

Hair Care Feature

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World-wide the hair care market is worth about 60 billion \$US of which about 12 billion \$US is spent on hair conditioners. Hair condition is measured by its strength, its gloss and its ease of combing. Loss of strength is attributed to environmental factors, mechanical and chemical damage and to diet and physiological stress. Natural hair shine is the result of a smooth hair fibre with an intact cuticle. Mechanical damage is caused by resistance to combing, which causes cuticle to be broken and chipped, and chemical damage is caused by oxidation hair dyes and bleaching compositions and by permanent waving. It can also be caused by poor shampoo products and it is the author's contention that use of a well-formulated shampoo virtually negates the need for a conditioning rinse.

Hair on a healthy human head grows by approximately 0.35mm per day so hair that is allowed to grow unchallenged for a year may be 100mm in length and 500mm after five years. When a hair follicle is first generated in the dermal papilla it is composed of three concentric layers. The medulla is the innermost layer and is not affected by hair care products or processes, the middle layer is the cortex which contains the pigment and can be modified through dyeing, bleaching, perming and straightening, and the outer layer is the cuticle, made up of tiny overlapping scales that protect the cortex. The hair shaft is lubricated as it emerges from the dermis by the sebaceous gland that produces sebum, which conditions the hair and skin.

Because each hair grows for many years it will be shampooed, conditioned, styled, cut and exposed to sun and wind innumerable times and may also frequently be blown dry, coloured, bleached or permed during its life cycle. Fortunately none of these treatments affects the growth of the hair in the hair bulb, even though some may seriously damage the hair shaft. The first signs of loss of condition are a roughness of the cuticle, caused by it being raised from the shaft and breakage along its edges. Eventually whole areas of cuticle may be lost and the hair loses its sheen and becomes dull, is rough to the touch and difficult to comb.

Mechanical damage caused by combing or brushing is a major cause of cuticle loss. Dry combing of hair leads to cuticle thinning or abrasive damage, and wet combing results in cuticle breaking or ablative damage. There have been several studies published in the Journal of Cosmetic Science on the subject. C. Robins [Ref 1] evaluated hair breakage by combing tresses and examining photographs of snags of hair fibres in combs. Robins reported that breakage involves hair-on-hair interactions, and broken fragment size suggests that breakage occurs primarily at or near the hair-comb interface.

Dr Alan Swift is well known for his studies of hair damage using a scanning electron microscope and his illustrated papers on the subject [Ref 2, 3] are well worth studying by all interested in hair product formulation. In the first paper Swift reported that sometimes the cuticle has been completely eroded away to reveal the underlying surface of the hair cortex at the tip ends of long hair. Rates of cuticle loss are greater when hair is combed in the wet than in the dry state and the rate of loss during wet combing is reduced if a conditioner is applied. It is generally accepted that the beneficial effects of the conditioner are in this case due to a reduction in the frictional forces between the comb and the hair surface. Dry combing of tangled hair can lead to massive localised loss of cuticle; wet combing of tangles is even more disastrous in this respect.

Swift also noted that increased rates of cuticle loss can be caused by previous toiletry treatments such as bleaching or permanent waving or by exposure to sunlight and he developed this further in the second paper [Ref 3]. Swift advanced the idea that at the hair's

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root end the non-keratins are the components normally plasticising the fibre against longitudinal shear stresses and these components are able to elastically accommodate shearing stresses between the much stiffer macrofibrillar elements. He also suggested that high environmental humidity increases this plasticity; the converse being that at low humidity the non-keratins, and the hair as a whole, will be more susceptible to longitudinal shear stress fracture. Free radicals attendant upon sunlight irradiation of hair introduce new and non-specific chemical cross-links into the hair's proteins. The effect of this will be proportionally greater in the non-keratins than in the keratin composite, given that initially the former contain far fewer chemical cross-links whilst the latter are heavily cross-linked by cystine disulphide bonds. Thus with increasing sunlight exposure the non-keratins lose their plasticity and become brittle.

Changes in hair as people age are also apparent and a study of the volume and bounce decrease in hair with ageing [Ref 4] found that this is not only caused by a decrease in hair diameter and fewer hairs per square centimetre of scalp but also by some internal changes in the hair. This reflects the comments by Swift that there are changes in cross-links between amino acids within the hair after exposure to solar radiation. There is also a loss of colour with age, caused by exposure to sunlight and loss of melanin. Melanin absorbs UV radiation and converts it into heat. Because of this, melanin provides a photochemical protection to natural hair colour and hair proteins and prevents their photodegradation. However, melanin pigments act sacrificially and become themselves degraded in the process of protecting the proteins from light. As a result, the protective effect of melanin pigments is lost and hair proteins undergo photo-oxidative cross-linking into higher molecular weight species [Ref 5]

The other major cause of hair damage is chemical processing. Two commonly used methods are permanent waving and hair colouring; both of which include an oxidation step. Permanent waving involves breaking cystine bonds with a strong reducing agent such as thioglycolic acid then restoring them by treatment with an oxidising agent, usually hydrogen peroxide. Not all the bonds are restored, resulting in a reduction in hair strength and delaminating of cuticle in large fragments. Treatment with hydrogen peroxide in a bleaching or hair lightening process can break down cuticle into small fragments

These causes of hair damage leading to poor hair condition and a loss of shine can be largely mitigated by the use of carefully formulated cosmetics. The use of a good quality shampoo is the first stage and mild surfactants were described in recent articles in SPC. This article will look at shampoo additives and post-shampoo products with particular emphasis on those that reduce hair damage and impart shine and gloss to hair.

There are various conditioning aids that may be added to the shampoo, usually a cationic polymer or a silicone compound. One of the most popular additives remains guar hydroxypropyltrimonium chloride, which is compatible with anionic cleansers but can present problems of solubility and clarity. The **AquaCat** series from **Aqualon** provides guar hydroxypropyltrimonium chloride in solution that is easy-to-handle and odour-free. It provides clear cationic conditioning to improve wet and dry combining of hair without build-up. The iC grade with Polyquaternium-7 also provides better colour retention than Benzophenone-4.

Two shampoo additives from **Alzo International** are polymers of isophorone diisocyanate (IPDI) and co-additives to provide differing functions but the same key properties of thermal

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stability, resistance to hydrolysis at extremes of pH, ease of use, effectiveness at low concentrations and superior substantivity. **Polyderm PPI-SA-15**; INCI: PEG-15 soyamine/IPDI copolymer; is a water-soluble hydroxy amine conditioner based on soya and **Polyderm SI-WS**, INCI: Bis-PEG-15 dimethicone/IPDI copolyol; is a water-soluble silicone copolyol emollient.

AC Polytherm, INCI: Diethylene glycol/DMAP acrylamide/PEG-180/HDI copolymer and dimethicone, from **Active Concepts** is a modified hydrophilic urethane polymer with silicone groups attached that is water-soluble, prevents moisture loss and protects the hair against heat styling. Its specific chemistry gives it the ability to absorb heat as well as seal in moisture, where it is able to almost completely retard the moisture loss from heat styling, so will also help with hair plumping.

Abil UV Quat 50, INCI: Polyquaternium-19, from **Evonik** is compatible with anionic surfactants so may be used in hair conditioning shampoos as well as conditioning rinses to provide efficient protection of the hair against UV-damage. As the product is cationic, it is substantive to hair keratin, forming a thin protective layer which absorbs damaging UV irradiation. **Crodasoft SCQ** from **Croda** is a mixture of Quaternium-91 and PPG-3 benzyl ether myristate that is suitable for adding to shampoo formulations to enhance hair softening and provide excellent wet and dry combing properties.

In response to the current interest in ingredients of natural origin that provide more than just label dressing **Gattefosse** have launched **Fruit Secrets**; a number of concentrated extracts rich in active substances such as vitamins, polyphenols, enzymes or fruit acids. All are suitable for shampoos; Apple Secrets is recommended for strengthening and volumising hair while Lemon Secrets and Orange Secrets are said to add shine and condition. A novel idea from the same company is **Original Extracts** as a substitute for the water normally used in cosmetic products. Water is obtained from fruits by flash distillation and supplied complete with all the natural trace elements, mineral salts and essential oils to be found within the fruit. The extract from grapefruit is said to be particularly suitable for adding gloss to hair when incorporated in shampoo.

Greentech also provide natural extracts for hair including Hibiscus sabdariffa (Karkade) extract to add lustre; Linden extract to improve hair volume and moisture content and to reduce static. A mixture of Ascophyllum, dulce, Irish moss, Neptune kelp and Wakame extracts are suggested for general hair conditioning. **Equisol** from **Variati & Co** is an extract of Equisetum arvense (horsetail) that contains high levels of silicon for cell restructuring and strengthening of hair. **Ace Bamboo Bioferment** from **Active Concepts** also has a high content of silica, is water-soluble and is offered as a natural alternative to silicone for shampoos and conditioning aids.

Hydrolysed proteins remain one of the most popular conditioning additives for shampoos and conditioners. They can be from many sources but have in common an affinity for areas of damaged hair, have film forming properties and hold moisture and provide shine. **Vari-Ker 100** from **Variati & Co** is described as a purified keratin lysate with hair restructuring and reinforcing properties specifically designed for leave-on conditioners and masques. **Vari-Ker WL** is wool based hydrolysed keratin, soluble in water and suitable for rinse off products and particularly for dyed hair treatment products. **Vari-Silk** is hydrolysed silk proteins in dry or aqueous formats to give enhanced moisturising and film forming properties.

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Also originating from silk, **Seriseal** from **Chemunion** is derived from sericin, a protein which acts as a cement between silk fibres. It is an aqueous solution of sericin with polyquaternium-7 and guar hydroxypropyltrimonium chloride, cetrimonium chloride and behentrimonium chloride in nanoparticle form and it has a very high affinity for human keratin. The nanoparticles also provide a greater surface area for adsorption. Seriseal has an anti static effect and promotes straightness and shine to hair.

Milk proteins are a source of essential amino acids required for the production of collagen, elastin and keratin. **Vevy EPCH** is hydrolysed milk proteins said to help repair split ends and improve hair damaged by dyeing and permanent styling. **Lactofil Moist** from **Gattefosse** is a milk based product which has excellent adsorption properties and creates a moisture absorbing film.

Cashmere has a particular appeal; it is the wool from Kashmiri goats and **Active Concepts** breaks it down by hydrolysis to produce **AC Cashmere Protein**; consisting entirely of water-soluble amino acids, it forms a highly hygroscopic film on hair, improves combing and adds shine. **Croda** also offer hydrolysed cashmere proteins among a number of others including ones based on cotton, Brazil nuts, milk, soya and wheat.

Combining the attraction of hydrolysed keratin, amino acids and silicone with controlled release based on a sub-micron delivery system, **Salvona** offer **HydroSal Silk** comprising acrylates/C12-22 alkyl methacrylate copolymer with PVA, keratin, hydrolyzed keratin, phenyl trimethicone, polyvinyl acetate and silk amino acids. This multifunctional product is described as a system infused with a unique protein-based active to protect the hair from aging. It shields the hair from the damaging effects of the environment including; UV light, pollution, chemical treatment, styling and cleansing, which cause a high level of protein degradation and lipid depletion, damaging the hair surface and speeding the aging process.

The first requirement of a hair conditioner is to reduce cuticle loss when wet or dry combing so detangling, lubricity and an acidic pH to lay flat the cuticle are the main criteria with added moisture content, extra volume, improved gloss, protection against colour loss and sealing of damaged areas on the hair shaft important attributes.

There are many materials offered for hair conditioners. Traditional ones have been based on alkyl trimethylammonium chlorides such as cetrimonium chloride but they are corrosive materials and Colipa Opinion No P 72 adopted by the SCCP in March 2007 states that the sum of the cetrimonium and steartrimonium chloride concentrations should not exceed 0.5%, and the total sum of behentrimonium, cetrimonium and/or steartrimonium chloride should not exceed a maximum level of 3%. Although only an opinion at this stage it is wise to move away from these materials. One alternative is to use the methosulphates, which are readily available and of which I have 43 listed besides cetrimonium, behentrimonium and steartrimonium methosulfate.

A methosulfate is part of **Fancor Anti-aging Hair Complex** from **Fanning Corporation**, a mixture of Crambe abyssinica seed oil, PEG-2 -dimeadowfoamamidoethylmonium methosulfate and hydrogenated polyisobutene. It is claimed that this blend of ingredients improves hair appearance and texture. The Crambe abyssinian seed oil moisturises and provides added lustre and emolliency while hydrogenated polyisobutene provides shine and slip and PEG-2 dimeadowfoamamidoethylmonium methosulfate enhances conditioning and durability of hair colour.

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Also incorporating a *Limnanthes alba* (Meadowfoam) derivative **SalSphere Vita Hair** from **Salvona** is said to be a unique composition of botanicals consisting of grape seed, meadowfoam, and mango that work synergistically to protect, nourish, and revitalise the hair and the scalp. SalSphere consists of solid hydrophobic submicron spheres that have a high cationic surface charge that enhances the deposition and retention of the botanicals onto hair and scalp from wash off applications. Also providing controlled release conditioning **Hairspheres AG**, INCI: Aqua, polyglyceryl-3-distearate, polysorbate 60, myristic acid, palmitic acid, stearic acid, guar hydroxypropyltrimonium chloride, wheat triticum vulgare flour lipids and avocado (*Persea gratissima*) oil, utilises Spherulite technology.

Because of their comparative mildness ester quats have gained in popularity as the foundation for cream-type hair conditioners; one to consider is **Varisoft EQ 65**, INCI: Distearoylethyl dimonium chloride with cetearyl alcohol from **Evonik**. It is based on stearic acid from a vegetable source, is biodegradable and readily emulsified. In half-head tests it is shown to out-perform cetrimonium chloride and be comparable to behentrimonium chloride.

Not all conditioning formulations are based on cationic surfactants. **Tefose HC**, INCI: Cetyl alcohol, glyceryl stearate, ceteth-20 and steareth-20 from **Gattefosse** is based on non-ionic surfactants making it compatible with the majority of cosmetic additives. It is said to provide stable emulsions over a broad pH range and to impart exceptional gloss to hair. It can be used with ethoxydiglycol, which is said to improve colour deposition on hair and to resist the formation of split ends.

Sunflohair, INCI: Helianthus annus (Sunflower) seed oil and phospholipids from **Lucas Meyer** is an Ecocert registered natural hair conditioner from sunflower oil and sunflower phospholipids. It reduces hair roughness and friction, and increases hair shine. Its liposome form allows it to penetrate the hair shaft to restore the natural lipid matrix and repair damaged structures. From **Zenitech LLC**: **Zenigloss**, INCI: Castor isostearate succinate is a naturally derived polymer which adds gloss and shine to hair and provides a smooth feel. A quaternised version is available under the name of **Zenigloss Q**, INCI: Polyquaternium 57, based on polymerised castor oil.

Shiny, healthy-looking hair is an ongoing priority for today's consumer. The provision of gloss to hair is often delivered through the use of silicones in formulas such as conditioners and shine sprays, where their relatively high refractive index and surface coating characteristics lead to films that add lustre to the hair. Dimethicone, dimethiconol, phenyl trimethicone and cyclomethicones are all added to shampoos, hair conditioners, hair serums, balms and sprays. Using materials with a silicone backbone onto which suitable reactive groups have been grafted can simplify formulation and improve end results.

Biosil Basics from **Biosil Technology** are a range of complexes formed from active amino acids and a highly reactive silicone backbone. When applied onto the hair, the reactive silicone crosslinks with the keratin, binding the polymer to the hair. The crosslink cannot be washed off and the material does not crosslink with itself. Four versions are available, each based on dimethiconol; Dimethiconol panthenol, Dimethiconol arginine, Dimethiconol cysteine and Dimethiconol methionene

Also from **Biosil** and combining silicone technology with cationic substantivity, **Bioplex Cetylsil S** is a complex of a fatty quaternary compound and a carboxy silicone with a molecular weight of 3200. The ingredient is based on cetrimonium chloride which has been

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complexed with a carboxy silicone polymer resulting in cetyl trimonium dimethicone PEG-8 succinate. In combination with other surfactants a clear base is formed where the Bioplex is driven onto the hair shaft for improved conditioning.

Polyderm SI-WI, INCI: Bis-PEG-15 dimethicone/IPDI copolyol from **Alzo International** is a silicone copolyol emollient suitable for hair conditioners to improve wet and dry combing and is said to improve the after feel in styling aids. Other silicone/IPDI complexes from Alzo are also offered as sheen additives for hair conditioners including one based on castor oil.

Capillisil is a 20% solution of silanediol salicylate from **Exsymol** offered as a high concentration of biologically active silicon to reduce hair loss and increase hair density.

Other silicone derivatives for hair care include a number from **Grant Industries**; **Granacrysil CRT-W** is a pre-emulsified version of isobutylmethacrylate/Bis-hydroxypropyl dimethicone acrylate copolymer for easy addition to shampoos, conditioners and other external water phase products and is recommended to improve colour retention. Amodimethicone has also long been popular as a conditioning additive and is available in emulsified form from A&E Connock, Dow Corning and Biosil, amongst others, the differences being in the emulsifier system used.

Crodamol STS, INCI: PPG-3 benzyl ether myristate from **Croda** is an innovative new ester offering major formulating and functional benefits to personal care systems. It is said to possess a silicone-like feel and with a refractive index of 1.496 it imparts exceptional hair glossing properties. Combined with its ease of emulsification and wider formulation compatibility, Crodamol STS is offered as an alternative to standard silicones.

Chitin derivatives are also available as alternatives to silicone. **Hydroxan**, INCI: Glycerin, propylene glycol, sorbitol, carboxymethyl chitin, panthenol and sodium hyaluronate is from **Atrium Innovations**. It is described as a perfectly balanced moisturising composition, based on the alliance of three complementary substances for strong reservoir and film forming effect. These benefits have been reinforced by the addition of a vitamin B5 precursor for enhanced moisturisation, hydration and softening of the hair.

Ref 1 C. Robbins; Hair breakage during combing; IJSC, Vol. 29, 6, pp 485-486, 2007

Ref 2 J.A. Swift; Fine details on the surface of human hair; IJSC, Vol.13, 3, pp143-159, 1991

Ref 3 J.Alan Swift; The Mechanics of Fracture of Human Hair; IJSC, Vol 21, 4, pp 227-239, 1999

Ref 4 Akira Mamada, Koichi Nakamura; A study of the volume and bounce decrease in hair with ageing using bending elasticity measurements; IJSC, Vol. 30, 5, pp 383, 2008

Ref 5 S.B. Ruetsch, B. Yang, Y.K. Kamath; Role of melanin and artificial hair colour in preventing photo-oxidative damage to hair; IJSC, Vol. 26, 5, pp 269, 2004

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