available in the market as swimming pool additives.

Table I
Experimental Design and Treatment Bath Compositions

Pretreatment	Water		Conditioner	
	Unoxidized	Oxidized	Unoxidized	Oxidized
Nominal pH = 6.0	Treatment Bath #1		Treatment Bath #2	
	—100 mg $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ dissolved in 100 ml distilled water			
	—100 ml 1:1000 prediluted Clorox added		Same as #1	
	—volume adjusted to 2000 ml with distilled water			
Nominal pH = 8.5	Treatment Bath #3		Treatment Bath #4	
	—100 mg $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ dissolved in 100 ml distilled water			
	—500 mg citric acid added		Same as #3	
	—100 ml 1:1000 prediluted Clorox added			
	—volume adjusted to 2000 ml with distilled water			
	—pH adjusted to 8.5 pH with NaOH			

EXPERIMENTAL

PREPARATION OF MATERIAL

The material was prepared in accordance with the experimental design shown in Table I. Natural white or blond hair (De Meo Brothers, New York, N.Y.) formed into eight tresses, approximately 0.5 g each, was used in the experiment. Four of the tresses were mildly oxidized by treating with a 3% aqueous solution of hydrogen peroxide adjusted to 10.5 pH using ammonium hydroxide. A drop of Triton X-100 was added to the solution to facilitate wetting of the hair. The oxidation treatment was carried out for a period of 15 min at 22°C. All tresses were then cleaned in warm methanol. Four of the tresses—two unoxidized and two oxidized—were immersed in distilled water and the other four were immersed in a commercial formulation of a quaternary ammonium compound (distearyl-dimethyl ammonium chloride) for 10 min for pretreatment and subsequently blow-dried for 2 hr at 22°C.

SIMULATED SWIMMING POOL TREATMENT

The experiment was carried out in four different simulated swimming pools or treatment baths—two at a low pH (6.0) and the other two at a high pH (8.5)—as shown in Table I. The compositions of the treatment baths are described in the table. It is to be noted that an attempt to prepare copper sulfate solution at 8.5 pH failed as the copper precipitated out in the form of copper hydroxide. For this reason citric acid was added in order to form the more stable copper citrate complex and thereby keep the copper in solution at the 8.5-pH level.

The various tresses were entered into their respective treatment baths and the treatment was given for a period of 1 hr at 22°C, with continuous stirring of the solution. The tresses were then rinsed thoroughly in distilled water and blow-dried at room temperature.

METHODS OF EVALUATION

The actual chlorine contents in the various treatment baths were measured spectrophotometrically using the ortho-tolidine method, standardized against iodine-thiosulfate titration (10). The actual copper contents in the treatment baths were determined by atomic absorption using a standard procedure (11).

The various hair samples generated in the experiment were evaluated for imparted color, copper content and physical location of copper absorption. The imparted color was examined visually. Copper content was determined by atomic absorption (11); for this purpose, the sample was prepared by dissolving 27 mg of hair in 6 ml of conc. HNO_3 , adding 1 ml of conc. HClO_4 to the solution, heating the solution to 200°C for 2 hr and making the volume up to 10 ml by addition of distilled water. The physical location of copper absorption was determined by energy dispersive X-ray analysis (EDXA) with the aid of a scanning electron microscope (SEM). For this purpose, the sample was prepared by flat-embedding the hair fibers in an epoxy resin block and cutting it across with a microtome so that the cross sections of the hair fibers can be mapped for copper. The resin block was mounted on a SEM stub and the surface to be examined was coated omnidirectionally with several hundred angstroms of carbon by vacuum evaporation to reduce the SEM charging artifact. The surface was then examined in a JOEL JSM-U3 scanning electron microscope equipped with an EDXA 707A energy dispersive X-ray analyzer. Maps for copper were made of the various hair cross sections using 100,000 X-ray counts, using a counting time varying between 15 and 75 min.

RESULTS

The contents of the four treatment baths before and after the treatments are shown in Table II. The results of the evaluation of the various hair samples are described in Table III. The EDXA-SEM photographs of cross sections of hair fibers from the tresses treated at the 6.0-pH condition are shown in Figure 1.

DISCUSSION OF RESULTS

GENERAL OBSERVATIONS

The copper depletion data (Table II) and the copper contents and imparted color of the hair samples (Table III) clearly indicate that hair absorbs the metal and consequently turns green when treated with a solution of a weak complex of the metal. This is the case with the experiment conducted at the 6-pH level. Little copper absorption and no color development occurred on treatment with the solution of the more stable copper citrate complex used at the 8.5-pH level. This lack of copper absorption cannot be attributed with certainty either to the stability of the citrate form

Table II
Initial and Final Contents of the Treatment Baths

	Treatment Bath #1		Treatment Bath #2	
	Initial	Final	Initial	Final
Cl ₂ ppm	2.7	0.24	2.7	0.15
Cu ⁺⁺ ppm	10.2	8.2	10.2	9.8
Actual pH	5.9	5.2	5.9	5.3
	Treatment Bath #3		Treatment Bath #4	
	Initial	Final	Initial	Final
Cl ₂ ppm	3.1	0.24	3.1	0.28
Cu ⁺⁺ ppm	10.6	10.5	10.6	—
Actual pH	8.6	7.5	8.6	7.4

or to the high pH without additional experiments. The EDXA-SEM photographs (Figure 1) show that the absorbed copper is primarily located in the peripheral region of the hair fiber.

The results also show that even mild oxidation enhances copper absorption, while pretreatment with a quaternary ammonium compound formulation inhibits the process.

The depletion data also register small reductions in the pH of the solutions and almost complete consumption of the chlorine from each of the treatment solutions. The high affinity of chlorine in hair and the resultant effects have been investigated in detail in another set of experiments in our laboratory. These factors fall beyond the scope of the present paper. As will be noted later, chlorine does not seem to play a role in green coloration of hair.

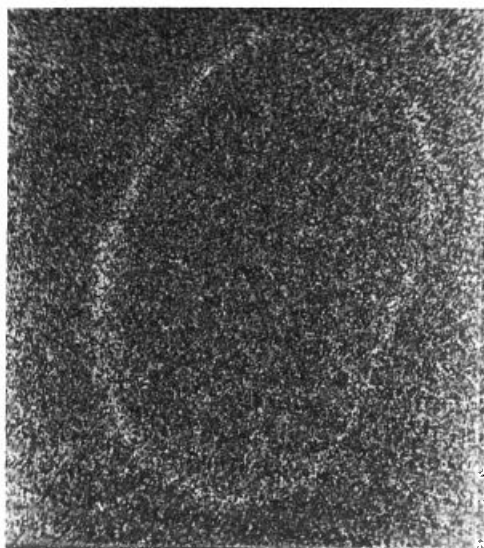
The mechanism of hair-copper interaction cannot be deduced from these results alone. Published literature in reference to interaction between copper and insoluble keratins (12-15), however, speculatively attribute copper-keratin complex formation primarily to side-chain carboxyl groups and, to a small degree, to amino groups, disulfide groups and their derivatives.

EFFECT OF MILD OXIDATION

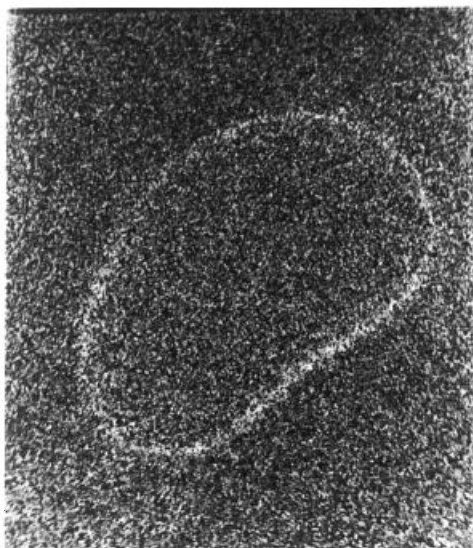
The larger amounts of copper absorbed by the oxidized hair are in agreement with the observations made by Edman and Marti (9), but these results cannot be readily

Table III
Evaluation of the Hair Samples

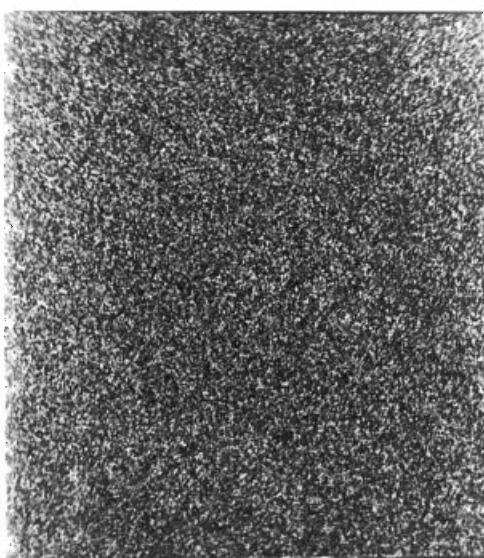
	Pretreatment	Water		Conditioner	
	Hair	Unoxidized	Oxidized	Unoxidized	Oxidized
pH = 6.0	Imparted color Cu ⁺⁺ content μg/g of hair	light green 1661	green 4545	none 128	none 366
pH = 8.5	Imparted color Cu ⁺⁺ content μg/g of hair	none 18	none 43	none 0	none 0



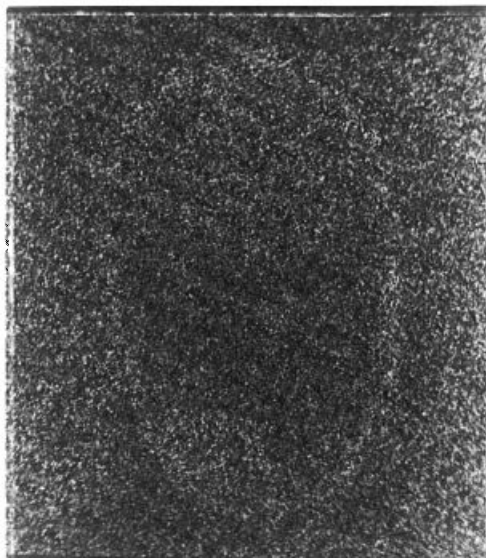
Unoxidized
(From Treatment Bath #1)



Oxidized
(From Treatment Bath #1)



Unoxidized
Conditioner Pretreated
(From Treatment Bath #2)



Oxidized
Conditioner Pretreated
(From Treatment Bath #2)

Figure 1. EDXA-SEM photographs of cross sections of the hair fibers treated with the copper sulfate containing simulated swimming pools at 6 pH. Effects of mild oxidation and conditioner pretreatment are evident, and they correspond with the results of Table III.

explained in the light of the above hypotheses. Our own amino acid data on mildly oxidized hair such as that used in the present experiment and some of the relevant literature (16) show that such oxidation causes little changes in carboxyl and amino group content. Hence these sites cannot be readily accepted as the copper binding

sites. Oxidation, even at mild levels, does decrease the half-cystine content and increase cysteic acid, and therefore the sulfonate groups perhaps participate, directly or indirectly, in copper absorption.

EFFECT OF CONDITIONER PRETREATMENT

The inhibition of copper uptake caused by the quaternary ammonium compound conditioner pretreatment is not surprising. The cationic active ingredient is likely to tie up the anionic metal-binding sites in hair, preventing copper absorption. The affinity of the conditioner to hair may be established from the results of another experiment conducted in our laboratory. The experiment involved a repeated process of immersion of hair tresses in a dilute aqueous solution of the conditioner, drying and subsequent treatment with a simulated swimming pool for an hour. Soxhlet extraction of the hair tresses with a 50/50 mixture of chloroform and methanol after 25 cycles of treatment yielded a residue amounting to about 5% by weight. This residue and the "sticky" feel of the hair before extraction suggested that the conditioner ingredients deposited on the hair to provide a coating which survived the swimming pool exposure in each cycle of treatment.

ATTEMPT TO REMOVE THE GREEN COLOR

Separate portions of the green colored unoxidized and oxidized samples (from Treatment Bath #1) were washed with a leading baby shampoo, a balsam and protein shampoo, or a strong aqueous solution of sodium lauryl sulfate. None of these washings removed the green color. Other separate parts of the green tresses were treated with ethylene diamine tetraacetic acid (EDTA) at 10 pH, dilute ammonium hydroxide or dilute nitric acid. The EDTA treatment imparted a golden-brown color, the NH_4OH treatment gave a silver gray color and the HNO_3 treatment left the green color unchanged. Thus no immediate method of removing the green color appeared evident.

ROLE OF CHLORINE IN COLORATION

In addition to the heretofore described experiment, another experiment was carried out by immersing water or conditioner-pretreated blond tresses in separate beakers containing about 12 ppm copper (in the form of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in distilled water adjusted to 3.8 pH using HCl. After several hours, the conditioner-pretreated hair turned very light green and the water-pretreated hair turned light green, suggesting that chlorine is not necessary for generation of the green color.

ANALYSIS OF A REAL-LIFE CASE

A sample of "green" hair collected from a young, female, regular swimmer with long blond hair which had developed streaks of green color was analyzed for copper content. Atomic absorption analysis showed that the "green" hair sample contained about 4220 μg of copper/g of hair. This value compares with the copper content of the oxidized hair treated with the copper sulfate solution at 6 pH for 1 hr in our experiments (Table III). The "green" and "normal" hair strands from the same subject

were cleaned in boiling methanol for several minutes and treated with a 0.0005 M aqueous solution of methylene blue dye at 11 pH for several minutes and subsequently washed in distilled water. The "green" hair strands acquired a much deeper blue stain than the "normal" hair strands. Since absorption of methylene blue from an aqueous solution is representative of the chemical hair damage (17), it is inferred that the "green" hair strands had suffered a greater degree of chemical damage. Optical microscopic examination further showed that the "green" hair strands had partially or completely lost the normal cuticle structure. All these results collectively suggest that the green streaks are caused by the enhanced copper absorption from the swimming pool by those parts of the hair fibers which have been subjected to extensive damage, either by a harsh cosmetic treatment or by cumulative exposure to the sun and weathering.

CONCLUSIONS

The results of the foregoing investigation may be summarized in the form of the following conclusions:

- a. Blond hair absorbs copper and acquires a green tint when exposed to swimming pool water containing copper in the form of a weak complex such as copper sulfate. Such absorption and consequent coloration does not occur when the copper in the pool water is in the form of a stronger complex such as copper citrate.
- b. The absorbed copper is primarily located in the peripheral region of the hair fiber.
- c. Oxidation of the hair by peroxide, even at a very low level, enhances copper absorption.
- d. Pretreatment of the hair with a formulated quaternary ammonium compound drastically reduces copper absorption and consequently inhibits green coloration.
- e. The absorbed copper and the resultant green color cannot be washed off by normal shampooing or treatment with a detergent.

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REFERENCES

- (1) L. B. Holmes and L. A. Goldsmith, The man with green hair, *N. Engl. J. Med.*, **291**, 1037 (1974).
- (2) L. C. Parish, Green hair, *N. Engl. J. Med.*, **292**, 483 (1975).
- (3) R. Cooper and J. Goodman, Green hair, *N. Engl. J. Med.*, **292**, 483-484 (1975).
- (4) L. A. Goldsmith and L. B. Holmes, Green hair, *N. Engl. J. Med.*, **292**, 484 (1975).
- (5) R. L. Lampe, A. L. Henderson and G. H. Hansen, Green hair, *J. Amer. Med. Assoc.*, **237**, 2092 (1977).
- (6) Anon., Army physicians weigh causes green hair, *C & E News*, June 6, 94 (1977).
- (7) T. E. Nappier, Green hair not due to F, *C & E News*, Dec. 19, 74 (1977).
- (8) J. Zercher, More green hair, *C & E News*, June 16, 64 (1978).
- (9) W. W. Edman and M. E. Marti, Properties of peroxide-bleached hair, *J. Soc. Cosmet. Chem.*, **12**, 133-145 (1961).

- (10) M. J. Taras, A. E. Greenberg, R. D. Hoak and M. C. Rand, "Standard Methods for Examination of Water and Waste Water," 13th ed., American Public Health Association: Washington, D.C., 1971; pp 117-123.
- (11) Perkin-Elmer, "Analytical Methods for Atomic Absorption Spectrophotometry: Standard Conditions," Reference Manual, September 1976.
- (12) S. Kokot, M. Fenghelman and R. M. Golding, An electron spin resonance study of the Copper (II) interaction with wool-keratin, Part I, *Text. Res. J.*, **42**, 704 (1972) Part II, *Text. Res. J.*, **43**, 146 (1973) Part III, *Text. Res. J.*, **44**, 523 (1974).
- (13) P. R. Brady, G. N. Freeland, R. J. Hine and R. M. Hoskinson, The absorption of certain metal ions by wool fibers, *Text. Res. J.*, **44**, 733-735 (1974).
- (14) M. S. Masri, "Binding of metallic ions to keratins," Proc. 5th International Wool Textile Res. Conf., Vol. III, 1-10 (1975).
- (15) R. E. Guthrie and S. H. Laurie, The binding of Copper (III) to mohair keratin, *Aust. J. Chem.*, **21**, 2437-2443 (1968).
- (16) L. J. Wolfram, K. Hall and I. Hui, The mechanism of hair bleaching, *J. Soc. Cosmet. Chem.*, **21**, 875-900 (1970).
- (17) J. Porter and C. Fouweather, An appraisal of human head hair as forensic evidence, *J. Soc. Cosmet. Chem.*, **26**, 299-313 (1975).