

## Hair Care Feature

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Developments in hair styling appear to have slowed in recent years. There was only one presentation dedicated to hair styling at In-Cosmetics and none appear on the programme for Formulate 2009. In the USA less than ten patents claiming hair styling compositions have been granted in 2009 and there was only one presentation on the subject at the IFSCC Conference, Melbourne, 2009 so has hair styling technology reached its zenith? Following is a round-up of the more recently introduced styling polymers with emphasis on those suitable for low VOC sprays and hair gels and also those with multi-functional attributes such as colour protection.

The presentation at In-Cosmetics was about acrylate hair fixatives sold under the Acudyne trade name by **Rohm and Haas**. Acudyne 180 is an aqueous acrylic emulsion polymer that upon neutralisation yields clear hair spray solutions and crystal-clear films on hair. Hydroxyl groups enable formulation compatibility with water or aqueous alcoholic systems while also being humidity resistant in sprays, gels, and mousses. Its minimal effect on viscosity makes it suitable for pump sprays and low VOC aerosols and it is said not to build-up on the hair. Acudyne 180 gives optimum film tensile strength and high humidity curl retention when about 50 to 70% of the polymer acid sites are neutralised with aminomethyl propanol. The films are very humidity resistant and at 92% relative humidity, the film absorbs only about 0.4% water after 24 hours.

Other Acudyne resins include DHR designed specifically for high performance 55% VOC aerosol sprays and pumps, said to deliver superior all day flexible hold and shine because of its unique dual phase combining a soft and a hard acrylic polymer. Acudyne SCP is a styling conditioning polymer that can be used in gels, mousse, spray gel, lotion and pomades and LT-120 is suggested for extreme hair styling products, such as, hair gels, styling aids and sprays because it offers a stiff hold with maximum humidity resistance and does not flake.

Polyquaternium-69 is the basis of Aquastyle 300 from **ISP**. Although not a new material it is still worth considering for hydro-alcoholic solutions and it may be used for clear and cream gels as well as aerosol and non-aerosol mousses, styling lotions, and sprays. In particular it appears suitable for hair gels and when incorporated at 4% it shows excellent humidity resistance with retained curl and enhanced shine. Interesting results are obtained if the Aquastyle 300 is combined in a gel with Carbopol Ultrez 21, which results in crystal clear gels with a synergistic effect on viscosity after neutralisation. ISP offers over forty styling and fixing polymers for hair care and further details may be accessed on line [Ref 1].

Hair gel science was the subject of the presentation in Melbourne [Ref 2] by Michael Philbin who described the use of molecular modelling in designing polymers suitable for use in hair styling systems. Over 5,000 new hair gel polymers were screened using virtual experimentation that is based on quantitative structure property relationships. This assumes that a polymer's properties are derived from its structure and that the different structural features can be characterized using molecular modelling. The method finds correlations among these molecular features and the critical product properties. The correlations can be used to predict the properties of other polymers so candidate polymers can be screened before making them in the laboratory.

Philbin also described tests performed on gels made with the selected polymers, which included gel clarity evaluations; hair stiffness and the work required to compress curls treated with the hair gels, and high humidity style retention tests used to measure long lasting hold.

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He also described a new flake quantification methodology developed using image analysis to determine the amount of flaking generated by each gel formulation on hair.

Carbomers are frequently used to produce styling gels but they have limitations because of incompatibility with cationic materials and they are very sensitive to electrolytes. **BASF** has recently launched Luvigel Advanced as a multifunctional cationic rheology modifier that, in combination with PVP and VP/VA copolymers, it improves setting properties and the overall performance of the hair styling gel formulation in terms of humidity resistance and low tack. It is a cross-linked copolymer of vinylpyrrolidone, vinylimidazole, 3-methyl-1-vinyl imidazolium chloride and methacrylic acid with the INCI name Polyquaternium-86. It is claimed that the cationic nature of polyquaternium-86 together with its tailor-made shear-thinning rheology provides properties like creamy texture and the ability to re-style the hair plus excellent combing behaviour without sacrificing gel clarity

**BASF** produces literature describing its extensive range of styling polymers and this can be accessed on its web site [Ref 3]. It lists the properties of all twenty-eight polymers with formulation suggestions for all types of hair products. Among the latest material introductions Luviflex Silk, INCI: PEG/PPG-25/25 dimethicone/acrylates copolymer, is a styling polymer containing silicone that combines excellent sensory properties with very good combability and wash-out properties. It was developed especially for hairsprays with little or no water content and it results in a pleasant soft, silky feel to the hair, making it easy to comb and providing it with natural, flexible hold. Luviset Clear, INCI: VP/Methacrylamide/vinyl imidazole copolymer, is designed to give crystal clear styling gels and it is compatible with a wide range of ingredients including cationic polymers and acrylate-type thickeners. It works equally well in mousses, setting lotions and alternative styling products, providing crystal clear, non-tacky, humidity resistant properties.

The UK distributor for BASF styling products is **Cornelius**, which has its own technical centre developing concept formulations that are often a little different to the norm. It has recently introduced a presentation about hair styling that includes such ideas as Chewwit Gum, Texture Butter, Candyfloss and Fluff-it. Chewwit Gum is described as a super stringy dense gum with unique chewwit sweet texture that is ideal for defining short hair styles. Texture Butter is for volume and texture on long hair and can be scrunched through wet or dry hair to boost curls. Candy Floss is a micro-emulsion that provides a ringing gel with stringy texture to create "messed up" styles on longer hair and Fluff-it is a fine coloured powder to lift roots or create a messed up "bed-head" look. It is sprinkled onto hair roots and rubbed in to boost volume and different pigments may be added to match or contrast the user's hair. These and other ideas are to be found on its web site [Ref 4].

DynamX Polymer, INCI: Polyurethane-14, AMP-acrylates copolymer, from **Akzo Nobel** is said to be for dynamic hairstyles and was developed to provide flexible, durable hold with memory performance and imparts excellent curl definition and frizz control when used in styling formulations. Fixomer A-30 from **Nalco** helps provide high curl retention in high humidity environment. Its INCI designation is Methacrylic acid/sodium acrylamidomethyl propane sulfonate copolymer. Fixomer 40 is Acrylates copolymer and is recommended for styling gels, mousses, waxes, creams and glazes to provide stiff, crunchy hold to spiky hair styles. It is non-flaking and contributes water repellence to formulations.

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Syntrans from **Interpolymer** are a range of acrylate polymers suggested for different styling product applications. The manufacturer claims Interpolymer's unique bimodal technology is designed to produce quick-setting hold, humidity resistance and effective curl retention in hair styling aids. Patent pending technology uses a bimodal interpenetrating network to deliver both cationic and anionic functions. Engineered hydrophobic and hydrophilic balance gives the bimodals a pleasant, natural feel without stiffness, flaking, or build-up and the films are easy to remove. They increase colour retention by limiting migration of molecules in and out of the hair shaft, and thereby contribute to vivid initial dye characteristics. Diaformers from **Clarient** are also acrylate-based and supplied as clear alcohol dispersions that are water-soluble and without the need for neutralisation. Viscolam MAC-30 from **Lamberti** is yet another acrylate polymer; it is recommended for strong hold hair gels.

Not all fixatives are acrylates or vinyl pyrrolidone based polymers. Baycusan C1001 from **Bayer Material Science** is an aqueous dispersion of Polyurethane-34. It gives a strong flexible hold and its concentration may be increased without significantly increasing viscosity, making it suitable for low VOC sprays. The key properties claimed are excellent high humidity curl retention; a strong elastic memory; non-tacky feel; high gloss and the ability to be easily removed without build-up on the hair. More suitable for styling gels is Eastman AQ 55, a sulfopolyester with the INCI name Polyester-5 from **Eastman Chemical Co.** that disperses directly in hot water without the assistance of surfactants or other additives

While still on the subject of styling it is often useful to examine newly granted patents for novel ideas that may be developed without contravening the patent itself. Among those recently examined USP 20090041683 claims the use of trimethyl pentaphenyl trisiloxane with at least one film-forming polymer for use in hair sprays. Such patents tend to list every film-former in the INCI Dictionary but Polysilicone-9 is specially preferred.

Silicones continue to dominate most areas of cosmetics; USP 20080305064 describes hair styling compositions containing a combination of a propylphenylsilsesquioxane resin and a phenylsilsesquioxane resin. USP 20090123405 describes a water-free, hair-care composition that claims to impart both style retention and shine to hair and is based on volatile silicones admixed with a non-volatile silicone and at least one hair fixative resin. The volatile silicone is preferably cyclomethicone at approximately 35 – 40% by weight and the non-volatile silicone is typically dimethicone or caprylyl methicone at approximately 2% by weight. Various acrylate polymers are suggested to provide hold and the solvent is either ethanol or aerosol propellant or both.

USP 20090074697 is entitled use of monosaccharides and disaccharides as complete replacements for synthetic fixative and styling polymers in hair styling products and is based on the use of modified starch and cellulose compounds and sugar based mono- and disaccharides. USP 20090226390 claims the use of a quaternary ammonium salt of hydroxyethylcellulose quaternized with diallyldimethyl ammonium chloride incorporated into a gel with polyquaternium-68.

Polyquaternium-68 is sold as Luviquat Supreme by BASF and is described as an innovative styling polymer for hair mousse providing ultra strong hold and outstanding curl retention even at high humidity levels. It is said to have impressive conditioning properties and gives fine hair more volume. A combination of Luviquat Supreme and panthenol results in a highly

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flexible polymer film with a tremendous resistance to breaking, ensuring a natural, flexible hold regardless of the weather.

For those looking for a more natural basis for hair styling Amaze XT from **National Starch** is dehydroxanthan gum. Described as a naturally derived, multifunctional styling polymer it was developed to provide outstanding long-lasting hold under highly humid conditions, without tack and flaking. Interestingly it provides a clear gel at 1% without the need for neutralisation or the presence of any other rheological additive. Its viscosity is related to its concentration and the resultant gel has shear thinning properties but rapidly regains viscosity once shearing forces are removed. Pullulan from **Hayashibara** is the natural starch-based polysaccharide, trehalose, which forms strong adhesive films on the hair that are readily removed by washing.

Another material recommended for forming hair styling gels is Hydrillian 9 from **Lipotec**. Its INCI name is Sodium acrylates/acrylonitrogens copolymer and it is described as a unique polymeric associative thickener and emulsion stabiliser. It forms clear pseudoplastic gels without the need for neutralising a form continuous films on drying that have a silky feel and reduced tack and drag compared to other gelling agents.

Hair styling waxes often give a feeling of stickiness when used, a problem claimed to be overcome by incorporating Inutec SP1 from **Orafti** into the product. Its INCI name is Inulin lauryl carbamate and only 0.2% to 1% is needed to improve the spreadability of high wax content products and to stabilise the emulsions. Inutec SP1 is an emulsifier for silicones and has the ability to incorporate silicones into hair mousse without causing collapse of the mousse. It can emulsify high levels of many different silicone compounds into the water phase and give exceptionally stable products.

Providing hold is not enough: products are also expected to provide volume and protect the hair from thermal styling appliances and its colour from fading in sunlight. The damaging effects of heating tools on the hair were the subject of two posters at the IFSCC Conference, Melbourne, 2009 [Ref 5, 6]. Repetitive use gradually promotes hair damage, producing split ends, fractures, rough surfaces, and making the hair feel dry. Hair that has been treated in this way shows surface blistering and the authors suggest that the heat applied boils water pre-existing inside the hair; the resulting water vapour then passes through the highly hydrophilic endocuticle layer; causing changes in the cuticle structure. The water vapour also lifts the cuticle surface, causing blistering; and repeated use would cause its detachment. The authors also undertook amino acid analysis of the hair protein, which showed a pronounced reduction in cystine and methionine and was suggestive of hydrolysis. The change in the amino acids was thought to cause change in the protein structure and this explains the loss of tensile strength in hair that has been repeatedly exposed to thermal styling.

Flexan II from **National Starch** is sodium polystyrene sulfonate that protects hair from thermal damage. Impressive photomicrographs at high magnification shows how it protects the cuticle by covering the hair shaft in a smooth flexible film that is heat stable up to 300°C and helps hair resist heat damage from hair dryers and curling irons. It is a highly anionic polymer with excellent electrical conductivity and quickly dissipates electric charge to prevent flyaway when used in shampoos and for skin care, its film forming properties tighten skin and smooth fine lines and wrinkles.

AC Polytherm from **Active Concepts**, INCI: Diethylene glycol/DMAP acrylamide/PEG-180/HDI copolymer and dimethicone, is a modified hydrophilic urethane polymer with

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silicone groups attached, which 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. Said to have a similar feel to silicones KiOsmetine-S 1000 from **Kiozyme** is chitosan succinamide, which is water-soluble and readily incorporated into hair products to impart moisture retention and conditioning properties and to protect the hair during thermal styling.

MiruStyle X-HP from **Croda** is an aqueous solution of sodium laureth-40 maleate/styrene sulfonate copolymer that also offers protection from thermal styling aids. Very complete descriptions of test protocols and the results obtained show that it is effective in protecting the hair from cuticle damage even when subjected to straightening irons at a temperature of 220°C. Other ingredients to protect hair from excess heat and moisture loss include a silicone quaternary emulsion called DC 57113 and aminopropyl phenyl trimethicone, DC 2-2078, both from **Dow Corning**. DC 2-2078 is a liquid amino phenyl silicone resin that imparts heat protection and straightening properties and shows good stability in high pH conditions, making it particularly suitable for use in products such as lye relaxers. It also provides high and lasting shine to hair when used in leave on or rinse off products.

**Evonik** supplies two silicone-based materials; Abil T Quat-60 protects hair during thermal styling and Abil UV Quat 50 improves colour fastness of hair dyes. Abil T Quat-60 is Silicone Quaternium-22 and it is said that it improves significantly the combability of wet and dry hair and leads to excellent manageability. It can be used universally in conditioning shampoos, hair rinses, balms, body washes and leave-in formulations and is suitable for clear formulations. The product is proven to be highly substantive to hair keratin because of its unique triple cationic charge and shows significant heat protection properties associated with the application of high temperature styling tools. Abil UV Quat 50 is Polysilicone-19 and being cationic, it is substantive to the hair keratin, forming a thin protective layer which absorbs damaging UV irradiation.

It is possible to find more natural-based ingredients for hair protection: plant-derived amino acids, a phosphated fluorinated polymer and date fruit are combined by **Active Concepts** to provide AC Volumising Complex, a material that is said to use a three-pronged approach to maximising volume and curl retention. AC Rice Curl Complex builds hair strength, as well as affording hair fixative effect and AC Cationic Rice Bran Extract is rich in ferulic acid and will prevent colour fade and can be used as a replacement for benzophenones. Tilicine from **Greentech** is obtained from fresh Linden buds rich in phytohormones, proteins and sugars and are suggested for improving hair volume and moisturising when added to styling gels and other hair products.

Marine Biopolymer from **Unipex** is a purified grade of chitosan that provides good styling properties when used in hair gels but and in addition it has antimicrobial properties. It carries a strong positive charge and binds electrostatically to the cell walls of microbes. In vitro studies show that 0.8% of Marine Biopolymer is sufficient to completely inhibit the growth of *Malassezia furfur*, one of the microbial agents associated with the appearance of dandruff.

Ref 1. <http://online1.ispcorp.com/>

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Ref 2 Advances in hair styling using polyvinylformamide and polyvinylalcohol fixative technology for clear gels; Michael Philbin *et al*

Ref 3 <http://www.cosmetics.basf.de/>

Ref 4 [http://www.cornelius.co.uk/Cosmetics\\_and\\_Personal\\_Care/Haircare/](http://www.cornelius.co.uk/Cosmetics_and_Personal_Care/Haircare/)

Ref 5 The new heat damage induced by hair ironing and the novel protective technology, "anti-blister" formulation; Reina Ikuyama *et al*

Ref 6 The effect of heat on the internal structure of hair using tensile and differential scanning calorimetry techniques, Alisa Roddick-Lanzilotta *et al*

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[www.creative-developments.co.uk](http://www.creative-developments.co.uk)