

Hair Care Feature

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John Woodruff

The author of this feature has a complete set of Journals of the Society of Cosmetic Chemists (JSCC) from Volume 1, No 1. 1947. In that issue the use of mercaptans in depilatories and permanent waving products were described [Ref 1]. The next issue described the chemistry of permanent waving [Ref 2] and a second item described the cold process [Ref 3]. An extract from the latter states “The desire of the human race to alter the natural pattern of the scalp hair is a rather strange phenomenon. Those with naturally straight hair wish it to be curly while those with naturally curly hair wish it to be straight”. It was not until May 1951 that the first paper referring to shampoos appeared [Ref 4] in which the authors claimed that in a shampoo the primary requisite is one of imparting a lustrous soft finish to the hair rather than one of efficient cleansing.

The first reference to polymers for hair styling was in 1957 in a paper on the use of polyvinylpyrrolidone (PVP) in cosmetics, which described its film-forming properties and its use to style human hair [Ref 5]. It was another three years before the use of vinyl acetate and its copolymers in hair styling were described [Ref 6] and it wasn't until 1966 that the first reference to the possible use of cationic conditioning agents was made [Ref 7].

Leaping forwards to 2014 current trends are still into ways of improving shampoo performance, improving hair conditioning, strengthening and adding thickness and volume to the hair fibre and into ways of styling it with polymers. According to Euromonitor the forecast by value for global hair care categories for 2014 is 30% for shampoos, 53% for conditioners and treatments, 8% for dyeing, 5% for styling and 3% for perms and relaxers. The forecast by units of sale virtually reverses the shampoo and conditioner figures to 58% and 29% respectively. The big change in the past 50 years has been the fragmenting of product categories beyond those aimed at the traditional greasy, normal and dry hair to products targeted by age, by hair colour, by ethnicity and gender and for those with sensitive scalps or with straight or curly, short or long hair.

The other big change has been the move away from traditional materials with proven efficacy towards those with a good marketing story that claim natural origins. An example is the replacement of alkyl and alkyl ether sulphates as the basis of shampoo by glucosides such as decyl glucoside or lauryl glucoside. For several decades silicones have been ubiquitous in hair care products but alternatives are slowly being introduced. Because of concerns about consumer and environmental safety, alternatives to the volatile cyclic siloxanes were the first to receive serious consideration. Neolight 100P from **Kokyo Alcohol Kokyo** is isodecyl neopentanoate; a low viscosity ester with a light dry texture comparable to cyclopentasiloxane and **Croda** offers Crodamol SFX [INCI: PPG-3 benzyl ether ethylhexanoate] as an alternative to volatile silicones to add lubricity to hair fibres.

Ever since their introduction in the mid-1960s hair conditioners have relied on a cationic surfactant with a fatty alcohol to provide a cheap but effective emulsion that gave smoothness and shine to the hair. Concerns about the toxicology of the traditional cationic surfactants has led to the introduction of much milder alternatives although most are still based on a cationic material and silicone.

The use of PVP, now more properly known by its INCI name of PV, continues in styling products as does that of vinyl acetate copolymers. Before PVP shellac was the natural material for hair setting lotions, this was before aerosols came into common use. It still has its followers and if properly formulated the products can be very effective however there are many alternatives capable of delivering the effect desired, whether from a gel, a lotion or a

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spray. A material available as Asensa NFF-11E is hydrolyzed corn starch that is offered as a natural alternative to PV by **Honeywell**.

Returning to shampoos, Peter Clark, **Innospec**, delivered a presentation at In-Cosmetics 2014 entitled "Formulating sulfate-free structured liquid surfactant formulations using Iselux SLC". It is an aqueous solution of sodium lauroyl methyl isethionate, sodium lauroamphoacetate and cocamide MIPA preserved with sodium benzoate. The presentation gives a good insight into the physical chemistry of surfactants in solution. The effects of various oils and rheological additives are described and because structured liquids are materials capable of suspending immiscible performance additives like natural and essential oils and silicones it is possible to formulate products with interesting properties.

Also from **Innospec** and at the same event Tony Gough gave an insight into advances in formulating high-performance, sulfate-free cleansing products. Gough illustrated his talk with a table of different sulphate-free surfactants giving both the advantages and disadvantages of using the materials. He also said that if a shampoo formulation required a surfactant that was highly foaming, mild, non-ethoxylated, naturally derived and could be thickened with salt then Iselux [INCI: Sodium lauroyl methyl isethionate] could be the answer.

There are many alternative surfactants to the traditional SLES/CAPB combination and these will be covered in a future feature. This article will focus on some of the additives designed to add functional properties to shampoo and some new hair conditioning actives.

Caring for the scalp has become an essential part of shampoo technology. Described as a highly effective first-aid kit for stressed, sensitive and irritated scalp Defensil Plus from **Rahn** is said to soothe hot and itchy skin when added to shampoo or hair conditioners. Containing blackcurrant seed oil and balloon vine extract in combination with sunflower oil concentrate it reduces inflammatory processes and helps regenerate the skin barrier damaged by chemical irritation. Aquarich from **Rahn** is a moisturiser comprising an extract of black oats [*Avena strigosa*] and plant-based lecithin that has a repair effect on hair and recent studies demonstrate that it prevents split ends and improves hair gloss and bounce back. Both these materials are Ecocert and COSMOS listed and NaTrue certified.

Amisoft was the world's first mild amino acid based surfactant and was launched by **Ajinomoto** in 1972. Since then Ajinomoto has continued as a foremost supplier of amino acids and amino acid-based materials. About 80% of human hair is keratin derived from amino acids so these ingredients find particular application in hair products. Amino acids are also essential for keeping the scalp well-nourished and amino acids such as L-cysteine, L-methionine and L-serine are known to promote hair growth.

ProdeW 500 from **Ajinomoto** is an amino acid blend, developed to provide moisturising, strengthening and colour-protection to hair and to repair surface damage. Ajidew ZN-100 [INCI: Zinc PCA], suppresses excess sebum secretion, leaving the scalp feeling clean and refreshed. Aquadew Spa-30 is a moisturiser for skin that has found application in hair products where it improves moisture levels and increases manageability. It protects the cuticles and helps prevent hair breakage and splitting. Research at Ajinomoto showed that Eldew forms lamella liquid crystals identical to ceramide. The addition of Eldew [INCI: Cholesteryl/behenyl/octyldodecyl lauroyl glutamate] to shampoos or conditioners is claimed to repair damaged hair and improve its strength.

Despite its cationic charge guar hydroxypropyltrimonium chloride is a shampoo additive that is compatible with anionic systems and which provides conditioning properties. An

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alternative is Dermofeel P-30 from **Dr Straetmans**. This is a plant derived hair and skin conditioner [INCI: PCA glyceryl oleate] suitable for certified natural cosmetics. It improves the smoothness and feel of the hair with a measurable combing force reduction of up to 50% and has a positive influence on foam quality and viscosity when added to shampoo. To avoid the use of silicones in 2-in-1 shampoos Dr Straetmans suggests incorporating isoamyl laurate, available with the trade name Dermofeel Sensolv. It is a polar oil that has a silicone-like sensorial profile and shows excellent skin compatibility.

Cashmilan LS from **Laboratoires Serobiologiques** is a partially hydrolyzed keratin from cashmere wool that is added to shampoos to increase the strength of fine and fragile hair and hair damaged by chemical treatments. Kelimor from **Kelisema** is a water soluble Moringa oleifera seed protein hydrolysate that is rich in free amino acids which can penetrate the hair shaft and short peptides which can replenish damaged hair. It has high substantivity on hair and protects its colour from fading and also it helps strengthen and repair damaged areas.

An interesting variation on shampoos is suggested by **Seppic** whereby encapsulated argan oil and Inula HC, which is an oily extract of Inula maritime, is added to sulfate-free shampoo to give long-lasting protection to coloured or damaged hair. Produced using Seppic encapsulation technology, the capsules are stabilised and suspended with the help of Eliclear 4U acrylates copolymer. Seppic also suggest adding Aquaxyl [INCI: Xylitylglucoside, anhydroxyxylitol, xylitol], claiming that it provides deep-down hydration while strengthening the hair and improving its appearance.

Aquaxyl may also be added to dry powder shampoos and hair conditioners. A formula for a dry powder shampoo suggested by **Seppic** comprises 27% by weight kaolin; 5% cyclodextrin; 45.7% tapioca starch, 10% cellulose; 0.3% fragrance; 1% Aquaxyl; 10% Sepimat SB and 1% Lipacide C8G. Sepimat SB is PMMA microspheres that have oil absorbing properties and Lipacide C8G is capryloyl glycine that has antimicrobial properties and protects the acid mantle of the scalp. The formula is suitable for sprays and freshens the hair to leave a satin finish and will add body and volume to fine hair. A source of specially processed kaolin with high oil absorption properties is ImerCare K from **Imerys**.

In general people are unkind to their hair; shampoos remove protective lipids; brushing and combing removes cuticle and results in split ends; perming, straightening and oxidation colouring causes even more damage and just exposing it to sunshine can result in colour fading and disruption of the hair shaft through the formation of peroxides within it. Treatments that can prevent or repair hair damage are therefore much sought after.

Lucas Meyer Cosmetics offers Sunflohair to provide colour protection and increase colour intensity of dyed hair; Phytensol as a natural hair straightener, Capixyl to prevent hair loss and Melitane to reverse greying hair. Sunflohair [INCI: Phospholipids, Helianthus annuus (Sunflower) seed oil] has a strong affinity with hair and is able to compensate for lipid loss by penetrating the hair fibre. It restores the lipid matrix and returns hair to its natural beauty. It can be used with semi-permanent and permanent hair dye to aid pigment fixation and is stable up to pH 12. Sunflohair is said to protect and repair hair fibres, act as a free radical scavenger and improve combing properties.

Phytensol contains specific phospholipids and glycine soja (Soybean) oil that adheres to hair fibre surrounding it with a smooth film, which straightens hair through a physical action. Phytensol contributes to the styling of curly and frizzy hair, which is often difficult to manage in conditions of high humidity. Capixyl is a combination of acetyl tetrapeptide-3 and Trifolium pratense (clover) flower extract for stronger, thicker and fuller hair. Melitane

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includes acetyl hexapeptide-1 that can be used as a natural photo-protector and as an inflammation modulator. Melitane stimulates melanin synthesis under UV-inducing conditions and helps reduce greying of the hair bulb.

Formulating shampoos presents two specific problems: the need to increase viscosity and the requirement to improve deposition of beneficial ingredients from a rinse-away product. A multi-functional material from **Lubrizonl** named Carbopol Silk 100 [INCI: Carbomer] may help solve both. It is claimed to exhibit synergistic effects with salt to increase viscosity, provide high suspending power and to impart pleasant flow and foam aesthetics to shampoo. It also increases deposition of silicone and cationic polymers due to coacervation enhancement to give better conditioning.

A presentation from **Ashland** called ASI Deposition Technologies gives a very clear description of how conditioning polymers such as **Ashland's** N-Hance SP-100, [INCI: Acrylamidopropyl trimonium chloride/acrylamide copolymer], form a coacervate with anionic surfactants to improve deposition. It also includes much useful information on shampoo and conditioning products formulation.

Introduced at In-Cosmetics 2014 by **Ashland** N-DurHance A-1000 [INCI: Polyacrylamidopropyltrimonium chloride] is described as a durable and substantive conditioning polymer for hair. It is compatible with anionic and cationic surfactants and may be added to conditioners and shampoo. Because it is positively charged the polymer is attracted to the negatively charged damaged hair leaving the hair with an excess of positive charge. When the hair is next shampooed the anionic surfactants start to form flocculates on the hair surface with the cationic polymer. During flocculate formation, hydrophobic lauryl groups from the anionic surfactant coat the hair surface, creating a hydrophobic layer. It is said to restore hair to a hydrophobic state and the benefits persist on the hair even after multiple washes yet does not cause build-up.

Emulsense HC by **Inolex** is described as a new era in natural cationic surfactants. Created using green chemistry and only natural and sustainable materials Emulsense [INCI: Brassicyl isoleucinate esylate, brassica alcohol] is said to be 65% cationic and 35% fatty alcohol and its performance as a hair conditioner is comparable to those based on traditional cationic ingredients. Another cationic material of natural origin is Laraquat from **Lonza**. Based on galactoarabinan (GA), a natural polysaccharide polymer harvested from the larch tree, quaternary nitrogen groups have been grafted onto the backbone of the polysaccharide, creating an ingredient substantive to hair. It is a mild, non-irritating and water-soluble polymer that provides lighter styling and a more weightless feel for leave-in products while still offering substantial conditioning benefits to hair.

Because of the need to reduce flyaway and hair surface roughness caused by using strong anionic shampoo materials cationic surfactants have long dominated the hair conditioner market. However with today's use of milder cleansing agents there are alternatives such as KeraDyn HH [INCI: Bis-ethyl(isostearylimidazoline) isostearamide] from **Croda**. Hair damage results in high levels of inter-fibre friction which restricts the free movement of individual hair fibres and the typical fluidity of movement and fibre alignment are lost. KeraDyn HH is designed to influence the surface properties of damaged hair, reducing inter-fibre friction and restoring healthy hair dynamics.

Two non-quaternary conditioners are proposed by **CR&D**; Hyalorice [INCI: Hydrolyzed glycosaminoglycans, hydrolyzed rice protein, hyaluronic acid] is an antistatic conditioner that relies on the positive charge created by the interaction of low pH hyaluronic acid derivatives

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with hydrolyzed rice proteins. The hair shows an improved softness and becomes more easily combed in dry and wet conditions. The second one is Hyaloat where the combined properties of hyaluronic acid and hydrolyzed oat protein allow it to give gloss and brightness to the hair. Hyaloat [INCI: Tremella fuciformis extract, Avena sativa seed extract, lentinus edodes extract] has a repairing action that reduces split ends and helps to prevent them, keeping the right ratio of water in the cuticle structure.

Luminescine from **Phenbiox** is a phytocomplex of hydrolyzed verbascum thapsus flower that is able to protect the hair from harmful high energy UV radiation, transforming it into a source of light that radiates directly from hair making it look shinier, younger and healthier. Also from Phenbiox a material trade-named Pro-Structure acts as a powerful antioxidant able to make the hair itself an antioxidant, binding the hair proteins. The treatment is long lasting; 3 days after treatment, the hair is still maintaining a high antioxidant capacity. A hair-care cosmetic formulation containing 1% of Pro-Structure [INCI: Hydrolysed walnut extract] is able to effectively protect the hair colour from degradation.

Croda offers many materials for hair care amongst which are Crodabond CSA [INCI: Hydrogenated castor oil/sebacic acid copolymer] that has been specifically engineered to seal down hair cuticles that have been damaged through physical and chemical treatments. It is incorporated into hair conditioners to lay the cuticles down and lock them into their original position, allowing consumers to carry on with their day-to-day hair cleansing and styling regime without any risk of inflicting further damage. Crodasone P is an advanced copolymer derived from Pisum sativum that offers proven protection against cuticle cracking caused by common hair styling practices such as blow-drying and combing. Due to its complex polymeric structure Crodasone P cross-links on drying to form a conditioning and protective network. Studies have shown that Crodasone P can reduce thermal cracking by 49% in an aqueous spritz and 38% in a conditioner system making it ideally suited for leave-on styling products and rinse-off applications.

Crodazoquat MCC [INCI: Behentrimonium methosulfate, Quaternium-87, cetearyl alcohol] restores hydrophobicity to hair and also adds shine and strength. To assess the detangling and conditioning capability of Crodazoquat MCC the wet and dry combing forces on coloured Asian, bleached Caucasian, and relaxed Brazilian hair were measured. A Crodazoquat MCC conditioner was compared to behentrimonium methosulfate and behentrimonium chloride conditioners. The force required to comb through a hair tress was measured and a reduction in combing force indicates how well a product is conditioning and detangling the hair. The wet and dry combing study revealed excellent detangling and conditioning from Crodazoquat MCC, measured by up to a 95% reduction in combing force on bleached Caucasian and relaxed Brazilian hair and it outperformed the other two conditioners for detangling and conditioning coloured Asian hair.

Cutissential 18-MEA 40 and Cutissential Behenyl 18-MEA are quaternized derivatives of 18-methyl eicosanoic acid (18-MEA), the primary lipid of the hair surface. The thin layer of lipids protects the hair from damage caused by chemical treatments, environmental stress and everyday grooming and the Cutissential range was developed as a means of replenishing 18-MEA and helping the hair to retain or regain its natural healthy appearance.

Products for sebum control, hair styling and for inhibiting hair loss are of particular interest to men so they will be described in the next issue of SPC under Male Grooming.

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Please note: Only the principal ingredients are listed under the INCI names and those interested are urged to contact suppliers for complete information and also for compliance with Ecocert, COSMOS or other certification bodies.

Ref, 1 McDonough, Everett G. The use of mercaptans in cosmetics, JSCC, Vol.1 27 -32 (1947)

Ref 2 Suter, Marcel J. Chemistry in permanent waving, JSCC, Vol.1 103 – 108 (1948)

Ref 3 Reed, Raymond E *et al.* Permanent waving of human hair, JSCC, Vol.1 109-122 (1948)

Ref 4 Barnett G, Powers D.H., A Quantitative method for the evaluation and study of shampoos, JSCC Vol.II 219-229 (1951)

Ref 5 Greenfield, I. Polyvinylpyrrolidone, its manufacture, properties and use in cosmetics, JSCC Vol. VIII.196-211 (1957)

Ref 6 Weitz, P. Vinyl copolymer in the cosmetic cosmos, JSCC, Vol. VX1 291-302 (1960)

Ref 7 Godfrey, K. Cationic emulsifiers in cosmetics, JSCC 17 17-27 (1966)

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