

Formulating Green Personal Care Products

Hair Care

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5.1 Introduction

Many formulators aim to create greener products, but the first question always is, Where to begin? In this chapter we discuss the history of hair preparations, pointing out that as synthetic chemicals are a relatively recent development, we have a huge back-catalogue of “green” hair preparations to learn from. We also discuss some of the ways that modern hair care products can be made greener. This task is not easy, but please do not be discouraged. Creating a green and sustainable agenda for hair care products represents one of the most exciting and challenging areas in formulation science. The range of products available for cleaning, styling and conditioning hair are considerable and consumers expect these products to perform well. The successful greener products must therefore be equal to or better than the products currently available. This means that hair care is the part of the personal care industry where the versatility and usefulness of plant derived alternatives to synthetic ingredients can be particularly well showcased.

It is important first to define the criteria for improving the green credentials of a product, in order to ensure that the formulation strategy meets the brand’s expectations.

For the purpose of this chapter, “greening of hair care” is defined as follows:

- Increasing the amount of sustainable plant derived material in the formula
- Improving biodegradability
- Reducing water content
- Reducing the generation of hazardous materials

Issues such as not using ingredients that have been tested on animals for cosmetic purposes, selecting materials that are made without using genetically modified organisms and preferring those that are produced via a Fair Trade or Community Trade agreements are not covered, but it is hoped that formulators setting out on the path to become greener will also consider these issues. Self-preserving formulas are, however, discussed, not because it is believed that parabens and other unpopular preservatives should be excluded from greener hair care products, but because it is understood that formulators are now finding themselves under pressure to develop products that are green and preservative-free.

5.2 Hair Care Market

The vanity of humans is such that the global hair care market is now valued at around \$4.7 billion (www.cosmeticsdesign-europe.com/Products-Markets/World-hair-care-market-victim-of-its-own-success). There are a vast number of different products used in hair care. The most common are shampoos, conditioners and treatments, as well as hairstyling preparations including setting lotions, mousses, hair sprays, lacquers, gels, gums, putties, waxes, lotions, serums, creams and pomades. Then there are also hair coloring, waving and straightening preparations. These hair products are designed to do many different things. They can clean, protect, add fragrance, give shine, give volume, improve mechanical strength and ease of combing, straighten or hold curls, and enable elaborate hair styles, condition hair and

color. The efficacy of most of these modern products is due to synthetic materials, which are excellent at doing what is required and are unfortunately often far from being green.

Hair care is a mature market, where manufacturers need to stretch themselves to remain competitive. Many companies are trying to win customers by emulating the success of the “natural” skin care market (see **Chapter 6**); however, they have two major constraints. Firstly, they dare not sacrifice product performance in order to become greener, and secondly, because the consumer expects to pay far less for hair care products than they pay for skin care products, hair care formulators will not necessarily be able to afford the more expensive green actives. For example, materials such as non-animal derived sodium hyaluronate can be found in hair products that retail for ~ \$40.00. Mass-market brands retailing at approximately \$5.00 would find it far too expensive to use said material at effective levels. That said it is interesting to note that Beiersdorf recently launched its mass-market Nivea diamond gloss shampoo, which is enriched with precious diamond particles. The ingredient listing clearly shows that the formula really does contain diamond powder, which is an expensive ingredient you would not expect to find in hair care products, and as it has no obvious benefits to hair care beyond giving the product the perception of luxury and shine, it is a very brave addition.

5.3 Tried and Tested Hair Care Ingredients

People have been caring for their hair for far longer than they have been making chemicals so logically there must be a huge back-catalogue of tried and tested green materials that can be considered when formulating green hair care products. The earliest hair preparations were likely to have been made with local, nonsynthetic materials and therefore they were truly green. The current debate on the causes of global warming has made the public very aware of the cost and implications of transporting materials across long distances. The fuel required to move materials adds to a product’s carbon footprint, thus reducing its greenness. Finding out about the traditional uses of local

materials, is therefore a good starting point for small- and medium-sized companies.

The hair care industry is global so it is not always easy for the large international companies to know what the term *local* means. Also, it is worth remembering that transporting a natural material from farther away may not be bad. For example, it would be worthwhile if a poorer community were benefiting from the trade. Furthermore if the material has been traded over long distances for thousands of years, it is likely to be special in some way. Fashions come and go but materials that have been used for generations have stood the test of time and are therefore likely to be potent. Traditionally traded materials have key properties. For example, frankincense, which has been traded on the Arabian Peninsula and in North Africa for more than 5,000 years, is a very important ingredient used in perfumery. Today the greener companies such as Neal's Yard Remedies follow the ancient tradition and use wild-harvested frankincense from Somalia. Tapping the resin from the frankincense tree causes the minimum impact to the tree and allows it to continue growing and providing more resin. The collective experience of our ancestors has left us a legacy of traded materials that have become strongly associated with hair care. These materials have great green credentials and can become the cornerstone of greener hair care products.

Table 5.1 breaks down natural, botanical materials commonly associated with hair care, alongside a brief description of their traditional individual uses.

Table 5.1 Examples of botanicals historically associated with hair*

Natural Material	Traditional use in hair care
Arnica <i>Arnica montana</i>	Traditionally a tincture is applied to the scalp to encourage hair grow.
Bearsfoot root <i>Polymnia uvedalia</i>	Often included in American hair ointments and lotions. Applied externally to stimulate hair growth.

Natural Material	Traditional use in hair care
Chamomile <i>Matricaria recutita</i>	Used for centuries to add luster and to bring out the highlights in blond hair. The active is trihydroxyflavone (apigenin). It is too large to penetrate hair. It coats the hair, giving a yellow cast. It often is used as a rinse after shampooing or added to hair brightening shampoos for use on blonde or light brown hair.
Castor Oil <i>Ricinus communis</i>	Castor oil is used to give shine and to encourage hair growth. Used in hair straighteners and dressing oils. Liquid brilliantines can be 15% castor oil
Citrus Fruits (Lemons, limes etc.)	Since the time of the ancient Egyptians, citrus juice has been used to clean hair and to leave hair shiny and smelling fresh. When soap was used to clean hair, citrus juice was used to rinse away the lime soap left deposited on hair that dulled it.
Elder <i>Sambucus nigra</i>	The Romans used elderberry juice as a hair dye. Nicolas Culpepper wrote in the 17th century that “the hair of the head washed with the berries boiled in wine is made black.” The seeds are rich in undecylenic acid and the juice contains tannins which can inhibit microbial growth, including fungal growth.
Field Larkspur <i>Delphinium Consolida</i>	A tincture made from the seeds is used to destroy lice and nits in the hair.
Great Mullein <i>Verbascum</i>	The boiled flowers produce a yellow stain. Dilute sulphuric acid, turns the yellow stain to a permanent green color, which then turns brown in alkalis. Roman women used infusions of the flowers to dye their hair a golden color. Lyte tells us, “the golden floures of Mulleyn stiped in lye, causeth the heare to war yellow, being washed therewithal,” and according to another old authority, Alexander Trallianus, “the ashes of the plant made into a soap will restore hair which has become grey to its original color.”
Tragacanth gum, Karaya gum and Gum Arabic.	Natural gums are used to set hair and as protective films – tragacanth gum is a white powder from Turkey, gum karaya from India (gives a softer film than gum tragacanth), and gum arabic comes from Western Africa.
Juniper <i>Juniperus</i>	The ancients used juniper berry juice to darken the hair and kept it from turning grey.

continues

Table 5.1 Examples of botanicals historically associated with hair**(continued)*

Natural Material	Traditional use in hair care
Henna <i>Lawsonia Inermis</i>	Henna India was used in India as early as 400 AD. The lawsone dye derived from the henna plant imparts a reddish cast to the hair. Henna enhances also gives hair an attractive shine.
Honey	Used to improve dry hair.
Indigo <i>Indigofera Tinctoria</i>	Combined with henna (Persian henna) to give a permanent black dye. Black henna or neutral henna are made from indigo. Indigo dye is now made synthetically from naphthalene.
Jasmines <i>Oleaceae and Jasminaceae</i>	Jasmine is used in India to make perfumed hair oils. The scent is absorbed by sesame seeds. The fragranced seeds are then pressed to make the oil. Interestingly, in Borneo women put Jasmine blossoms in their well-oiled hair at night.
Lavenders <i>Labiatae</i>	Lavender oil adds fragrance, and the oil from <i>Latifolia</i> or <i>Spica</i> is claimed to promote hair growth.
Lettuce <i>Lactuca sativa</i>	This is an ancient treatment used to stimulate hair growth. The Egyptians applied chopped lettuce patches to bald spots. Lettuce was associated with Min, the Egyptian god of virility.
Mustards <i>Brassica</i>	Oil expressed from the hulls is used to promote hair growth.
Nettles <i>Urticaceae</i>	Key ingredient in hair tonics designed to prevent hair loss and leave hair soft and glossy. Tonics can be made by simply simmering the leaves in water or boiling the entire plant in vinegar and water.
Olive <i>Olea Europaea</i>	Used to help condition hair and to make it shine. Olive oil oxidation on the hair results in yellowing.
Rosemary <i>Rosmarinus officinalis</i>	Used as spiritus Rosmarini, in hair growth stimulating lotion designed to prevent premature baldness. Rosemary infusions made with borax were used to clean hair and prevent scurf and dandruff.
Common sage <i>Salvia officinalis</i>	A strong infusion is applied to the scalp, to darken the hair.

Natural Material	Traditional use in hair care
Scotch Thistle <i>Onopordon acanthium</i>	Pliny the Elder states, and mediaeval writers repeat, that a decoction of thistles applied to a bald head would restore a healthy growth of hair.
Sugar (sucrose)	Used to set hair styles.
Shellac	Used to hold hair and add shine. It is produced by female lac insect (<i>Iaccifer lacca</i>) to surround her eggs which are laid on certain Indian, Malaysian or Thai trees. It forms a slightly yellowish very brittle film.
Walnut <i>Juglans nigra</i>	Culpepper wrote that “walnut ... being taken in red wine, and stay the falling of the hair, and make it fair, being anointed with oil and wine. The green husks will do the like, being used in the same manner.” The crushed unripe walnut shells produce a brown color. That is used to deepen the color of dark brown hair. Walnut or indigo when added to henna make hair black and brown.
Yucca <i>Ornithogalum</i> <i>Liliaceae</i>	Over the deserts of the southwestern United States and Mexico, the tuberous rhizomes of large species of Yucca (also belonging to the order <i>Liliaceae</i>) are called Soap Root, and have the same uses as those of the Californian variety of <i>Ornithogalum</i> . There is said to be no better tonic or stimulant for the hair than a free application of a solution of this juice in alcohol, water, or glycerine. Besides the Saponin, it contains a large number of raphides, which probably add mechanically to the stimulation.

*The information contained in this table was taken from A Modern Herbal, first published in 1931, by Mrs. M. Grieve. The reader is encouraged to contact expert ethnobotanists or do their own research using historic and ethnobotanical literature, as it is not possible to list all the botanicals that have been associated, throughout history with hair care in this chapter.

Multinational companies benefit from their strong buying power and their efficiency. Formulating fewer products for larger markets allows them to take advantage of the economy of scale. Also, the well travelled, loyal customer expects to find their favorite products behaving the same wherever they are purchased. Developing products designed to use the materials available in each local area where a multinational operates has been considered and is occasionally practiced but because it requires extra staff and can incur technical problems, it has not become common practice amongst the multinationals.

Thankfully, it is far easier for small companies to take advantage the local natural resources. This is one of the niche markets that are difficult for the multinationals to control.

5.4 History of Hair Care

5.4.1 The Ancient World: Egyptians, Greeks and Romans

The vanity of humans is also such that the manipulation of one's appearance can be found amongst some of our earliest records. For example, hieroglyphic writing has lead experts to believe that ancient Egyptians would wear wigs, shaving their heads (or cutting their hair short), possibly to prevent infestation. Artifacts from the Egyptian Bronze Age include razors (circa 3,500 BC) and there are images showing shaving and the nobility wearing heavy, curly black wigs in ceremonies. Traces of resins, myrrh, and aromatic woods, palm oil and wine have all been found in ancient tombs. It is believed that materials such as beeswax, henna and fragrant substances made by steeping botanicals and or gum resins in oil, were used for hair care. Henna paste is simply made by mixing the dried leaves of Egyptian private *Lawsonia alba* with water. Its use is very green and remains popular today. Henna stains hair with a reddish hue. The exact color depends on when the leaves are harvested, the pH and what other botanicals are included in the paste. Young immature leaves are used for green henna, which yields the more delicate shades. The active is lawsone, which is a progressive dye, i.e. it is small enough to penetrate the hair where it is slowly oxidized over one to two days to become a larger molecule trapped in the hair and seen as permanent color. Henna is perfect for shampoos for lifting brown, chestnut colored hair, giving it auburn highlights. Hennaed black hair has red highlights, which are seen best when strong light hits the hair.

The red shades produced by henna alone can be modified by including:

- Alkaline substances to make hair browner
- Acid (acetic acid) to make Hennaed hair redder

- Metallic salts (copper or silver) and pyrogallol to make hair blacker and or more brown
- Adding vegetable dyes such as walnut or indigo also makes the hair blacker or browner

The beeswax and resin found in ancient Egypt are thought to have been equivalent to modern setting lotions. Grey hair was treated then with finely ground horn or with products made by boiling ox blood together with oil. Although it is believed they often shaved their heads, ancient Egyptians had treatments for baldness. These were based on astringent plants such as Juniper berries and also included chopped lettuce. Hieroglyphics clearly show the ancient Egyptians rubbing oils (believed to be castor oil and olive oil) into their hair and scalps. Some ancient Egyptians used a naturally occurring salt, which largely consisted of sodium carbonate and sodium bicarbonate, mixed with oils and talc for cleansing their hair and bodies. We've even learned that the ancient Egyptians concocted potions using hippopotamus fat to control dandruff.

Records from ancient Greece show that citizens shaved their heads in order to improve their appearance and so it would be churlish not to credit the early Greek barbers with being the forerunners of our modern hair care industry. Experts generally consider that the golden age of ancient Greece is the origin of many of today's hair styles. Some of the most prized ancient Greek art depicts men and women using hairbrushes and carefully curling their hair into ornate styles. These detailed images show ancient Greek women with long braided hair, frequently arranged on top of the head or in ponytails. These styles benefited from being set in some way and there is evidence that also used were setting lotions based on gums.

The ancient Greeks generally had dark hair and they felt the rarer blond hair was goddess-like; it is therefore not surprising to discover that hair lighteners are amongst the earliest recorded Greek hair preparations. They made their hair color lighter using solutions of potassium salts, yellow flower petals and even pollen. They deliberately sat

in the sun after these solutions had been applied to help bleach their hair; however, as they also wanted fair complexions, they must have taken great care to keep only their hair in the sun. This type of hair lightening must have been successful as there are also 4th Century BC records of hair was being lightened using similar ointments. These are based on olive oil, citrus juice and pollens. Some of these preparations even included metallic gold dust. Similar materials are used today; however, it is worth noting that gold was voted “Allergen of the Year” in 2001 by the American Contact Dermatitis Society. It not surprising therefore to find that gold is now more commonly found in a product’s name than in its list of ingredients.

Hair played a major role in ancient Greek rituals. An jar from ancient Greece, owned by the State Hermitage Museum in St. Petersburg, Russia, clearly shows liquid being poured from an urn onto a young man’s long hair, while a winged angelic figure looks on. We know that washing and cutting hair was part of the “rites of passage” practiced by the ancient Greeks. It is hard to be exactly sure about all the materials used at that time but there are records of olive oil, lanolin and citrus extracts and juices being used on hair. They also tried to fight hair loss using remedies based on botanicals such as wormwood.

Complicated hair styles were also popular in ancient Rome. Dyes were made by boiling walnut shells with various other plant materials. A raw egg applied to hair and combed through with a lead comb to form lead sulphide deposits would have turned grey hair black. Metallic salts are small enough to enter the hair. Copper and iron salts have also been used through the ages to color hair. The Romans seemed to prefer golden-red hair and the richer ladies were prepared to go to great lengths to get the hair color they desired. Ovid wrote a poem that when roughly translated (Guy Lee, Viking Press, 1968) goes as follows: “I told you to stop using that rinse, and now you have no hair to tint. Why couldn’t you let it be? You’ve only yourself to blame. You were asking for trouble applying that concoction. But thanks to our German triumph you’re quite safe. One of the women prisoners can send you hers.” The poem suggests that the dye mixtures being used could be so strong that overuse might cause more harm than good!

Personal care was important to ancient Roman society, and many within enjoyed communal bathing. The term “spa” comes from the roman *Sanus per Aquam*. Wherever the Romans settled they introduced their favorite Mediterranean plants, such as lavender. Lavender oil was used to clean hair as well as for general cleansing. Beer, vinegar and lemon juice were also used by ancient Romans to help keep their hair color. Their hair setting solutions could be made from egg white and gum arabic.

5.4.2 Ancient China and the Far East

Whole books have been written on ancient Chinese customs. For long periods unmarried Chinese women wore their hair long and braided, whereas older women would tie their hair back in knots. The comb was special in ancient China. They could be made from gold, jade, ivory, hawksbill shell and rare woods. The rarest combs, used only by ladies in the imperial court, were from exotic sources such as rhino horns. The rhino horn, like ox horn, was believed to reduce heat and toxic materials from the blood and cure headaches. Dandruff treatments included using combs made from horn. One of the oldest Chinese pharmacology texts, the *Bencao Jing*, mentions lovage root extract being used on the scalp to invigorate blood and improve circulation. Dull hair could be restored using preparations based on red ginseng (*Panax Ginseng*), and Chinese knotweed (*Polygonum Multiflorum*) was used to blacken hair. Hair could be cleaned using gleditsia fruit mixed with spices and fragrances. Jasmine and Mandarin were popular fragrances in ancient China.

Shaved heads and short stiff pony tails are how ancient Japanese men are portrayed. However, like most human societies, hair was important and there were times when high rank and beauty was associated with longer hair. Long loose hair became far more ornate in the 17th century and was heavily lacquered. Early hair lacquers were made from natural polymers such as shellac and vegetable gums; gum arabic and gum tragacanth gum are especially effective. In the mid 20th century, Helene Curtis (now part of Procter and Gamble)

introduced *Spray Net*, which was one of the first synthetic versions of hair lacquer. The scented synthetic polymer could be sprayed more easily and kept the hair stiff and firm. *Spray Net* was also claimed to include actives that stiffened hair by lowering the amount of minerals in the hair root. Successful hair sprays used today are mainly based on scented, strong flexible synthetic polymers such as polyvinylpyrrolidone, copolymers with vinyl acetate and copolymers with maleic anhydride, and include silicones that make the hold last a bit longer and give shine. When greening these formulas, it is sensible to consider the natural polymers used in the ancient recipes for hair lacquers but also to remember that the performance of hair sprays has advanced. Simply going back to the products from the past will not be acceptable.

5.4.3 The Middle East and Spain

A cosmetics school was started by Ziryab in what is now southern Spain in the ninth century. Artifacts such as soap moulds and records show that Muslim chemists had replaced cruder soap-like products with more sophisticated fragranced, colored soaps bars and liquid soaps. They used vegetable oils including sesame oil and olive oil, and aromatics such as thyme. Al-Razi (865–925), is given credit for being the first chemist to formulate these soaps. Al-Zahawi wrote in his book, the *Kitab al-Tasrif*, (known in Europe at that time as *Concessio ei data qui componere haud valet*), descriptions of hair dyes that changed blond to black and hair waving lotions. His hair care products included ingredients such as rose water and essential oils. Middle Eastern literature is therefore strongly recommended as a source of inspiration for greening modern products. When discussing the history of this region it is important to mention henna. This plant has long been popular in the Middle East. Persian Henna has been used continually since ancient times, and in the late 15th century it is clearly depicted being used to stain womens' hands and feets in the surviving art.

5.4.4 Medieval Europe and the “New World”

Spanish records of hair tonics being made from boiled quince fruit peel in medieval times and images of hair washing can be found in many historic European documents. Medieval woman are pictured washing lice out of hair. It is likely that the figures are “wise women” and the “wash” would have been based on harsh lye soap mixed with local herbs. These hair cleaning remedies were green shampoos in all but name. Fairer hair has continued to be popular amongst Europeans throughout the ages, and bleaches made by combining various yellow flowers, and even saffron with pungent plants such as onions, are to be found amongst early treatments.

Adventurers and explorers brought ideas and materials back from wherever they ventured. They observed the behavior of indigenous people in the New World and either emulated or adapted it to better suit their own ways. Lovers of chocolate have to thank Don Cortes for bringing cacao back to Spain in the 16th century and making it sweeter to suit European tastes. Europeans went on to introduce their preferred botanicals such as sugar cane and cacao trees into Africa, as well as into countries such as the islands of the Caribbean, Malaysia and, later, Australia. Products using exotic naturals are still very much in vogue today, but their peak of popularity must have been when the New World was first being discovered. The Spanish were responsible for introducing many Mayan, Incan and Aztec materials including avocado, which was believed at first to be “skin food” and remains popular today for many uses, including hair conditioning. Later, South American cinchona bark (named by Linnaeus after the Countess of Chinchon, the wife of the viceroy of Peru who was said to have used it to cure a life-threatening fever) was used in hair treatments as an astringent. Today we use many other South American botanicals including Brazil nut oil and babassu oil hair care products.

In the 1700s, Native Americans living in the Sonora desert in what is now Arizona were seen by Father Junipero Sierra to be pressing a rich material from jojoba seeds and using the liquid to improve dry skin and hair. Jojoba oil was later shown by chemists to actually