

**Silicones as a Color-Lock Aid in Rinse-Off
Hair Care Products**

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Abstract

Technology for permanent hair colorants has evolved significantly over the past decade, and consumers have high expectations for these products. Bright, intense color that lasts without degrading through shampoos and normal wear is a must. Other sensory characteristics such as shine, body, lustrous feel and manageability are also linked to color retention. For this reason, specialized shampoos and conditioners have been designed specifically for hair treated with permanent colorants.

The objective of this study was to develop a method of measuring color maintenance, and also to identify silicones that show potential for retaining permanent color. Rinse-off conditioner formulations were used as the initial focus. Bleached Caucasian hair shows excellent color reproducibility, and it was used in the study to develop the analytical method. Hair swatches were pretreated with a commercial colorant in a red tone. To determine color retention versus time, color measurements were taken with a colorimeter, and evaluations were conducted for sensory characteristics such as shine, wet detangling, combing and flyaway.

To replicate the normal conditions of wear and shampooing over time, a protocol was developed to include up to six wash cycles coupled with UV exposure cycles. A variety of silicone types were evaluated in a prototype rinse-off conditioner, including amine-functional silicones, silicone elastomers, a silicone polyether, high molecular weight silicone emulsions and a silicone polyamide. Color measurements were taken after exposure in UV chamber, and hair was evaluated for its sensory attributes.

Results of rinse-off conditioner evaluations indicate that silicones show excellent potential for their ability to aid color lock for permanent hair color products. Similar studies are in progress with shampoos to evaluate the usefulness of silicones in maintaining the color of permanent-colored hair.

Market Trends

A survey of global hair care market trends indicates that consumer use of hair colorants has significantly increased over the past three years.¹ Because hair colorants are known to damage the hair cuticle and leave brittle, dull and dry hair, consumers with colored hair seek specialized treatments to maintain healthy colored hair.

Previous studies demonstrate that, when incorporated in permanent or semi-permanent colorants, amodimethicone and its derivatives boost color beauty and help to prevent color fading from washing and UV exposure.²

This article presents the results of a study demonstrating that silicones can help preserve color beauty when incorporated in rinse-off conditioners. It consists of three parts:

- A market study designed to further understand the importance of treatments dedicated to colored hair.
- Development of a test method to ensure that claims related to color maintenance can be substantiated.
- Determination of the best silicone candidates for color lock.

Consumer Requirements

Hair can be subjected to considerable damage over a very short period of time. It can face cycles of bleaching, permanent waving and coloring. Its length might change from short to very long, its form from straight to curly, and vice versa.

In the midst of style and color changes, consumers expect to maintain healthy-looking hair, despite the potential damage brought by treatments such as colorants, bleaches and permanents. The desired look can be achieved by the use of premium conditioning treatments with the objective of protecting or repairing hair without negatively impacting its volume.

Consumer demands give rise to the need for specialized and sophisticated colorant products with a wide range of shades and nuances. Consumers typical-

ly are looking for easy-to-use, convenient products that fit a busy lifestyle, and they value highly differentiated products. They may also seek products that convey a sense of fun and have unexpected textures while still providing sophisticated care.

These trends and consumer requirements challenge formulators to develop products that provide multiple benefits beyond conditioning, such as shine, fast drying, volume, and the perception of moisturization. When viewing commercial shelf space, it's clear that consumer demand has pushed cosmetic manufacturers to create product line extensions, with highly differentiated products that are personalized to the specialized needs of each consumer.

Market Study

In 2002, a market study was conducted using supermarkets, hair salons and Internet web sites. More than 57 products dedicated to colored hair were identified from the top ten hair care manufacturers, showing that this market is mainly composed of shampoos (35%) and rinse-off conditioners (56%), with leave-on conditioners present at 9%.

Claims for color protection were present in only 50% of the products, suggesting that the consumer need for color protection is not entirely fulfilled. Claims related to hair shine were found in 50% of the products, indicating that shine is an important benefit related to the beauty of colored hair. Secondary claims such as hair beauty, strength, suppleness and softness also were found, suggesting that consumers view feel as another important characteristic of colored hair.

The ingredients mentioned in the INCI list for products dedicated to colored hair also were studied and compared to those used in products dedicated to damaged hair. These ingredients were very similar, with the exception of sun filters in some of the products developed for colored hair.

Silicone penetration was found to be already very high, with some products containing more than one silicone. Dimethicone and amodimethicone are the silicones most frequently found in these products.

The market data showed that:

- Today's colored hair care treatment market is mainly composed of rinse-off conditioners and shampoos.
- Claims of color protection are more linked to hair beauty (e.g., shine, softness and suppleness).
- Silicones are already used for benefits other than color maintenance.

These observations suggest that consumer needs purely linked to color maintenance are not fully fulfilled, opening the door to the study of silicones as color maintenance guards. To substantiate consumer-perceivable claims, it was imperative to develop a method that would allow the measurement of color loss in a reproducible manner.

Method Development

A method for measuring hair color from a colorant base using a colorimeter/spectrophotometer is already well established. This approach demonstrated that certain silicones such as Dow Corning® 2-8566 Conditioning Agent, Dow Corning® 2-8177 Emulsion and Dow Corning® 8500 Conditioning Agent are excellent color guards when incorporated in semipermanent or permanent colorants.² This test method was adapted to the objective of the current project related to color maintenance from hair care treatments.

For the current study, we used slightly bleached hair, which provides the best color reproducibility when treated with a permanent colorant. Twenty measurements per swatch were performed in order to optimize standard deviation.

Additionally, we tested parameters such as shine, moisturization perception (feel), volume and combing using methods developed at Dow Corning.

Three parameters that compose the color were studied using the colorimeter:

- L* values indicate the level of darkness (color intensity)
- a* values indicate the redness intensity (from green to red)
- b* values indicate yellowing level (from blue to yellow)

The influence of washes, UV exposure, shampoo and rinse-off treatments were analyzed to understand their impact on hair discoloration. We observed that hair begins to discolor after about 90 hours of UV radiation, which represents four intensive hours of exposure each day for approximately 26 days. This suggests that UV exposure is not the main parameter affecting hair discoloration. Rather, washing is the main parameter affecting fading. Significant color loss could already be observed after just one shampooing. Rinse-off conditioner applications also contribute to hair discoloration. The presence of UV filters in rinse-off conditioners help to protect minor color loss due to long-term UV exposure.

These parameters helped us devise test methods and better understand variations linked to hair discoloration. As a result, silicones could be tested as protective agents against color fading due to shampoo and rinse-off application cycles.

The Solution For Hair Color Maintenance

Because the market study showed that rinse-off conditioners have the highest product penetration, we decided to focus the first part of this study on rinse-off conditioners. Based on the market study, we developed a base formulation using the ingredients most frequently found in current commercial rinse-off conditioners (see Table 1).

Different silicone families were tested, including dimethicone, phenyl trimethicone, amodimethicone and derivatives, alkylmethylsiloxanes, silicone elastomers, a silicone polyether, and a silicone polyamide (see Table 2).

The procedure mentioned earlier in method development was used. Flat, slightly bleached Caucasian hair swatches were colored with a leading brand commercial permanent colorant and treated with 14 cycles of the following steps:

1. Shampooing using a commercial normal hair shampoo (without silicone)
2. Treatment with a rinse-off conditioner (with and without silicones)
3. Exposure for 7 h (~2 days) in a UV chamber

Table 1. Rinse-Off Conditioner Formulation Used to Test Color Retention

INCI Name	Function	Wt. %
Hydroxyethyl cellulose	Thickener	1.5
Cetrimonium chloride	Conditioning/emulsifier	0.3
Cetyl alcohol	Coemulsifier	1.0
Benzophenone-3	UV filter	1.0
Silicone active	Conditioning agent	2.0
Deionised water	Carrier	to 100.0
Phenoxyethanol (and) paraben	Preservative	0.1
Tocopherol acetate	Fortifying agent	0.1
Glycerin	Hydrating agent	1.0
Citric acid	Neutraliser	pH: 3.5

Table 2. Silicone Families Studied

Siloxane Type	Description	Dow Corning Solution
Amine functional	Microemulsion	Dow Corning 2-8177 Emulsion
	Derivative polymer	Dow Corning 8500 Conditioning Agent
	Polymer	Dow Corning 2-8566 Conditioning Agent
Elastomer	In cyclopentasiloxane	Dow Corning 9040 Silicone Elastomer Blend
	Oil-in-water suspension	Dow Corning 9509 Elastomer Suspension
Dimethicone	Divinyl/dimethicone/dimethicone copolymer; > 100,000,000 cSt o/w	Dow Corning HMW 2220 Nonionic Emulsion
Polyamide	Nylon-611/dimethicone copolymer (and) PPG-3 myristyl ether	Dow Corning 8178 Gellant
Polyether functional	PEG/PPG 14/14	Dow Corning 5330 Fluid
Phenyl functional	Phenyl trimethicone	Dow Corning 556 Cosmetic Fluid
Alkyl functional	Cetyl dimethicone	Dow Corning 2502 Cosmetic Fluid

A colorimeter was used for color measurements. Because the hair coloration step is very sensitive, we observed that it is very difficult to obtain swatches with identical coloration. This was perceived visually, but also documented by differing L*, a* and b* values from one swatch to another. To eliminate variations, we adapted the following calculation of L*, a* or b* by:

$$\Delta E = \sqrt{L^{*2} + a^{*2} + b^{*2}}$$

1. calculating the difference between time 0 (colored swatches untreated) and time t (colored swatches treated with a shampoo, rinse-off conditioner *without* silicone and exposed to UV radiation). This was expressed in % versus the starting swatch color at time 0. For example, for the L* value,

$$L^* = \{(L_t - L_0) * 100 / L_0\} \text{control}$$

2. calculating the difference between time 0 (colored swatches untreated) and time t (colored swatches treated with a shampoo, rinse-off conditioner *with* silicone and exposed to UV radiation). Again, for the L* value,

$$L^* = \{(L_t - L_0) * 100 / L_0\} \text{silicone}$$

3. calculating silicone contribution to color maintenance. For example, for the L* value,

$$L^* (\%) = \{(L_t - L_0) * 100 / L_0\} \text{control} - \{(L_t - L_0) * 100 / L_0\} \text{silicone}$$

Results confirmed that amodimethicone is a very good candidate for protecting hair against color fading from washes. These results ensure that the study method was properly designed. However, the use of amodimethicone in shampoos and conditioners is already widely patented.

With the method validated, we next looked at alternative products patented by Dow Corning or having already sufficient prior art. Several also showed excellent color protection:

- Dow Corning® HMW 2220 Nonionic Emulsion (a macroemulsion of ultra high molecular weight dimethicone copolymer)
- Dow Corning® 9509 Silicone Elastomer Suspension and Dow Corning® 9040 Silicone Elastomer Blend
- Dow Corning® 8178 Gellant (a silicone polyamide)
- Dow Corning® 8500 Conditioning Agent (an amodimethicone derivative)
- Dow Corning® 5330 Fluid (a silicone polyether)

Table 3 summarizes the silicones that are useful for maintaining each of the three color components. Different silicones affect the durability of color-treated hair in different ways.

Several explanations suggest why silicones are good protective agents against color fading:

- Although most colorant does not penetrate the hair cuticle, a portion remains on the upper layers of cuticle and can easily be removed when hair is washed. When deposited on hair, silicone forms an external homogeneous film that helps color stay on the hair.
- In many applications, silicones act as a synergistic agent. For example,

Table 3. Comparison of Color Improvement Using Various Silicones

L* (darkness)	B* (anti-yellow)	A* (redness)
<ul style="list-style-type: none"> • Dow Corning 2-8177 Emulsion • Dow Corning 2-8566 Conditioning Agent • Dow Corning 8178 Gellant 	<ul style="list-style-type: none"> • Dow Corning 2-8177 Emulsion • Dow Corning 2-8566 Conditioning Agent • Dow Corning 8178 Gellant • Dow Corning 9509 Elastomer Suspension • Dow Corning 9040 Silicone Elastomer Blend 	<ul style="list-style-type: none"> • Dow Corning HMW 2220 Nonionic Emulsion • Dow Corning 5330 Fluid • Dow Corning 2-8177 Emulsion • Dow Corning 8500 Conditioning Agent

quaternary agents condition hair in synergy with silicones. It has also been suggested that a synergistic deposition mechanism between the colorant and the silicone can occur. This would lead to a redeposition of the colorant in the presence of silicone when hair is washed.

- Silicones have very low surface tension and help the colorant spread on hair and form a homogeneous film. In addition, because of this spreading behavior, silicone may help the colorant further penetrate the hair cuticle.

Based on sensory evaluations, we observed that the silicones tested did not negatively affect hair volume but provided a smooth, nongreasy feel, with what we referred to as “ultra” shine, and improving wet detangling.

Conclusion

In conclusion, we observed that:

- The hair colorant market is global in expansion, fueled by a proliferation of consumers with colored hair, an increase in coloration frequency and a wide range of color shades (from nuance to extreme).
- Consumers are seeking color intensity and beauty.
- Color maintenance and shine are the most important claims of color protection treatments.
- Color beauty is mostly affected by washes.
- Silicones are currently used for benefits other than color maintenance. This study helped identify new silicone families to preserve color and go beyond conditioning to provide ultra shine, improved drying time, moisturization, styling benefits, and a smooth and light feel without negatively impacting hair body and volume.

We also demonstrated that Dow Corning proposes a broad solution offering from formulation ideas to substantiated consumer benefits and claims with innovative technologies. In addition to Dow Corning® 2-8566 Conditioning Agent and Dow Corning® 2-8177 Emulsion, other silicone materials that show promise for use in these applications include silicone polyether (Dow Corning® 5330 Fluid), an emulsion of ultra high molecular weight dimethicone (Dow Corning® HMW 2220 Nonionic Emulsion), silicone elastomers (Dow Corning® 9040 Silicone Elastomer Blend and Dow Corning® 9509 Silicone Elastomer Suspension) and silicone polyamides (Dow Corning® 8178 Gellant).

References

1. Euromonitor Cosmetics and Toiletries (2002).
2. Gomes, A., et al., The use of silicones in hair colorant formulations, Dow Corning white paper (2000).

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