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Advancements in polymers used in hair care: a review

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Abstract

Polymeric materials gained rapid significance in professional cosmetics formulation due to their large variety of functions. They are critically important for the creation of modern cosmetics and personal-care products. Polymers used in hair care represents promising means as film formers in hair fixatives, emulsifiers in hair-colorants, conditioning agents for hair, thickeners, rheology modifiers and sun protection agents. In the present paper different polymers which are used in hair care are classified on the basis of their application, along with their examples and mechanism of action.

Key words: Polymers, Fixative, Styling, Conditioning, Thickening, Coloring polymers.

Introduction [1-8]

Polymers have become increasingly important components of cosmetic over the past few decades. The term "polymer" derives from the ancient Greek word πολύς (polus, meaning "many, much") and μέρος (meros, meaning "parts"), and refers to a molecule whose structure is composed of multiple repeating units, from which originates a characteristic of high relative molecular mass and attendant properties. Most of the polymers are organic compounds that are chemically based on carbon, hydrogen, and other non metallic elements; they have very large molecular structures. Some polymers are obtained from natural resources and are then chemically modified for various applications, while others are chemically synthesized and used. Polymers, both natural and synthetic, are created via polymerization of many small molecules, known as monomers. Their consequently large molecular mass relative to small molecule compounds produces unique physical properties. The polymers used in hair care typically have low densities and are largely used as film formers, coloring agents, conditioning agents, thickeners and sun protection agents. In this paper, the polymers have been classified on the basis of their applications along with their examples.

Hair Styling and Fixative Polymers [9-14] do exactly what their name implies: they fix the hair in place. Traditionally, hair fixative polymers have been applied to the hair as sprays, lotions, gels and mousses. Polyquaternium-69 is a type of advancement in Styling and Fixative Polymer. Polyquaternium-69 has been designed by polymerization of vinyl pryrrolidone, vinyl caprolactam, DMAPMA, and the alkylated quaternary DMAPMA+- C12H25CL. It is a hydrophobic polymer, yet water soluble and predominately non-ionic with a weakly cationic nature providing a broad range of compatibility with cosmetic ingredients including anionic gellants.

Thickening and Rheology Modifier Polymers [15-18] are long, branched or unbranched molecules which provide thickening effects simply by entanglement, cross-linking or

cluster formation. They all are extensively used in gels, oils, emulsions and nanoemulsions to increase the viscosity and thickness of the particular product by giving it more richness and a smooth and creamy performance. Carbopol Ulterez 10 Polymer is a type of advancement in Thickening and Rheology Modifier Polymer. Carbopol Ultrez 10 is a cross-linked polyacrylic acid polymer that provides efficient rheology modification with enhanced self-wetting for ease of use. Carbopol. The self wetting properties eliminate the need for mechanical dispersers and have the outstanding ability to suspend and stabilize formulations.

Hair Coloring and Highlighting Polymers [19-25] act as thickeners for oxidation dyes, conditioners and hair-protectors. The thickeners used in hair care are classified as associative thickeners, hydrophobically modified ethoxylated urethanes (HEUR), alkylmethicones and aminosilicones and nonassociative thickeners. Acrylates/Steareth-20 Methacrylate Copolymer is a type of advancement in Hair Coloring and Highlighting Polymer. Acrylates/steareth-20 methacrylate copolymer is a Hydrophobically-modified Alkali Soluble Emulsion (HASE). It provides synergistic interaction with surfactants, particulates and hydrophobic raw materials as well as enhanced stabilization.

Conditioning and Cleansing Polymers [26-28] are effective hair modifiers designed to deposit, adhere and adsorb to proteins of the hair. They improve the hair manageability and make the hair softer and smoother. They are classified as cationic conditioning polymers, nonionic conditioning polymers and silicone polymers. Polyquaternium-74 is a type of advancement in Conditioning and Cleansing Polymer. Polyquaternium-74 is an amphoteric polymer used to deliver high conditioning and delivery performance in rinse- off personal care applications. It gives light hair feel and has strong affinity with dimethicone to boost deposition.

UV and Sun protection Polymers [29-30] are designed to provide substantive, broad-spectrum UV-A and UV-B protection to hair; they protect the hair fiber structure (both inside and out) against damage caused by the sun exposure. They maintain the tensile strength of the hair after UV exposure, and have an excellent toxicity profile. Polysilicone-19 is a type of advancement in UV and Sun Protection Polymer. Polysilicone-19 is a silicone copolymer with methoxycinnamic acid, cocos alkyl and cationic groups.

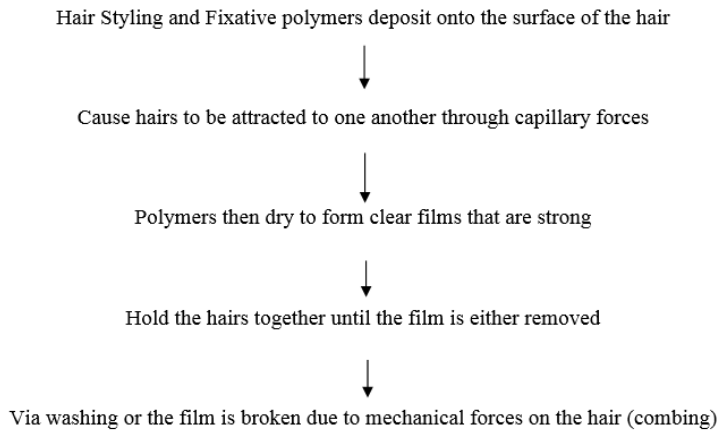
Classification of Polymers Used In Hair Care On The Basis Of Their Application

1. Styling and Fixative Polymers
2. Thickening and Rheology Modifier Polymers
3. Coloring and Highlighting Polymers
4. Conditioning and Cleansing Polymers
5. UV and Sun Protection Polymers

1. Styling And Fixative Polymers [9-14]

Hair fixative polymers do exactly what their name implies: they fix the hair in place. Different film polymers have different humidity resistance properties, which determine both the holding power and the lack of tack in humid climates. The higher the humidity resistance of fixative polymers the higher is its curl retention (CR). Styling polymers are often used as source of "hold" in styling products. These polymers generally function by forming films that spot-weld and seam-weld the hair in the desired style. These tiny welds suffer enormous stress due to the natural movement of the hair. Hair style fixation should be achieved with a tiny amount of styling and fixative polymer applied from "Hair Sprays, Setting/Styling Gels and Lotions, and Mousses."The hair styling and fixative polymers must not phase-separate. The mechanical properties like body, bounce, increased hair volume; non-clumping, lack of extreme stiffness, non-hygroscopic nature and less cohesion of the polymer film should be maintained. Examples of most commonly used hair fixatives are: polyquaternium-11, polyquaternium-4, polyquaternium-46, polyquaternium-16, polyquaternium-39, polyquaternium-2, polyquaternium-28, VP/methylacylamide/vinyl imidazole copolymers, PVP, PVP-VA, acrylates type copolymers, butyl or ethyl esters of PVM/MA copolymers, and guar derivatives like guarhydroxypropyltrimonium chloride.

1.1 Mechanism of Action (MOA)[9-14] includes the following steps:



1.2 Classification of Polymers used as Styling and Fixative Polymers:[9-14]

- Homopolymers: Polymers that contain only a single type of repeat unit are known as Homopolymers. They consist of long molecular chains in which each link is an identical monomer. Polymer nomenclature is generally based upon the type of monomer residues comprising the polymer.
- Random copolymers consist of long molecular chains which comprises of two different monomers which are arranged randomly along the chain. They have a solubility parameter that is intermediate between homopolymers made from the same monomers.
- Block copolymers are the monomers of homopolymer blocks joined together. In block copolymers the molecular blocks are covalently linked, but the segregation is limited to micro domain or nano domain dimensions. This limited segregation leads to polymer alloys in which glassy micro domains confer mechanical rigidity, and rubbery micro domains confer shock-absorbing properties. These materials are thermoplastic elastomers that can display enhanced mechanical properties when compared to the homopolymers. Amphipathic block copolymers contain polar blocks that confer the desirable attribute of facile removal of the polymer from hair by shampooing. The cosmetic and styling properties can be enhanced by the inclusion of a non-thickening amphiphilic block copolymer in a fixative formulation based on a conventional hair fixative polymer.
- Graft copolymers are branches consisting of one type of monomer which are "hung" from a main chain consisting of another type of monomer. For graft copolymers the technique of free-radical polymerization by reaction with a nitroxide and the RAFT (reversible addition-fragmentation chain transfer) polymerization technique can be applied

1.3 Applications of Styling and Fixative Polymers:[9-14]

- Hair Sprays: Hair sprays meet the requirement for a quick- dry preparation which imparts just sufficient rigidity to the set to keep them in place and control loose ends during the day, while not detracting from the natural sheen of the hair. The objective of a hair spray is to deposit onto the dry hair an invisible film to protect it against all external agents that are likely to change its desirable features. Most of the hair spray consists of more than one polymer. All components must be considered and these comprise fixative polymers, solvent, propellant, adjuvant and the value system of the aerosol. Thestyling and fixative polymer sprays should be a compromise between adhesion &elimination, and tightness & lightness. The film should not be sticky or tacky to the touch and should hold the hair, but at the same time leave it free to move. The spray should be very fine and also the force of the spray should be gentle, it should not be wet, which means that the characteristics of the spray should allow it to be of a fineness not to wet the hair but also not to dry before reaching the hair. Styling and fixative spray should be spread over a wide area in a short period and dry quickly. The film should be relatively flexible to follow the movement of the hair without breaking. The film should be substantive to the hair but should be soluble enough to be shampooed off easily. Formulation for styling and fixative polymer sprays generally consist of an amphoteric polymer constituting either of (a)a hydroxyl-containing ethylenically unsaturated monomer (which provides hydroxyl functionality to the polymer) or(b) an acid-containing ethylenically unsaturated monomer (which provides carboxy functionality to the polymer) or(c) an amine-containing ethylenically unsaturated monomer (which provides amine functionality to the polymer) or(d) an ethylenically unsaturated monomer devoid of acid, amine and hydroxyl content. As this polymer composition is insoluble in water, acid neutralizing agent is added for the process of solubilization.
- Setting/Styling Gels and Lotions: Styling gels and lotions are pseudo plastic in nature to enable easy removal from the jar and ensure smooth application on the hair. Setting lotions are intended to strengthen and maintain for an extended period a temporary deformation imparted by waving. The solution of a polymeric material is deposited on the shampooed hair which after setting and drying leaves a flexible film that ensures the cohesiveness and hold of the hair style and also protects it from the effects of humidity. The lotion is based on the synthetic polymers which are soluble in hydro alcoholic solutions. A hair fixative gel is a cosmetic product which is widely used to create and maintain a variety of hairstyles. Two important properties desired in hair gel products are stiffness and hold, which are controlled by the fixative polymer in the formulation. When a gel is applied to the hair, a polymer–fiber composite is created that is morphologically similar to high performance fiber composites used in load-bearing applications. Formulation for styling and fixative polymer setting/styling gel and lotion mostly consist of (a) hydro alcoholic solution, (b) film-forming polymers (which are usually cationic), (c) plasticizers (which are used for increasing the flexibility of the film and providing resilience to extensive handling), (d) additives(which is used for enhancing sheen, softness and disentangling), (e) perfumes, and (f) colorants.
- Mousses: Hair mousse is a toiletry added to hair for extra shine and volume without any clumps or buildup. It often comes either in spray or cream form. Mostly, hair mousse is purple inside the can, but when released the isobutylene makes it an off-shade white in color. Depending upon the nature of fixative, hair styling mousses provides a strong, flexible hold to the hair with a natural look. Mousses are commonly applied to wet hair before blow drying and are combed through without rinsing, to distribute

the product through the hair. The hair is then styled and dried. Mousses are packaged either in aerosol form or as a non-aerosol pump and they typically dispense thick, creamy white foam. Mousses can improve wet hair manageability by lowering combing forces. They reduce flyaway and minimize static. Fixative mousses claim to add body while providing conditioning benefits. Styling mousses enhance body and style retention. Formulation for Styling and Fixative Polymer Mousse consist of (a)resins (which are generally cationic, cationic and neutral, cationic and anionic, or amphoteric),(b) water (which provides the medium for the formula), (c) alcohol (which helps to reduce tack and acts as a VOC), (d) hydrocarbons which are the most commonly used as a propellant that dispenses the product out of the can), (e) non-ionic emulsifier/surfactant (which helps in generating the foam), and surfactants (which is used for lowering the surface tension to help spread the polymer film over the hair surface and to support the foam character of the product).

1.4 Type of Advancement in Styling and Fixative Polymer:Polyquaternium-69 [9-14]

Polyquaternium-69 is a water-soluble, quaternary polymer composed of (a) vinyl caprolactam (VCL)(which increases the hydrophobicity and provides increased film flexibility and durability of hold), (b) vinyl pyrrolidone (VP) (which provides initial stiffness on hair after drying), (c) dimethylaminopropylmethacrylamide (DMAPMA) (which imparts conditioning and provides smoothness of the film and flexibility of hold), (d) and methacryloylaminopropyllauryl -dimonium chloride (MAPLDAC) (a hydrophobically modified quaternary monomer which provides durability, substantivity and the associative behavior of the polymer with hydrophobically modified gellants). Together, these monomers combine to provide the enhanced styling benefits of polyquaternium-69. Polyquaternium-69 is a hydrophobic polymer, yet water soluble and predominately non-ionic with a weakly cationic nature providing a broad range of compatibility with cosmetic ingredients including anionic gellants. It is also synergistic with hydrophobic gellants and has extremely low flaking and broad raw material compatibility. It provides improved humidity resistance and excellent high humidity curl retention. It provides enhanced frizz control and mechanical properties without compromising basic attributes such as gel clarity, stability, mousse foam properties, and low VOC requirements. It is more durable, has elastic hold, and increases shine and luster.Polyquaternium-69 can be easily incorporated into various styling products such as clear and cream gels, aerosol and non-aerosol mousses, styling lotions, and sprays. Advanced formulation of polyquaternium-69 comprise of (a) polyquaternium-69 (which is used in combination with another styling polymer, copolymer 845 (VP/Dimethylaminoethyl Methacrylate Copolymer)). This combination increases the conditioned feel of hair both in the wet and dry state. (b) Palmitamidopropyltrimonium Chloride (PATC)(which is added primarily to raise the cloud point of the concentrate to enhance stability, but its auxiliary benefits are evident in increasing the quality of the foam and conditioning aspects to hair, both in the wet and dry state). The formula is made to be 6% VOC. This particular formulation has increased curl formation and style memory.

Utility: Low VOC regulations have driven the researchers to create fixatives that can be delivered from aqueous solutions. In this context Polyquaternium-69 provides hydrophilic-hydrophobic balance which leads to an excellent high humidity curl retention, increased durability of hold, anti-frizz effects under high humidity and high utility in meeting low VOC requirements.

2. Thickening And Rheology Modifier Polymers [15-18]

Polymers comprising of long, branched or unbranched molecules provides thickening effects. The mechanism of action of thickening polymers can be attained by entanglement, cross-linking or cluster formation. They are extensively used in gels, oils, emulsions and nanoemulsions to increase the viscosity and thickness of the particular product by giving the product more richness, smooth and creamy performance.

2.1 Mechanism of Action (MOA) of Thickening and Rheology Modifier Polymers is: [15-18]

- Entanglement (like cooked spaghetti): In the procedure for polymeric thickening, polymer chains are dissolved in a solvent, which entangles much the same way soft, cooked spaghetti noodles wrap around each other. Solution viscosity increases as the polymer concentration increases simply because more and more chains are trying to occupy a limited space. As the polymer concentration increases, it becomes more difficult to separate individual polymer chains by the application of force over a given area.
- Cross-linking (bind to each other to form large netlike structures): Cross-linking polymers (that is, hooking two polymer chains together by periodic insertion of a difunctional monomer that can react with both chains) radically alters their properties. An optimum level of cross-linking is required to maximize the polymer's viscosity performance i.e. solution polymers must be able to extend and uncoil in solution so that chain entanglement can occur. Cross-linking assures and enhances the ability of polymers to overlap. At the same time, it effectively increases the molecular weight of the polymers.
- Cluster formation (sit together forming micro lumps): In the procedure for cluster formation grafting the hydrophobe along the length of the hydrophilic backbone of the polymer is achieved. The hydrophobic domains of the polymeric thickeners behave like surfactant hydrophobes and find themselves forced together by their unfavorable interactions with water. As the polymer concentration increases, the hydrophobic interactions evolve from

intramolecular to intermolecular. These interpolymeric associations create transient, noncovalent and interpolymeric cross-links further leading into formation of cluster or micro lumps.

2.2 Classification of Thickening and Rheology Modifier Polymers:[15-18]

- Polyethylene Glycols (PEGs): Polyethylene glycol is synthesized by the interaction of ethylene oxide with water, ethylene glycol, or ethylene glycol oligomers. The starting materials used for synthesis of PEG polymers with low polydispersity index (narrow molecular weight distribution) are ethylene glycol and its oligomers. PEG polymers thicken by surrounding themselves with a sheet of water (cluster effect).In most of the cases they are water-soluble at all use levels. PEG shows a high solubility in organic solvents and, therefore, end-group modifications are relatively easy. They provide emulsifying properties which helps to stabilize emulsions. Examples of widely used PEG-thickeners are PEG-150 distearate, PEG- 7 glycerylcocoate, and PEG-200 hydrogenated glyceryl palmate and PEG-120 methyl glucose dioleate.
- Carbopol Polymers: Carbopol polymers have greater ability to thicken, suspend and stabilize aqueous formulations. They have been the standard in the personal care industry for forty years in a wide variety of applications such as gels, creams, lotions and suntan products.
- Acrylate Copolymers/Carbomers: A carbomer is a homopolymer of acrylic acid with a high molecular weight, which is cross-linked with several polyalcohol allyl ethers. It's the polyalcohol portion that confers a carbomer with its high water solubility, unusual in polymers of this size. Carbomers crosslink each other by forming a net, due to which carbomers can help to greatly stabilize emulsions, thereby allowing the formulator to decrease the amount of primary emulsifiers but still hold the emulsion together. Hence, carbomers are excellent agents to form stable, high-viscosity creams and lotions. Another important feature of carbomers is their ability to suspend hard-to-dissolve agents like pigments, particles, antidandruff agents or other polymers. Carbomer is an excellent thickening agent and is consistent from batch to batch. It does not support bacterial growth, and is hypo-allergenic. It also has a particularly nice "skin feel," producing solutions and gels that feel rich and luxurious to the touch. Examples of Acrylate Copolymers/Carbomers are Carboxymethylene polymer, Carboxyvinyl polymer, Acrylates/C10-30 alkyl acrylate crosspolymeretc

2.3 Applications of Thickening and Rheology Modifier Polymers: [15-18]

- Hair Styling Gels: Hair Styling Gels are aqueous compositions that are usually thickened with cross linked poly (acrylic acid); namely the carbomers. Carbomers confer yield stress and shear thinning characteristics on aqueous systems. In order to develop water- soluble fixatives nonionic derivatized starches, poly-*N*-vinylacetamide, amphoteric urethanes, and dehydroxanthan gum have been introduced. Copolymers containing up to 10 weight percent of 2-acrylamido-2-methy 1-1 -propane sulfonic acid or its salts in combination with anionic or nonionic monomers provide a better balance between conflicting requirements of good curl retention at high humidity but they can be removed from hair by merely rinsing with water. An extension of this class of polymers has been introduced in the form of fluorine modified comb polymers based on acryloyldimethyltaurine acid.
- Nanoemulsions: Oil-in-water nanoemulsions are liquid/liquid dispersions in which the droplet size is less than 100 nm. These small droplet size emulsions are transparent and the droplets can be stabilized by a shell of emulsifiers, which are structured as lamellar phase that completely wraps each droplet. Nanoemulsions, are similar to regular emulsions by virtue of the fact that they are thermodynamically unstable and the small droplet size is achieved by subjecting the system to enormous shear energies using homogenizers or dispersers. Nanoemulsions often need to be thickened to be acceptable to consumer expectations. Two conventional ways to thicken a nanoemulsion is (a) by increasing the concentration of the dispersed oil phase (which is usually not an option for the cosmetic formulator because it usually leads to compositions with an undesirable oily or greasy feel), and (b) by adding conventional polyionic thickeners, but these thickeners usually cause flocculation and/or coalescence of the nanoemulsion and destroy the transparency for which the nanoemulsion was made in the first place.
- Oils: Useful compositions have been thickened by particulates such as clays or fumed silica; structuring waxes, triglyceride gellants such as glyceryltribehenate, and silicone elastomers. Block copolymers such as hydrogenated styrene/isoprene block copolymers are useful as gellants. Silicones thickened by elastomers tend to have unacceptably high viscosities.

2.4 Type of Advancement in Thickening and Rheology Modifier Polymer: CarbopolUlterez 10 Polymer [15-18]

CarbopolUltrez 10 Polymer is a cross-linked polyacrylic acid polymer that provides efficient rheology modification with enhanced self-wetting properties which eliminates the need for mechanical dispersers.This new polymer is unique because it is exceptionally easy to disperse and requires no mixing. CarbopolUltrez 10 will self-wet in minutes after the polymer is put on the surface of water. In addition, carbopolultrez 10 is a universal polymer, offering a wide range of performance properties valuable in many personal care applications and, are suitable for general thickening for gels, creams and lotions. Since the dispersion viscosity of carbopolultrez 10 is extremely low, adding additional

ingredients when making a formula is easy, reducing processing time in a formula. This polymer is highly efficient for cost effectiveness, and has improved aesthetic properties (i.e. less tacky feel than traditional carbomer polymers, providing excellent gloss, clarity and smoothness desired in gel products). CarbopolUltrez 10 polymer has outstanding ability to suspend and stabilize formulations. It can be polymerized in toxicologically preferred solvent system, cyclohexane and ethyl acetate. Advanced formulation of carbopolultrez 10 polymer mainly uses the liposome formula which demonstrates the use of carbopolultrez 10 as an additional thickener. This formula does not use soap or surfactant based emulsifiers which could damage the liposome structure, but is instead emulsified with acrylates/c10-30 alkyl acrylate cross polymer, which is a primary emulsifier and can emulsify very high amounts of oils at low usage levels. Both polymers are added using the indirect addition technique, whereby the polymers are dispersed in the oil phase.

Utility: Cross-linked polyacrylic acid polymers have been developed as polymeric emulsifiers for efficient rheology modification with enhanced self-wetting for ease of use. CarbopolUltrez 10 polymer is a unique, multi-purpose carbopol polymer that is the easiest to disperse, has a low dispersion viscosity, requires no mixing to disperse, and makes processing easier, less time consuming, more cost efficient, provides high efficient thickening, excellent clarity, and a non-tacky elegant feel in gels, cream, and lotions.

3. Coloring And Highlighting Polymers [19-25]

Hair Coloring and Highlighting Polymers act as thickeners for oxidation dyes, conditioners and hair-protectors. The thickeners used in hair care are classified into associative thickeners, hydrophobically modified ethoxylated urethanes (HEUR), alkylmethicones & aminosilicones and nonassociative thickeners. The formulations for thickened oxidation dye compositions must be stable and should be readily rinse-able from the hair with water. The compositions must have desired rheological properties, and the dye mixture should allow rapid diffusion of the dye precursors. The mixture should contain conditioning agents and should have comparable viscosities.

3.1 Mechanism of Action (MOA) of Thickened Oxidation Dye Compositions: [19-25]:

Polymeric oxidation dyes are made up of dye precursors, which are colorless compounds that can penetrate the hair fiber. Traditional Hair Coloring Systems usually contains oxidative 'permanent' dyes which comprises of 2-part kits : Dye precursor alkaline solution and Oxidizer

3.2 Classification of Thickeners used as Hair Coloring and Highlighting Polymers: [19-25]

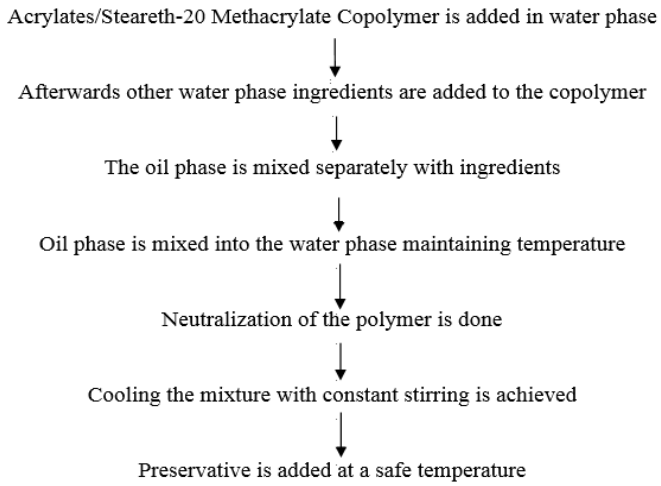
- Associative Thickeners: These thickeners consider the structure of the thickeners with their reported performance in oxidation dyeing. They can be further classified as anionic, cationic, amphoteric, nonionic, and hydrophobically modified alkali swellable.
- Hydrophobically modified Ethoxylated Urethanes (HEUR): This class enhances color intensity from thickened oxidation dyes. Once the hair has been dyed with either a direct dye or an oxidative dye, the color must be maintained. Examples for this class are: PEG-180/octoxynol-40/TMMG copolymer, PEG-180/laureth-50/TMMG copolymer, and polyether-1.
- Alkylmethicones & Aminosilicones: They play a significant role in color retention. They provide more uniform dyeing along the length of the fiber, improve hair softness and pliability and have good shampoo fastness properties. Examples for this class are amodimethicone and trimethylsiloxyamadimethicone
- Nonassociative Thickeners: They are highly suitable for hair lightening. Examples for this class are cross linked acrylic acid homopolymers, nonionic guar gums, and dimethylaminoethyl methacrylate homopolymers and copolymers quaternized with methyl chloride.

3.3 Type of Advancement in Hair Coloring and Highlighting Polymer: Acrylates/ Steareth-20 Methacrylate Copolymer[19-25]

Acrylates/Steareth-20 Methacrylate Copolymer is a Hydrophobically-modified Alkali Soluble Emulsion (HASE). HASE polymers are synthesized from an acid/acrylate copolymer backbone and a monomer that connects the hydrophobic groups as side chains. The polymer is made through emulsion polymerization and is synthesized from acrylic acid, acrylate esters and a steareth-20 methacrylate ester. Mechanism of Actioncomprises of two mechanistic components that work jointly to produce the observed thickening. The first component is polyion swelling, which occurs when the polymer is neutralized with base and becomes a polyelectrolyte; the resulting polyion swells as a result of mutual ionic repulsion of the carboxylate ions that are covalently attached to the polymer chain. In the second mechanistic component, swollen thickener molecules are hydrophobically associated to form an overall network structure. The hydrophobic associations between the macromolecules are easily disrupted by shear and are reformed into a new conformation when the shear force is ceased. A characteristic feature of acrylates/steareth-20 methacrylate copolymer is its highly associative andpseudo plastic nature. This polymer has broad pH range stability, and is also used as an emulsion and foam stabilizer. The polymer is salt & shear tolerant, has instant neutralization/thickening property and has high yield value. Advantage of acrylates/steareth-20 methacrylate copolymer includes it's easy to handle and non-hygroscopic nature. The polymer has increased manufacturing efficiency. The polymer is able to formulate clear products and can be used with electrolytes. It has synergistic interaction with surfactants, particulates and

hydrophobic raw materials and provides enhanced stabilization. The polymer is compatible with nonionic, anionic, zwitterionic and some cationic surfactants and has the ability to stabilize suspensions. It thickens and stabilizes hydrogen peroxide and does not promote or support contamination, unlike natural thickeners. The polymer has flexibility in choice of preservative system and is supported by comprehensive environmental, health and safety data.

Advanced Formulation of Acrylates/Steareth-20 Methacrylate Copolymer comprise of: [19-25]



Utility: Hydrophobically-modified Alkali Soluble Emulsions are being extensively used in hair-coloring products to gel the product on the substrate, but to simultaneously allow good color development. Acrylates/Steareth-20 Methacrylate Copolymer a rheology modifier is an anionic hydrophobically modified alkali-soluble acrylic polymer emulsion (HASE) with unusually high aqueous thickening and stabilizing efficiency. This polymer is a liquid, cold-processable product that instantaneously thickens upon neutralization providing ease of handling and increased manufacturing efficiency.

4. Conditioning And Cleansing Polymers [26-28]

The Conditioning and Cleansing Polymers are effective hair modifiers designed to deposit, adhere, or adsorb to proteins of the hair. They improve the hair manageability and make the hair softer and smoother. These are classified as cationic conditioning polymers, nonionic conditioning polymers and silicone polymers. Cationic polymers are preferred as they are hold by the negatively charged hair proteins by electrostatic forces, whereas nonionic polymers are easily washed off by surfactants. Silicone polymers are a diverse family of synthetic inorganic polymers based upon polydimethylsiloxane.

4.1 Mechanism of Action (MOA) of Conditioning and Cleansing Polymers is:[26-28]:

A conditioner improves the quality of the surface to which it is applied particularly improvement involves the correction or prevention of certain aspects associated with surface damage. Conditioning of the hair must be a continuous process, as both substrates are in a constant cycle of shedding and renewal. Hair damage results from both mechanical and chemical treatments that alter the physical structures of the hair. Conditioning agents cannot enhance repair, but can temporarily increase the cosmetic value and function of the hair shaft until removal of the conditioner occurs with cleansing. Several mechanisms by which conditioners can improve the cosmetic value of the weathered hair shaft are (a) by increasing shine, (b) by decreasing static electricity, (c) by improving hair strength and (d) by protecting against ultraviolet radiation. Conditioning the hair can mitigate this hair damage by improving sheen, decreasing brittleness, decreasing porosity, and increasing strength.

Polymeric conditioners help hair look and feel better by improving the physical condition of these surfaces. Hair conditioners are intended primarily to make wet hair easier to detangle and comb and to make dry hair smoother, shinier, and more manageable. Cationic polymers are very efficacious conditioning agents because of their substantivity to the respective substrate, which is directly attributable to electrostatic interactions between oppositely charged sites on the hair shaft and on the polymer backbone. Conditioners typically remain on the fiber surface, reducing combing forces & flyaway, and in some systems, providing enhancement of volume, curl retention, body and manageability.

4.2 Classification of Conditioning and Cleansing Polymers:[26-28]

- Cationic Conditioning and Cleansing Polymers: Cationic polymers (positively charged) are preferred as they are hold by the negatively charged skin/hair proteins by electrostatic forces, as all cationic polymers carry a quaternary ammonium compound they are called polyquaternium-X, where X is simply sequentially chosen. Examples include polyquaternium-6, polyquaternium-7, polyquaternium-11, etc.
- Nonionic Conditioning and Cleansing Polymers: Nonionic polymers when present in a dried state are very hydrophobic, but when hydrated, are quite hydrophilic. This dual functionality is characteristic which allow them to spread quickly over the surface of hair, driven primarily by their low surface tension on these protein substrates. They are easily removed by surfactants (unlike mineral oil and other oily conditioners) and hence are easily washed off during shampooing and rinsing.
- Silicone Polymers: Silicone polymers are a diverse family of synthetic inorganic polymers based upon polydimethylsiloxane that can be prepared and modified in numerous ways in order to produce materials suitable for a wide range of applications. Silicones used in hair care products are typically long, flexible molecules with a backbone comprised of thousands of repeating units of some

variation of – (O-Si-O) - linkages with differing organic (carbon-containing) pendant groups attached to the central silicone atom. These are typically liquid at room temperature and are oily in their consistency. They are most often insoluble in water, but are sometimes modified with ethylene glycol groups or other atoms to render them as water-soluble. The physical properties of silicones cause them to adsorb onto the surface of hair and to spread out, forming a smooth film, which increases slip along and between hair strands and decreases combing forces. This renders them as superior conditioner agents and detanglers. Additionally, they provide thermal protection, which reduces structural damage incurred from the use of heated styling tools. They have also been found to increase the longevity of color in dyed hair. Silicone polymers have a high refractive index, which allows them to impart an extraordinary level of gloss to the hair, which gives the appearance of shiny, glamorous tresses.

Most commonly used silicone polymers are (a) cyclomethicones (which are used to provide transient shine with no buildup and prevention against clogging or windowing of pumps), (b) dimethicones (which are used to provide shine, improved feel and softness. It is also used as resin plasticizer, helps reducing static electricity and resistance against humidity), (c) dimethiconecopolyols (which are used as resin plasticizer, emulsifier, and foam stabilizer. It also helps in reduction of irritation to the hair), (d) alkyl-modified silicones (decyldimethicone, stearylmethicone, andcetylmethicone) (which are used to improve volume/body, and combing properties), silicone resins (silsequinoxanes, siloxysilicates) (which are used to provide improved volume/body and humidity resistance**),** and silica (which is used as antifoamer, thickener and suspending agent).

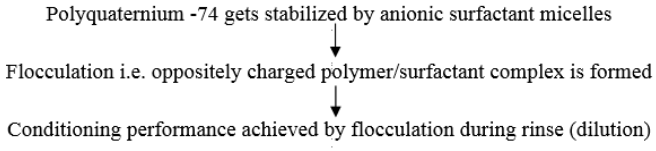
4.3 Applications of Conditioning and Cleansing Polymers:[26-28]

- Shampoo: Shampoo is defined as suitable detergents for the washing of hair, packaged in a form which is convenient for use. Raw materials used in the formulation of a shampoo are (a) surfactants (which can be classified as primary/principle surfactants and secondary/auxiliary surfactants), (b) foam boosters, (c) conditioning agents, (d) additives, (e) preservatives, (f) sequestering agents, (g) viscosity modifiers (which are used as thickening or thinning agents), (h) opacifying or clarifying agents, (i) fragrance, (j) color, (k) stabilizers (which are used as suspending agents), (l) antioxidants and (m) UV absorbers. Primary/Principle surfactants (lauryl sulfate and sodium or ammonium laureth sulfate) are used to provide detergency and foam. Primary surfactant has fine ability to clean sebaceous soil, while providing excellent lather and viscosity building properties. Secondary/Auxiliary surfactants (amides such as cocamonoethanolamide (cocamide MEA), betaines) are used to improve detergency, foam, and hair condition. A characteristic consideration of shampoo is that they should have ease of spreading and ease of rinsing. They should possess abundant lathering power and efficient soil removal efficiency. They should comprise of ease of combing and setting wet as well as dry hair. They should provide lustre of hair, efficient speed of drying and safety.
- Conditioners: Conventional conditioner formulations are based upon lamellar gels or emulsions using either ceto-stearyltrimethylammonium chloride or distearyldimethylammonium chloride as cationic surfactants and ceto-stearyl alcohol as co-surfactant. These products form a gel matrix that confers conditioning benefits from rinse-off products. Polymeric conditioners can improve wet combability and ameliorate electrostatic charging of the hair. Conditioners must provide ease of wet and dry combing and should minimize porosity. They should smooth, seal and realign damaged areas of the hair shaft. Conditioners should impart sheen and a silken feel to the hair and should possess the property to moisturize. They should provide some protection against thermal and mechanical damage and should add volume/body to the hair. Polyquaternium-10 (cationic hydroxyethylcellulose), polyquaternium-6 (polydiallyldimethylammonium chloride homopolymer) and polyquaternium-7 (which is a copolymer of diallyldimethyl --ammonium chloride and acrylamide), are found in conditioner formulations.
- Conditioning Shampoos: Conditioning shampoos are intended primarily to cleanse and secondarily to improve manageability and promote desired feel & appearance they confer the wet hair attributes (i.e. hair softness and ease of wet-combing), and the dry hair attributes (i.e. good cleansing efficacy, long-lasting moisturized feel, and manageability with no greasy feel). The mechanism of action of conditioning shampoos introduced the concept of polymer-surfactant complex coacervates that phase-separate and deposit on the hair during rinsing. Polyions in aqueous solution are surrounded by an electrical double-layer of counterions and the location of the counterions with respect to the polyion is determined by a balance between chemical potential and electrochemical potential, called the "Donnan Equilibrium." Surfactant ions contain a large hydrophobic group and this makes them intrinsically less soluble in water than inorganic ions such as chloride or bromide. When surfactant ions interact with an oppositely charged polyion, they bind strongly and displace the water-soluble inorganic ions from the polyion; that is, they ion-exchange. Once the surfactant ions bind, hydrophobic interaction between the hydrophobic surfactant tails causes the polymer-surfactant complex to phase separate. If the surfactant concentration is sufficiently high to form micelles or hemi-micelles along the polyion chain, then the polyion is resolubilized. Conditioning shampoos are formulated within the range of surfactant concentrations that correspond to this solubilized regime. If

this solubilized complex (shampoo) is diluted to a concentration in the vicinity of the critical micelle concentration, then the complex coacervate phase separates. The separated phase is deposited on the hair during rinsing.

4.4 Type of advancement in Conditioning and Cleansing Polymers: Polyquaternium-74 [26-28]

Polyquaternium -74 (molecular weight: ~1.2 M) is amphoteric copolymer, i.e. bearing both cationic and anionic charges. Cationic charge density of polyquaternium -74 varies from 0 meq/g to 1 meq/g as a function of pH. It is used to deliver high conditioning and delivery performance in rinse- off personal care applications. It gives light hair feel and has strong affinity with dimethicone to boost deposition.
Mechanism of Action (MOA)



Polyquaternium -74 must have the ability to improve wet combability and should be anti-static. It must restore disrupted cuticle and should provide aid of active delivery (flocculation during rinsing). It should neutralize the negative charges of most shampoos and hair proteins and help hair lie flat. It should ionically bond itself to hair and possess antimicrobial properties.Polyquaternium -74 has(a) volume enhancing properties (i.e. they re-firm hair from root and thicken hair shaft), (b) anti-dandruff properties (i.e. they eliminate fungus), (c) repairing properties (i.e. they restore damaged keratin fiber), (d) moisturizing properties (i.e. they nourish hair from inside), (e) shine providing properties (i.e. they smoothen the hair surface), and (f) color protecting properties (i.e. they lock and revive the color). Advanced formulation of polyquaternium -74 polymer comprise of (a) water, (b) dimethicone (which is used to boost deposition), (c) polyquaternium-74 polymer, (d) laureth-7, sodium benzoate and (e) phenoxyethanol, (which acts as a preservative).
Utility: Amphoteric polymers are highly used to deliver high conditioning and delivery performance in rinse- off personal care applications. Polyquaternium-74 is a synthetic high performance conditioning polymer whose flocculation and deposition characteristics enable it to match or outperform traditional conditioning polymers in detangling, overall hair conditioning, shine enhancement and buildup reduction when combined, as shown here, with a submicron dimethicone emulsion.

5. UV And Sun Protection Polymers [29-30]

UV and Sun Protection Polymers are the breakthrough in hair care technology for the effective broad spectrum UV-protection of hair. UV and Sun protection polymers are multifunctional UV-absorbing polymers for use in both leave-in and rinse-off hair care products, including shampoos, conditioners and non-aerosol hair styling products. They are designed to provide substantive, broad-spectrum UV-A and UV-B protection to hair. They protect the hair fiber structure, both inside and out, against damage caused by sun exposure, and maintains the tensile strength of hair after UV exposure. It works well in formulations over a broad pH range, from 4 to 10. They have excellent toxicity profile, which is fully water soluble, and is also compatible with a variety of surfactants and in formulations containing up to 95 percent alcohol.
Exposure to ultraviolet radiation depletes the protective lipids found on the surface of the cuticle. This increases combing forces necessary to detangle hair, which generally results in formation of split ends and breakage. UV-B radiation (280-320 nm) cleaves disulfide bonds (S-S) in the cuticle which depletes cystine in the structure, and thus damages the protein structure of the protective cover of the hair strand. This process increases surface roughness and porosity, which results in frizz, tangling, and ultimately, breakage. The surface of human hair is highly hydrophobic, which helps to seal moisture into the hair shaft, protect it from the environment and mitigate effects from fluctuations in humidity that can cause structural damage. UV-B breaks down tryptophan found in the protein structure of the hair and create a more highly negatively charged surface, which becomes more hydrophilic and less capable of moisture retention and more susceptible to ill effects of the environment. Ultraviolet radiation also penetrates into the cortex of the hair where it breaks down protein structures within the hair strand, compromising the mechanical integrity of the hair. This results in a lower tensile strength which ultimately enhances easy breakage of hair. UV-A radiation in the cortex reacts with both natural melanin pigments and chemical dye molecules, causing photo bleaching and yellowing, both definitely undesirable effects. UV and sun protection polymers have greater charge density which enhances its substantivity to the surface of hair. Also, as a lighter weight, water-soluble polymer, it has no greasy tactile sensation. The novel twist to the polymer structure is the inclusion of groups capable of absorbing UV radiation at the ends of the pendant groups. These portions of the molecule transform the harmful, high energy UV radiation into a lower energy form (infrared) that is emitted as heat. This sun protection quality is perhaps the most valuable contribution UV and sun protection polymers makes to any personal care product formula.

5.1 Type of Advancement in Heat Repair and Sun Protection Polymer: POLYSILICONE-19 [29-30]

Polysilicone-19 is a silicone copolymer with methoxy-- cinnamic acid, cocos alkyl and cationic groups. Polysilicone-19 provides efficient protection against UV-

damage. It is a photo protective polymer, which is specifically designed for protection of hair against UVB and UVA. As polysilicone-19 is cationic, it is substantive to the hair keratin, forming a thin protective layer which absorbs damaging UV irradiation. Polysilicone-19 protects hair color against fading in the sun light and fiber integrity against damage by UV irradiation. They have high substantivity to hair surface from rinse-off applications. Polysilicone-19 is compatible with anionic surfactants. It can be used in anionic post treatments for colorants with or without polycationic ingredients.In the advanced formulation of polysilicone-19 polymer, polysilicone-19 is applied into the oily phase of an emulsion like formulation e.g. conditioner, balm or hair mask. In shampoo formulations polysilicone-19 is mixed with a concentrated surfactant (anionic nonionic or amphoteric) before further dilution with aqueous ingredients.

Utility: Silicone copolymers with methoxycinnamic acid, cocos alkyl and cationic groups are significantly used as UV-absorbing polymers providing heat repair and sun protection. Polysilicone-19 provides efficient protection of the hair fiber against UV-damage. It is a photoprotective polymer, which is specifically designed for UVB and UVA protection of hair

Conclusion [1-8]

Polymeric materials are critically important to the creation of modern cosmetics and personal-care products. Low VOC regulations have driven the researchers to create fixatives that can be delivered from aqueous solutions. In this context Polyquaternium-69 provides hydrophilic-hydrophobic balance which leads to an excellent high humidity curl retention, increased durability of hold, anti-frizz effects under high humidity and high utility in meeting low VOC requirements.

Cross-linked polyacrylic acid polymers have been developed as polymeric emulsifiers for efficient rheology modification with enhanced self-wetting for ease of use. Carbopol Ultrez 10 polymer is a unique, multi-purpose carbopol polymer that is the easiest to disperse, has a low dispersion viscosity, requires no mixing to disperse, and makes processing easier, less time consuming, more cost efficient, provides high efficient thickening, excellent clarity, and a non-tacky elegant feel in gels, cream, and lotions. Hydrophobically-modified Alkali Soluble Emulsions are being extensively used in hair-coloring products to gel the product on the substrate, but to simultaneously allow good color development. Acrylates/Steareth-20 Methacrylate Copolymer a rheology modifier is an anionic hydrophobically modified alkali-soluble acrylic polymer emulsion (HASE) with unusually high aqueous thickening and stabilizing efficiency. This polymer is a liquid, cold-processable product that instantaneously thickens upon neutralization providing ease of handling and increased manufacturing efficiency.

Amphoteric polymers are highly used to deliver high conditioning and delivery performance in rinse- off personal care applications. Polyquaternium-74 is a synthetic high performance conditioning polymer whose flocculation and deposition characteristics enable it to match or outperform traditional conditioning polymers in detangling, overall hair conditioning, shine enhancement and buildup reduction when combined, as shown here, with a submicron dimethicone emulsion.

Silicone copolymers with methoxycinnamic acid, cocos alkyl and cationic groups are significantly used as UV-absorbing polymers providing heat repair and sun protection. Polysilicone-19 provides efficient protection of the hair fiber against UV-damage. It is a photoprotective polymer, which is specifically designed for UVB and UVA protection of hair

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