A recent on-line or virtual conference [Ref 1] brought together some of the leading cosmetic ingredient suppliers whose representatives gave presentations on various aspects of hair care. That given on behalf of **Croda** was entitled Vital Ingredients for Healthy Hair and it was shown that products promising to improve the health of hair were showing a dramatic, 22% from 2011 to 2012, increase in sales.

Healthy hair is naturally coated with protective lipids, in particular 18-methyl eicosanoic acid plus palmitic and oleic acids. These lipids are responsible for giving hair its natural hydrophobic properties and coat the surface of neighbouring cuticle cells to maintain and restore the visual appearance of healthy hair, giving it shine, smoothness, bounce and elasticity.

18-methyl eicosanoic acid (18-MEA) is the most abundant lipid on the hair surface and thus is most susceptible to depletion by mechanical attrition of the cuticle and UV exposure. High pH products such as cold waves, hair colouring and hair relaxers also tend to remove 18-MEA from the cuticle. **Croda** suggested two materials to restore loss lipids: Cutissential Behenyl 18-MEA [INCI: Behentrimonium methosulfate, C10-40 isoalkylamidopropylethyldimonium ethosulfate, cetyl alcohol] and Cutissential 18-MEA 40 [INCI: C10-40 isoalkylamidopropylethyldimonium ethosulfate, dipropylene glycol]

Traditional conditioning lotions were benzalkonium or cetrimonium chloride with cetearyl alcohol but although the majority of mass market conditioners have little changed improved systems are available. Either of the two **Croda** Cutissentials could form the basis of a conditioning lotion, which are generally cationic in nature. Cationic materials are substantive to hair, which is rendered anionic by its amino acid content. Areas of damaged cuticle expose a greater concentration of amino acids, which make them a target for cationic materials and also for proteins and peptides.

A material from **Croda** designed to take advantage of this is Keramimic 2.0, an aqueous solution of laurdimonium hydroxypropyl hydrolyzed keratin, which is said to replicate the peptide sequences naturally found in the cuticle and cortex of human hair. There are different types of keratin proteins in the hair, each with a different amino acid composition and therefore each containing different levels of cystine, which plays a key role in hair cohesion and gives hair its structural integrity.

A lack of cystine in the hair caused by chemical and environmental aggressors will affect its manageability and strength. By treating hair using keratin derivatives with chemical similarity, hair keratin can be protected and its condition improved. The cationic properties of Keramimic 2.0 make it substantive to hair and it may be added to shampoos or conditioning lotions to improve hair condition and strength.

Ashland Speciality Ingredients have a number of conditioning agents in its portfolio; a new one is N-Hance 4572 {INCI: Guar hydroxypropyltrimonium chloride, acrylamidopropyltrimonium chloride/acrylamide copolymer]. It has a high charge density and high molecular weight and is said to enhance the deposition of silicone and oils onto hair allowing for up to a 50% reduction in silicone materials in 2-in-1 shampoos. Less silicone and oils in the shampoo improves product foaming and by ensuring an even spread of the oil over the entire length of hair it appears less heavy, is well lubricated and has good wet and dry combing properties.

Not all hair conditioning materials are cationic; KeraDyn HH from **Croda** is Bis-ethyl (isostearylimidazoline) isostearamide, which is compatible with most shampoo surfactants and conditioning agents. Its polyamine backbone provides multiple points of attachment to the hair, which makes it highly substantive and it is said to give hair bounce and shine. Its multiple branch-chains have a lubricating action, which reduces inter-fibre friction. Haiaqueouster DCS [INCI: Bis-ethoxydiglycol succinate] is a water-soluble ester from **Kokyu Alcohol Kogyo** that is shown to have detangling and anti-static properties when incorporated in hair mists and conditioning products. Biosil Basics DL-Methionine 30 [INCI: Dimethiconol methionine] is based on reactive silicone with both reactive and cationic sites on the molecule. The cationic site binds selectively with negatively charged substrates such as hair delivering the amino acid methionine in a rinse off product. This amino acid is thought to retard premature hair loss and to improve the texture and quality of hair. **Biosil** produces a number of hair improvement products based on reactive silicone with amino acids or panthenol.

Protecting Hair

Hair damage is the result of chemical and mechanical abuse and heated tongs and flat irons that raise the temperature of the hair shaft to 150°C or even higher are a major problem. Products that offer thermal protection were a subject of interest at the virtual conference [Ref 1]. **Ashland** proposed Gafquat 755N [INCI:Polyquaternium-11] or Styleze CC-10 [INCI: VP/DMAPA acrylates copolymer] as materials that aided curl retention in leave-on products and built body by coating the hair with a clear, non-tacky film that also offered thermal protection.

Other materials providing thermal protection from **Ashland** included Styleze W [INCI: Polyquaternium-55] that also reduces colour leaching from dyed hair and Styleze 2000 [INCI: VP/acrylates/lauryl methacrylate copolymer] that gives synergistic thickening in carbomer gels that can be water-white, clear and alcohol-free. Styleze XT3 [INCI: Aqua, polyimide-1, PVM/MA copolymer, caprylyl glycol] is claimed to maintain desired hair shape over multiple washes, to provide brilliant shine and to protect hair against heat styling damage.

Sphingoceryl VEG LS 8712 [INCI: Octyldodecanol, hydrogenated coco-glycerides, Helianthus annuus *(Sunflower)* extract] from **Laboratoires Sérobiologiques** is described as a complex of botanical phytoceramides-6 that may be added to permanent wave systems to protect the hair. It is oil-soluble and may also be added to conditioning products to restore lost hair lipids on dry hair.

Keravis from **Croda** is an aqueous solution of hydrolyzed vegetable protein pg-propyl silanetriol, a material that is substantive to hair that can be used to improve its resistance to breakage. It is said that its penetration of the cuticle builds strength from within to increase resistance to tensile forces and to withstand bending stresses and at the same time it lubricates and protects the hair surface, preventing cuticle abrasion and loss.

Another silanetriol from **Croda** is trade named Crodasone Cystine, which is an aqueous solution of cystine bis-PG-propyl silanetriol. It is an anionic material at pH 9.5 and is designed to protect hair undergoing chemical treatments and thermal

styling. It bonds covalently to hair keratin to form a high molecular weight film that is polymerised by heat or on drying and is said to improve curl retention after perming and to enhance the sheen of hair by repairing damaged cuticle. Croda has developed a 4-stage hair smoothing system based on Crodasone Cystine and details are available from the supplier.

Hair can be straightened with flat irons or by the use of hair relaxers. Relaxers are based on sodium, guanidine, lithium, or potassium hydroxide and all work at high pH and significantly damage and weaken hair. **BASF** have introduced a new material trade named Plantasil Relaxcare that is a mixture of potassium silicates, caprylyl/capryl glucoside and glycerin. It is claimed to be stable at high pH and penetrate into the hair as a pre-relaxer to offer protection to it during the relaxer process and to stabilise the hair structure following treatment. Salon test results from BASF show that hair treated with a relaxer formula containing 1% Plantasil Relaxcare had improved manageability, softness and shine and showed significantly less loss of resistance to breakage than hair treated with the same relaxer but without Plantasil Relaxcare.

Hair Styling

BASF claimed that styling gels, waxes and creams are the fastest growing products in the styling market. Conventional gels are usually based on carbomer thickeners so the choice of styling polymers and consequently the setting performance is limited. BASF have introduced Luvigel FIT [INCI: Acrylates/C10-C30 alkyl methacrylate copolymer] as a new thickener for high end styling which allows manifold combinations with many styling polymers. It is a hydrophobic alkali swellable emulsion (HASE) type thickener and it enables very stiff hold or a normal hold with reduced polymer content.

Obtaining a strong hold from an aerosol delivery system is the claim made by **DSM Nutritional Products** for its Tilamar Fix A140 styling polymer. Specifically designed for ultimate hold and fast drying without stickiness in aerosol sprays this acrylates copolymer also delivers high humidity curl retention for long lasting styling. It is suitable for aqueous based formulations such as VOC55 aerosols and non-aerosol pump sprays.

Dow Personal Care has a range of styling materials available under its Acudyne trade name that are based on acrylic technology developed by Rohm and Haas. Different variations are recommended based on the type of film and strength of hold required. Recent introductions include Acudyne Shine, a styrene/acrylates copolymer with a very high refractive index that gives gloss to hair, and Acudyne 1000, that gives high hold with a crunchy feel.

For styling **Wacker Silicones** has a new material named Belsil P 1101 [INCI: Crotonic acid/vinyl C8-12 isoalkyl esters/VA-bis-vinyldimethicone crosspolymer]. This is a silicone-polyvinyl acetate block copolymer that gives styling products a strong hold combined with quick drying time, high water compatibility and a silky feel. Wacker describes it as a silicone hybrid hair styling resin that combines organic chemistry for hold, solubility and curl retention with silicone chemistry for smoothness and a silky touch plus easy combing and resistance to humidity. It is supplied as an alcoholic solution and requires neutralisation when being processed Hair Care Feature 1st Published in SPC - 2012 John Woodruff into the final composition and it is suitable for both aerosol and pump spray products and for use with flat iron styling tongs.

Natural styling and conditioning

Consumers not only want their hair to look natural, many want the means to make it so to be based on natural ingredients. Natpure Film AP from **Sensient Cosmetic Technologies** is a low viscosity solution of pullulan, sorbitol, trehalose and acacia senegal gum that combines to coat hair with a clear, flexible film with good hold. It can be dispensed from a pump spray or incorporated in styling gels and waxes. Asensa NFF11from **Honeywell** is a starch-based biopolymer that imparts shine, frizz control and a natural feel with curl resistance, even in high humidity. It can be formulated in water based systems without the use of solvents.

Keramare from **Provital** helps restructure keratin fibers, improving the integrity of the ortho-cortex and protecting hair against thermal treatments. Its active ingredients are Cystoseira compressa extract and zea mays (corn) starch. Also from **Provital** is Keracyn, active ingredient Cynara scolymus (Artichoke) leaf extract, which is claimed to prevent the degradation of keratin and lipids by its anti-oxidant activity.

Natural conditioning aids are also available. Amihope LL [INCI: Lauroyl lysine] from **Ajinomoto** is an amino acid based organic powder derived from plant fatty acids and naturally occurring amino acids. It provides slip and skin feel to natural shampoo and conditioner formulations, as well as offering a pearlescent effect and excellent hair control from root to tip. **Rahn** suggest Aquarich [INCI: Glycerin, aqua, Avena strigosa seed extract, lecithin] as a shampoo additive that improves gloss and bounce back of hair after blow drying as well as enhanced skin feel and foam during washing.

Amisol Trio is a conditioning aid from **Lucas Meyer** that includes phospholipids, glycolipids, phytosterols and linoleic acid extracted from the cell membrane of soybeans. It covers and smoothes cuticle scales to preserve or improve hair condition and provides super-fatting properties and improved moisture balance to make the hair look radiant and healthy. Rep'Hair by **Solabia** is behenyl/stearyl aminopropanediol esters, a ceramide-like molecule obtained from two saturated vegetal fatty acids, behenic acid and stearic acid. It is claimed to restore lost lipids, smooth the cuticle and add gloss and strength to hair.

Biostyle CGP from **AkzoNobel** is a non-ionic hair fixative polymer having greater than 50% natural content. It is a unique, graft polymer produced via the reaction of maltodextrin and vinyl pyrrolidone [INCI: Maltodextrin/VP copolymer] that is claimed to provide exceptional clarity and consumer preferred rheology. Structure Style, also from **AkzoNobel**, is a starch-based rheology modifier and film former [INCI: Hydroxypropyl starch phosphate] that provides thickening and hold in hair styling products. It can be used as a stand-alone polymer, replacing both traditional fixatives and rheology modifiers with a single ingredient or in conjunction with traditional rheology control polymers to create economical and aesthetically pleasing styling products.

There are many materials claimed to improve hair health and condition but penetrating the cuticle to deliver them into the cortex is a problem. High pH systems lift the cuticle but also cause damage; Vecorexin from **Lipotec** is claimed to be a

cationic liposome type delivery system that anchors to the hair cuticle. It shows good resistance to removal by washing, giving more time for the actives to penetrate to the internal layers of hair. Tests published by Lipotec demonstrate its substantivity and resistance to washing and greatly enhanced penetration of actives into the cortex. Vecorexin incorporating various actives including d-panthenol, silk protein, keratin, tocopheryl acetate and bifidobacterium ferment with superoxide dismutase are available and are recommended for hair conditioning products that are designed to replace lost hair lipids and restore its physical condition.

Protecting Hair Colour

Hair colouring is beyond the scope of this article but protection or enhancement of hair colour may be considered an important part of maintaining hair condition. Loss of hair colour is the result of oxidation caused by UV radiation. UV rays lead to photo-oxidation of the protein structure through the oxidation of specific amino-acids, especially tryptophan and cystine. UVB is absorbed by hair and is the source of natural photo-damage through deterioration of keratin and thus of hair integrity. UVA is mainly responsible for the photo-fading of artificial hair colour. A material claimed to inhibit these effects is a polyphenol-rich lychee extract available as Litchiderm from **Laboratoires Sérobiologiques**.

Litchiderm, [INCI: Butylene glycol, Litchi chinensis pericarp extract] is a syrupy amber liquid that is added at 1 - 2% to hair shampoos and conditioners. Its polyphenol content ensure its free radical scavenging properties and it is able to reduce colour fading of dyed hair as well as protect hair against the toxic effects of oxygen radical stress.

SilkRom [INCI: Acrylamido propyltrimonium chloride/acrylates copolymer] from **Bozetto Performance Chemicals** is used in order to improve manageability, provide glossiness, and softness to the hair texture and to protect hair colour. It is cationic in nature so is substantive to hair, which remains through subsequent hair washing to prevent colour being leached from the hair shaft. As with all materials mentioned in this article, extensive data is available from the supplier to demonstrate its efficacy.

Amodimethicone is known to protect hair from colour fade and also to offer thermal protection but its insolubility makes it a difficult material to work with. **A&E Connock** supplies it as trimethylsilylamodimethicone or in emulsion form with either C11-15 Pareth-7, laureth-9 and trideceth-12 or with trideceth-12 and cetrimonium chloride to make it easier to incorporate in formulations.

Wacker Silicones supplies amodimethicone/morpholinomethyl silsesquioxane copolymer as a micro-emulsion with trideceth-5 trade named Belsil ADM 8301 E or the same copolymer with trideceth-10 as a macro-emulsion named Belsil ADM 6300 E. Both are suggested as additives to conditioners at 2% to offer thermal protection and to give enhanced colour retention. **Wacker** launched Belsil OW 1500 at In-Cosmetics 2012; it is a polyether-modified siloxane, [INCI: PEG/PPG-20/20 copolymer, PEG-/PPG-20/20 dimethicone] with applications in skin creams, liquid pigmented products and in hair conditioners.

Silicones and their derivatives can give outstanding conditioning properties to hair products but are not permitted in products seeking natural or organic certification

from Ecocert or other bodies. Alternatives include Daikon radish oil and meadowfoam oil from **Natural Plant Products** and the Lexfeel N series of silicone alternatives from **Inolex**. Meadowfoam and Abyssinian oils are also available from **Elementis Specialties** and these and many others were described at length in SPC February 2012.

VibraRiche from **Croda** is a quaternary ammonium compound, Rapeseedamidopropyl ethyldimonium ethosulfate, which is substantive to hair and said to combine conditioning properties with enrichment of hair colour. It is claimed to give vibrancy to dyed hair and to inhibit colour fade and loss through repeated washing. Nequat DBS from **Alzo International** is a combination of stearyl alcohol, stearamidopropyl ethyldimonium ethosulfate, dimethyl lauramine and dimer acid that is claimed to offer detangling, conditioning and colour enhancement properties.

Chemyunion supplies numerous products for hair care, one of which is Hidrahair O2, specifically aimed at protecting hair from UV radiation. It is described as a natural complex of tocols and ferulates derived from rice, soya and palm supplied as a solution in butylene glycol. Meadowquat HG-70 [INCI: PEG-2

dimeadowfoamamidoethylmonium methosulfate] from **Elementis** was launched as a material to enhance fragrance deposition on skin and hair but it also improves colour deposition in hair colouring products.

It is not only dyed hair that suffers from colour fade. Natural hair colour is also affected by UV exposure and harsh environmental conditions, including chemical and thermal treatments but most of all, by ageing. Melanin, the primary determinant of hair colour, is synthesized in melanocytes located in the hair bulb but with increasing age less melanin is produced and hair that has lost most of its melanin is gray; hair that has lost all of this pigment is white.

Chromafend Biofunctional from **Ashland** is an aqueous/glycolic extract of hydrolysed linseed claimed to help conserve melanin in the hair follicle by boosting tyrosinase expression, which is part of the melanin production process and it significantly boosts the expression of PAR-2 which is involved in melanin transfer from melanocytes to keratinocytes. Also from **Ashland** is Procataline Biofunctional, an aqueous/glycolic solution of Pisum sativum (pea) extract that may help hair follicles maintain antioxidant protein levels and sustain a positive environment for hair growth and to favour healthier, younger looking hair by preserving melanin from oxidation.

Lanatellis from **Unipex** is a botanical complex of green tea (Camellia sinensis) and chrysanthellis (Chrysanthellum indicum) with a powerful free radical scavenging action. The different constituents of Lanatellis act in synergy to trap and neutralise free radicals and inhibit lipid peroxidation, thus preserving hair strength and colour. Oleox [INCI: Hydrolyzed olive fruit] from **Phenbiox** is rich in polyphenols with antioxidant activity that protects hair from free radical damage and colour fade.

Stimulating Hair Growth

Male pattern baldness, more properly called androgenic alopecia, removes a significant number of hair product consumers from the general population. Although the majority are quite happy living without hair it is doubtful that any looked forward

Hair Care Feature 1st Published in SPC - 2012 John Woodruff to losing it. Much work has been done in order to stimulate hair growth and to extend the life cycle of existing hair.

Mibelle Biochemistry launched AnaGain at In-Cosmetics, Asia 2012. Described as a novel active which stimulates hair growth and fights hair loss its active ingredient is Pisum sativum (Pea) sprout extract. It is claimed to reactivate hair growth by directly targeting the dermal papilla cells that are key to the hair growth cycle. AnaGain boosts the expression of the noggin gene, which results in a shorter resting period, and it also enhances the expression of the fibroblast growth factor-7 gene. This in turn stimulates the proliferation of hair germ cells to trigger the anagen growth phase.

Follisync Biofunctional from **Ashland** is an aqueous/glycolic extracts of Vicia faba seeds that is claimed to boost hair renewal proteins such as Ki67 and keratin-15 to preserve cells that are critical for stimulating hair growth and to boost keratin-14 expression for a strong hair structure. Also from **Ashland**, Dynagen Biofunctional is a hydrolysed yeast protein that is shown to increase the time span of hair in the anagen phase, thus prolonging hair life.

From Lucas Meyer there is Capixyl [INCI: Butylene glycol, water, dextran, acetyl tetrapeptide-3, trifolium pratense (clover) flower extract] designed to encourage hair growth. It addresses the main causes for hair loss and like many anti-aging actives, it helps firm the skin with the idea of anchoring hair follicles.

Theories about the cause of Androgenic alopecia are many and varied and are almost certainly related to genetics and hormonal effects. One theory is that the 5- α - reductase enzyme converts testosterone to dihydrotestosterone (DHT), which attacks the dermal papilla leading to progressively shorter, finer hair and finally no further growth. Canadian Willowherb from **Unipex** inhibits the 5- α -reductase enzyme, thereby prohibiting the conversion of testosterone into DHT and therefore prolonging hair growth. Canadian Willowherb also has anti-irritant and anti-inflammatory activity.

5-α Avocuta [INCI: Butyl avocadate] from **Expanscience** is derived from Avocado oil. It inhibits the 5-α-reductase enzyme from converting testosterone into DHT and reduces excess sebum in skin and hair by inhibiting stimulation of the sebaceous gland. **Indena** also supplies a material claiming anti-androgenic activity by inhibition of 5-α-reductase enzyme activity; it is Sabalselect [INCI: Serenoa repens oil] said to prevent hair loss and to modulate sebum production.

Minoxidil is approved by the FDA as a treatment for androgenic alopecia and is available from **Crestchem** as Kodil. It is medically and scientifically proven to stabilise hair loss and stimulate new growth. Kopexil from **Crestchem** is diaminopyrimidine oxide that is claimed to strengthen hair, increase hair thickness and accelerate hair growth. It is suggested that collagen forms around the hair follicle causing hardening and shrinking over time. Kopexil blocks collagen formation and also dilates blocked vessels to bring increased supply of nutrients to the dermal papilla.

Zymo Hydroxysteroid Dehydrogenase Complex, from **IRA Laboratories** is an innovative enzyme specifically designed to help stop hair loss caused by androgenic alopecia. The enzyme 3-α-hydroxysteroid dehydrogenase [INCI: Hydroxysteroid

Hair Care Feature 1st Published in SPC - 2012 John Woodruff oxidoreductase] works by catalysing the degradation of dihydrotestosterone in the hair follicle.

It should be noted that only the principal ingredients of mixtures are listed and full disclosure should be sought from the suppliers.

REF 1: Haircare Ingredients 2012; virtual conference and expo organised by Cosmetics Design.

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