HOUSEHOLD AND PERSONAL PRODUCTS INDUSTRY

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Features

69

Columns

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Recent Trends In Hair Care Polymers

New polymers and polymeric systems continue to drive hair care innovation. Here's a review of some of the most interesting chemistries available.

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THE RECENT patent literature is a source of information on the relative priorities of major companies and, therefore, serves as a predictor of market direction. In this article, recent patents and patent applications have been scrutinized in an attempt to summarize trends in polymers for hair care and put them together in a "snapshot."

Maintaining a hairstyle in the rain, or even while bathing is a worthwhile objective for research and development, and L'Oréal researchers have patented hair-fixative systems that allow a hairstyle to be retained upon extended exposure to water, yet is easily removed by shampooing. The styling polymer composition contains 5-40% by weight of a water-dispersible linear sulfonic polyester with a glass transition temperature of between 50-100°C (e.g., Diglycol/CHDM/Isophthalates/SIP sold under the tradename Eastman AQ copolyesters).[1] A second styling system is based on a mixture of sulfonic polyesters and high molecular weight nonassociative polyurethanes, sold by Noveon, (PPG-17/IPDI/DMPA exemplified by Noveon's Avalure UR-450

Cationic polyelectrolytes are usually used for their conditioning properties, and many hair-fixative polymers and preferred gellants are anionic. However, attempts to simultaneously achieve both attributes by direct combination of cationic and anionic polyelectrolytes are often thwarted because mixing solutions of cationic polyelectrolyte and anionic polyelectrolyte usually causes the two polymers to interact and separate from solution as a symplex. To overcome this incompatibility, BASF researchers have premixed cationic copolymers based upon vinylimidazole with a copolymer containing acidic groups and then dispersing this preformed complex in a carrier such as a hair gel.[3]

An alternative approach is to use a polyampholyte as one of the components.[4] A polyampholyte is a polymer that contains both cationic and anionic groups on the same molecule. In this context, styling and/or fixing can be obtained simultaneously with good hair disentangling and feel by combining hair fixative polymers with an amphoteric starch; e.g., starch modified by (2-chloroethyl) aminodipropionic acid provided by National Starch.[5,6]

The thickening properties of hydrophobically modified alkali-swellable/soluble thickeners have been improved by combining these polymers with a polysaccharide hydrocolloid gum (such as xanthan gum). This combination alters the gel textures from brittle/cuttable to more flowable, shear thinning.[7]

One Shampoo, Multiple Benefits

Multiple attribute shampoos have been the norm for more than a quarter of a century. During the past 30 years there has been steady improvement on conditioning shampoos that aid in detangling, wet-combing and dry combing. The original successful conditioning shampoos of the 1970s were based on the formation of coacervates of cationic polymer (such as polyquaternium-10 or guar hydroxypropyltrimonium chloride) and anionic surfactants. More recently, a new cationic galactomannan, cationic cassia, has been introduced.[8] Polycationic/nonionic block copolymers synthesized by the new technique of living free radical polymerization reportedly confer surface deposition,[9,10] and improved foaming.[11]

Polyquaternium-7 (a copolymer of acrylamide and diallyldimethyl ammonium chloride) is a very old cationic polymer that has been used for its qualities as a hair conditioner. This polymer

is solution-polymerized and supplied at the relatively low concentration of 8-10% as an aqueous solution. Now, improved conditioning performance is possible from polyquaternium-7 produced in the form of beads by inverse suspension polymerization.[12] Comparative wet-combing measurements of conditioned hair form the basis of the claimed improvement.

Anionic surfactants are generally preferred for shampoos due to their superior cleaning and foaming properties. However, at the levels used in shampoos, these surfactants can be irritating to the eyes and the skin. The irritation can be ameliorated by combining nonionic, amphoteric[13,14,15,16] and/or cationic surfactants with the anionic surfactant shampoo base. However, this approach sacrifices the foamability of the shampoo composition. The inclusion of a hydrophobically-modified, crosslinked anionic acrylic copolymer (identified as Carbopol Aqua SF-1[17] from Noveon) in an 8% anionic surfactant base produces a composition that gives good foaming and cleansing and is substantially free of ocular sting.[18]

There has been steady improvement on conditioning shampoos that aid in detangling.

Certain nonionic "amphiphilic" polymers synergistically improve hair conditioning from silicone-containing conditioner compositions.[19] Polyether urethanes are a particularly useful class of amphiphilic polymers in this respect and Akzo Nobel's Elfacos T210 and Elfacos T212 are two examples. Improved conditioning is due to better wet-combing and dry-combing and by more uniform and more deposition of silicone on the hair surface. The uniformity of deposition is deduced from X-Ray Photon spectroscopy and Scanning Electron Microscopy of treated hair when the amphiphilic polymer is included in the conditioner formulation. *[The word amphiphilic is creeping into our scientific jargon like a pernicious weed and it is often used inaccurately. Amphiphilic—from the Greek roots amphi (dual) and philo (loving) literally means "dual-loving—conveying that the substance interacts favorably with each of the oils and water phases. This could mean that the substance readily dissolves in each of the oil and the water phases. Amphipathic (the Greek root patho means suffering) is a more appropriate term for a molecule that preferentially resides at the oil/water interface and, therefore,* suffers *both phases.]*

Polymeric urethane ester quaternary compositions have been claimed and these are disclosed as bringing about hair-conditioning properties.[20]

The drive to develop clear conditioning shampoos is distinguished by the development of new variants of guar hydroxypropyltrimonium chloride[21] and the inclusion of microemulsified silicone droplets into conditioning shampoo base.[22] Deposition of silicone gives conditioning benefits but residual silicone can cause the hair to lose volume and style, which is apparently ameliorated by using microemulsified silicone droplets.

Multiphase Cleansing

There continues to be a trend toward products that exist as separate phases in the bottle but, when mixed during application, provide added benefit.[23] Procter & Gamble researchers developed multiphase cleansing compositions in which the phases can be arranged to form visually attractive patterns inside a transparent container.[24,25,26] Phases comprise an aqueous cleansing phase,[27] a conditioning-benefit phase[28] and a non-lathering structured phase.[29] A recent example of compositions disclosed for moisturizing and conditioning[30] contains a phase of petrolatum in water emulsified with Emulsifying wax NF (Polawax from Croda) and co-emulsified and structured using hydroxypropyl starch phosphate (Structure XL from National Starch). The product is formed by injecting both phases into a bottle that rotates at 250rpm during packaging.

There is a desire to develop conditioning shampoos that bestow both conditioning and styling benefits. Such styling/conditioning shampoos and their use are reportedly due to the inclusion of an aminosilicone and a styling polymer.[31] The styling polymer is described as having a drawing power of greater than 5cm when evaluated by the TA-TX2 texture analyzer (from Stable Micro Systems).[32] This "drawing" measurement is performed by compressing and penetrating the product with an aluminum disc, withdrawing the disc and measuring the breaking length of the drawn fiber formed as the cylinder is withdrawn. This length is defined as the "drawing power." These styling shampoo patent applications[31] cite Ultimer from Ondeo-Nalco as an exemplary polymer that displays the desired drawing properties. This acrylamide and dimethylaminoethyl acrylate copolymer is a dispersion poly-

merized in saline. During the past decade, the texture analyzer has measured the properties of hair fiber assembly,[33,34,35] conditioners,[36] hair gels[37] and hair fixatives.[38,39]

The Role of Polymers

Polymers play several roles in hair color, acting as thickeners for oxidation dyes and conditioners and hair-protectors to mitigate the harsh effects of coloring. Thickeners include a range of associative thickeners (anionic, cationic, amphoteric, nonionic and hydrophobically-modified alkali swellable as well as hydrophobically-modified ethoxylated urethanes). Alkylmethicones and aminosilicones play a role in color retention. Non-associative thickeners boost hair lightening.

Casperson listed the following conditions of thickened oxidation dye compositions:[40]

1. The formulations must be stable to insure a reasonable shelf life.
2. The compositions formed by mixing the lotion and developer must have rheological properties to allow the applied composition to readily distribute the dye throughout the hair mass and avoid dripping or running from the hair during the color development period.
3. The dye mixture, as applied to the hair, should allow rapid diffusion of the dye precursors from the dye mixture into the hair fiber.
4. The thickened mixture should be readily rinseable from the hair with water.
5. The mixture should contain conditioning agents that leave the hair easy to detangle while wet and should feel smooth and be readily managed when dry.
6. The lotion and developer should preferably, but not necessarily, have comparable viscosities in order to facilitate mixing.
7. The dyeing effect should be rapid, with a dyeing time preferably under 30 minutes.

The oxidation dye compositions are usually thickened to localize the dye action on the hair and to prevent the formula from flowing down the face and into the eyes. Originally, thickeners such as Carbomers,[41] hydroxyethylcellulose or low HLB surfactants were used but they dulled hair color.[42] The original thickeners were replaced with several types of associative thickeners[43] to improve the brightness and intensity of the colored hair. Indeed one recent invention claims that two different anionic association thickeners give better stability than one in these compositions.[44] Combinations of acrylates/C10 30 alkyl acrylate crosspolymer (Carbopol ETD 2020 from Noveon) and acrylates/beheneth-25 methacrylate copolymer (Aculyn 22 and 28 from Rohm & Haas) are mentioned in the patent. Peroxide bleaching similarly requires thickened systems that will not run into the client's eyes. This is achieved by adding pulverulent bleaching powder to peroxide prior to application. However, hydrogen peroxide solutions having a titer of more than 40 volumes should not be used for cosmetic use. Nevertheless, there is a temptation for hair stylists to increase the bleaching performance by using stronger hydrogen peroxide.

L'Oréal researchers reported that they overcame these drawbacks by discovering a bleaching powder that is storage stable and can form homogeneous, stable, ready-to-use bleaching compositions that are easy to apply and remain where applied without running or diffusing onto the areas of the hair in which bleaching is not desired.[45] The compositions cause intense and homogeneous bleaching without rendering the hair coarse. Moreover, these compositions encourage safety in the salon, because if aqueous hydrogen peroxide of greater than 40 volumes is used, the thickened compositions are inhomogeneous and unstable; they run and leave the hair course. These pulverulent bleaching powders contain polymers

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