The Use of Cationizing Reagents in the Preparation of Conditioning Polymers for Hair and Skin Care

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Key Words

Conditioning polymers, cationic polymers, cationizing reagents, cationization processes

Abstract

Cationic compounds with quaternary ammonium functional groups are used extensively in personal care product applications. One important class of such quaternary ammonium compounds is cationically charge-modified polymers derived from various animal and plant sources, including guar gum, cellulose, proteins, polypeptides, chitosan, lanolin, starches and amino silicones. These polymers have a demonstrated utility as substantive conditioning agents in hair care formulations and have also found wide acceptance in skin care products.

Cationic conditioners are known to revitalize the hair: protecting against environmental damage and offseting the physical stress created by daily styling procedures such as blow-drying, bleaching, coloring, combing and perming. These cationic derivatives act as conditioning and thickening agents in hair care applications and also exhibit skin protection properties, due to their functional surface properties and their emollient smooth feel.

An overview of cationizing reagent chemistry and the various commercial methods for producing cationic conditioning polymers are described.

The Conditioning Mechanism

A product is considered to be a conditioner if it improves the quality of the surface to which it is applied, particularly if this improvement involves the correction or prevention of certain aspects associated with surface damage.

Conditioning of the hair and skin must be a continuous process, as both substrates are in a constant cycle of shedding and renewal. The main difference between hair and skin is that skin is basically a living organ that replaces its outermost layer on a frequent basis. Hair, in contrast, is basically dead material derived from a few live cells deep within the skin surface.

Thus, conditioning agents for skin can affect the homeostatic processes of growth and repair by supplementing the body’s renewal mechanisms. Conditioning agents for hair have no effect on growth and cannot affect cellular repair. Rather, they can only temporarily improve the cosmetic appearance of damaged hair and must be reapplied as removal occurs.

For skin to appear and feel normal, the moisture content of the upper layer must be above 10%. Moisture is lost through evaporation under low humidity conditions and must be replenished with water from the lower epidermal and dermal layers. Once skin damage has occurred and the barrier has been damaged, reconditioning can occur only if the loss of moisture is retarded. This is the goal of moisturizers, which function temporarily until skin integrity can be re-established.

Hair damage results from both mechanical and chemical treatments that alter any of 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. Most hair damage occurs as a result of grooming habits and exposure to chemicals used for esthetic purposes, such as shampooing, drying, combing, brushing, styling, dyeing, permanent waving, and to environmental factors, such as sunlight, air pollution, wind, seawater, and chlorinated swimming pool water. There are several mechanisms by which conditioners can improve the cosmetic value of the weathered hair shaft by increasing shine, decreasing static electricity, improving hair strength and 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 and skin 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. Skin conditioners primarily moisturize, while providing protection from the drying effects of the sun, wind, and contact with harsh detergents.

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 or skin surface and on the polymer backbone. Conditioners typically remain on the fiber surface, reducing combing forces and flyaway, and in some systems, providing enhancement of volume, curl retention, body and manageability.

Modern conditioners are designed to provide one or more of the following functions:

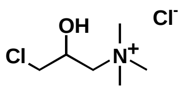
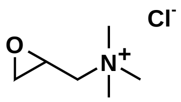
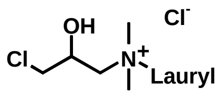
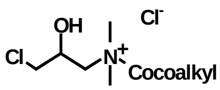
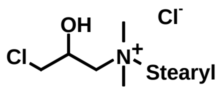
- provide ease of wet and dry combing
- smooth, seal and realign damaged areas of the hair shaft
- minimize porosity
- impart sheen and a silken feel to the hair
- provide some protection against thermal and mechanical damage
- moisturize
- add volume and body
- eliminate static electricity

Production of Conditioning Polymers Using Cationic Reagents

The oligomers or polymers used as the chemical precursors for cationic conditioning agents contain either hydroxyl, amino or mercapto functional groups as part of their monomer structure. These reactive groups are available for a wide range of chemical reactions, such as etherification or esterification. In the case of the cationic moieties, quaternary ammonium groups are grafted onto the polymer backbone and become covalently bound. These cationic groups enhance the polymer's substantivity to anionic substrates, such as hair and skin.

The introduction of longer chain alkylquat groups onto the polymer substrate produces a family of products having distinct physical and conditioning properties. Here, the effect of a cationic substrate is combined with functional properties normally associated with fatty acid quats like manageability, lubricity, anti-static properties, surface activity and biocidal activity.

The reagent products that are used for the cationic modification of polymeric substrates are quaternary ammonium salts with a reactive chemical end-group. They are commercially available in the stable chlorohydrin form or, in the case of the trimethylammonium reagent, also in the reactive epoxide form. The range of commercially available cationizing reagent products is shown below in Table 1.

Table 1. **Commercially Available Cationizing Reagents**			
Empirical Structure	Commercial Abbreviation / Chemical Name	Molecular Weight (g/mol)	CAS Number
	CHPTAC[a] (3-chloro-2-hydroxypropyltrimethylammonium chloride)	188.10	3327-22-8
	EPTAC[b] (2,3-epoxypropyltrimethylammonium chloride)	151.64	3033-77-0
	CHPDLAC[c] (3-chloro-2-hydroxypropyldimethyldodecylammonium chloride)	342	41892-01-7
	CHPCDAC[d] (3-chloro-2-hydroxypropylcocoalkyldimethylammonium chloride)	360	690995-44-9
	CHPDSAC[e] (3-chloro-2-hydroxypropyldimethylstearylammonium chloride)	426	3001-63-6

The Cationization Process

Figure 1 (below) illustrates the initial step in the cationization process, which is the chemical conversion of the cationizing reagent from its stable chlorohydrin form to its corresponding reactive epoxide form. This conversion is achieved by reacting equimolar quantities of alkali with the chlorohydrin. The resulting epoxide can then further react, again under alkaline conditions, with the hydroxyl or amino groups on the polymeric substrate. The resulting product is a substrate with a chemically bound quaternary ammonium group, which imparts a cationic charge.

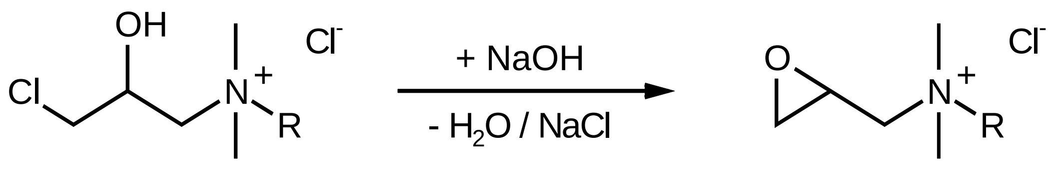


Figure 1. Conversion of a Chlorohydrin Reagent to the Epoxide Form

If the reagent used is in the chlorohydrin form, then equimolar quantities of sodium chloride and water are generated as reaction by-products. Some producers of cationizing reagents offer the EPTAC type product, which already exists in the reactive epoxide form. Using such EPTAC cationizing reagents circumvents the formation of salt during the cationization process, but usually at somewhat higher cost.

The main side reaction in the cationization process is the hydrolysis of the epoxide with water to form the respective 2,3-dihydroxypropyldimethylalkylammonium chloride (Figure 2).

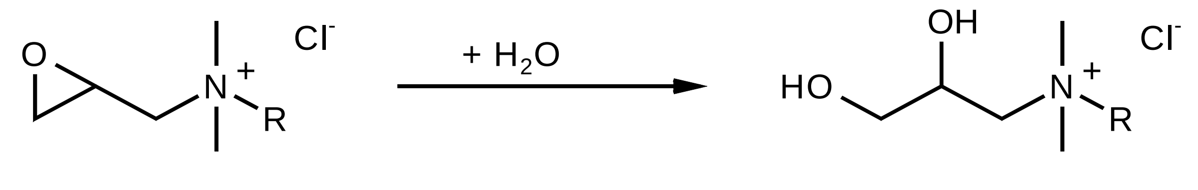


Figure 2. Formation of the Diol By-Product

Figure 3 illustrates the reaction of hydroxyethyl cellulose (HEC) with a cationizing reagent in its epoxide form to form the corresponding cationic cellulose ether. Such a cationization reaction is commonly employed to produce the conditioning polymer, Polyquaternium-10.

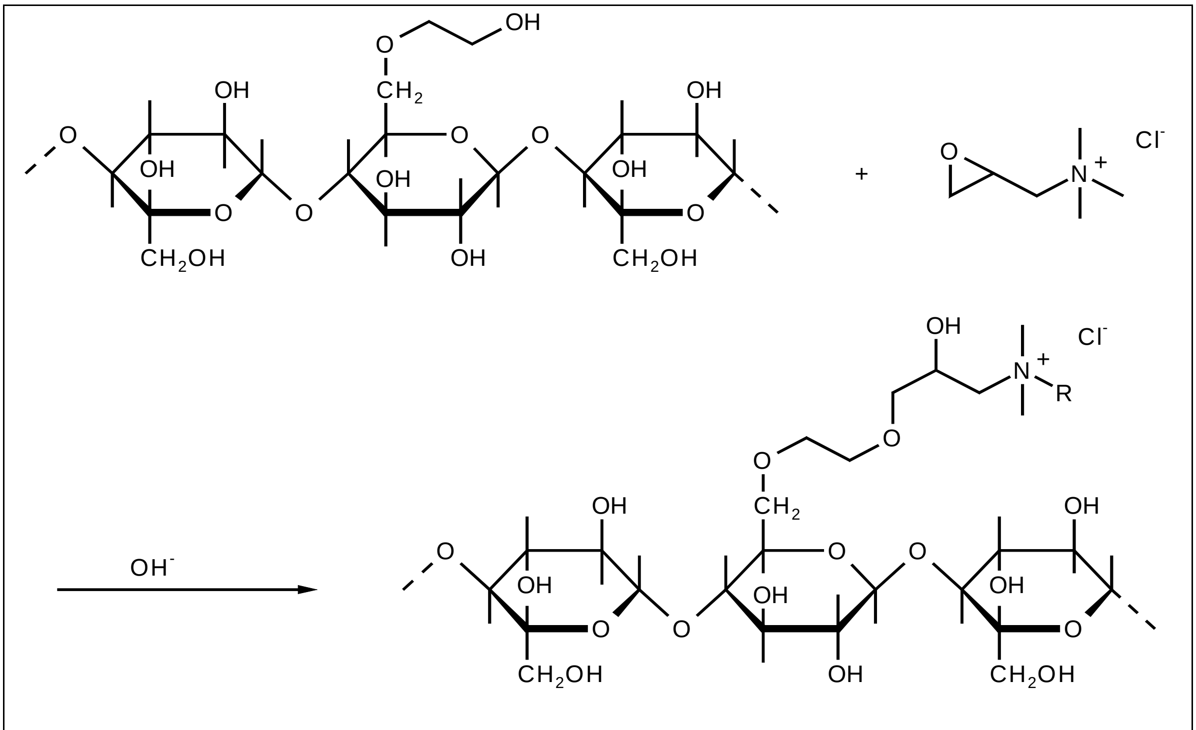


Figure 3. Cationization of Hydroxyethyl Cellulose

Homogeneous and Heterogeneous Cationization Processes

Polymeric substrates are either reacted in homogeneous or heterogeneous systems. The choice of the system partly depends on the physical state of the substrate, as they are available either as an aqueous solution or as a solid. Examples of polymers sold as aqueous solutions include protein hydrolysates, oligomers, methyl glucosides and the lower sugars. Examples of polymers in the solid form include starch, guar, cellulose and their derivatives.

Those substrates that are already in the liquid form are reacted in solution in a homogeneous system. Here, the substrate solution is mixed with the cationizing reagent and sufficient alkali to convert the chlorohydrin form into its reactive epoxide form (stoichiometric alkali) and to bring the pH up to the required alkalinity for the reaction to proceed (catalytic alkali). This solution is then maintained at elevated temperatures for up to 24 hours in order to completely consume the epoxide form of the reagent. Subsequently, the final mixture is neutralized with an acid to a neutral pH. In general, no further purification is performed.

The substrates that are natural solids are reacted in heterogeneous systems in order to maintain the granular form. These can either be reactions in dispersions (wet process) or in a quasi-dry state (dry process). Reactions in dispersions use either water as a solvent, for water insoluble substrates, like starch or guar splits, or organic solvents, for water soluble substrates like guar and cellulose derivatives. The major organic solvents used are alcohols or ketones, such as isopropanol or acetone.

In the dispersion system, a slurry is prepared from the substrate with the respective solvent. Then the reagent and the alkali are added sequentially in order to form the reactive epoxide (when the chlorohydrin form is used), and additionally, to bring the alkalinity up to its required reaction pH. The mixture is then reacted from a few hours up to 30 hours, at temperatures ranging from 30°C to 80°C. The dispersion is then neutralized with organic or inorganic acids, filtered, and the solid cationic substrate is washed several times in order to remove the reaction by-products, as well as any salts. In those systems where organic solvents are used, the preferred reagent is EPTAC, as less salt has to be removed from the final product.

The wet or slurry type of cationization reaction is shown schematically in Figure 4.

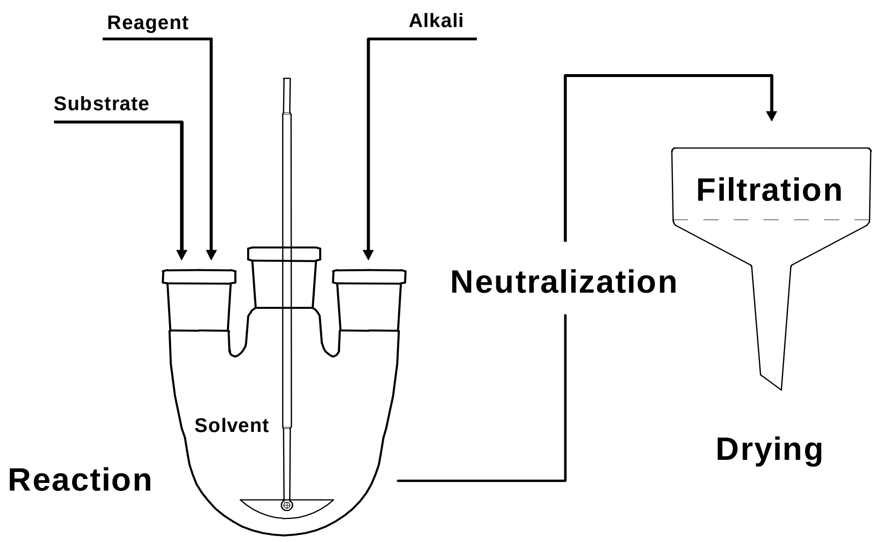


Figure 4. Wet or Slurry Cationization Process

In the dry system, the solid substrate is mixed vigorously in an intensive mixer along with the cationizing reagent, some additional water, and the necessary alkali. This mixture is then either reacted at ambient or elevated temperatures (up to 80°C) in reaction/storage bins or in the mixing equipment as such. After the reaction is completed, solid organic acids are added for neutralization purposes. The final product does not require any further purification.

A typical dry cationization process is illustrated below in Figure 5.

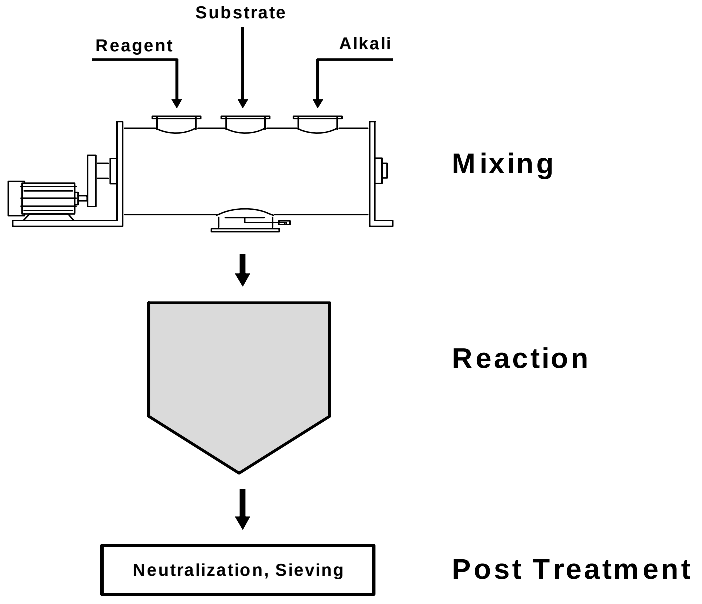


Figure 5. Dry Cationization Process

Commonly Used Cationic Oligomers and Polymers

The common quaternary oligomers and polymers used as conditioners in hair and skin care applications are based on guar gum, cellulose, proteins, polypeptides, chitosan, lanolin, starches, sugars and amino silicones. These are described in greater detail below.

Quaternary Guar Derivatives

Native or hydroxypropylated guar can be modified with EPTAC or CHPTAC to introduce cationic charges onto the molecule (Figure 6). Cationic guar is perhaps the most widely used cationic conditioning polymer in the personal care formulary.

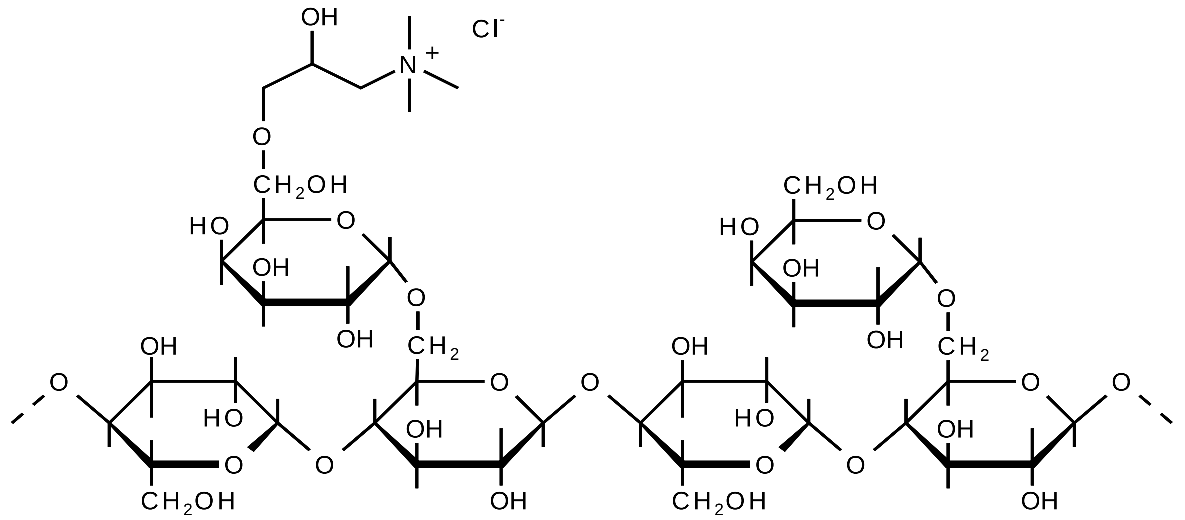


Figure 6. Guar Hydroxypropyltrimonium Chloride

Quaternary Cellulose Derivatives

The main cellulose derivatives commercially chosen for cationic modification are hydroxethyl cellulose (used in the synthesis of Polyquaternium-10, as shown in Figure 3) and hydroxypropyloxyethyl cellulose, with different molecular substituent patterns. However, hydroxypropylated and carboxymethylated cellulose derivatives may also be used.

Quaternized Proteins

Cationic proteins and polypeptides, derived from various plant and animal sources, are common conditioning agents. These products include plant-based proteins and their hydrolysates (such as wheat, rice, soy, corn, and other vegetables) and animal-based proteins and hydrolysates (such as milk, collagen, and keratin). Because of their similarity to the proteinaceous structure of hair and skin, they are naturally adsorbed. Proteins are non-occlusive film formers, which bind water and enhance the ability of the skin to absorb and maintain moisture. This results in more supple and smoother skin and a protective colloidal effect.

The cationic derivatives of proteins neutralize static charges, reduce fly-away and friction damage from styling, enhance shine and manageability, increase tensile strength of hair, have good film-forming properties and can smooth the hair shaft (split-end repair products). Because of their chelating power, they are useful in improving skin compatibility of anionic surfactants and have a high foaming power

Quaternary Lanolin

These natural products have many applications in cosmetics, particularly in the area of hair care products because of their compatibility with anionic surfactants.

Quaternary Chitosan

Chitosan is the de-acetylation product of chitin, which is a major component of the exo-skeletons of invertebrates. It is reacted with propylene glycol and then further quaternized with the cationic reagents.

Quaternary Natural and Plant Actives (Sugar Derivatives)

These raw materials are derived from short to long alkyl chain sugars, such as those found in sugar cane. The sugar or alkylpolyglucoside backbone is then quaternized with cationic reagents. The end-producsts provide substantivity to skin and hair much more so than their nonionic APG precursor.

Lauryl methyl gluceth-10 hydroxypropyldimonium chloride (reaction product from CHPDLAC) is a substantive conditioning humectant. It is a skin moisturizer, adjusting the skin‘s moisture content in line with the humidity.

Another common conditioning polymer is cationic honey, which has demonstrated improved moisture binding to skin and hair and penetrates hair to repair it.

Quaternary Starches

Starch is a polysaccharide containing anhydroglucose units. The hydroxyl groups of the molecule are quaternized with the cationization reagent. So far, the use of cationic starches as personal care conditioners is somewhat limited in scope, with a few exceptions. However, new derivatives like hydroxyethyl starch or hydroxypropyl starch may help to enhance the conditioning power of the cationic derivatives and provide better film forming properties.

Amino Silicones

Silicones offer a route to conditioning benefits without the buildup associated with dilution-deposition shampoos or the limpness associated with traditional rinse conditioners. They increase the hair's luster and ease wet combing. Applied to dry hair, they lubricate the fibers and ease dry combing.

New Product Developments

Hydroxyethyl cellulose (HEC) derivatives containing both a trimethylammonium group as well as a dimethyllaurylammonium group have recently been introduced to the market. They are produced from EPTAC and CHPDLAC and have unique properties in hair care formulations.

Besides for the trimethylammonium group containing reagents, the long alkyl chain reagents may also be used in reactions with hydroxyethyl cellulose. For example, Polyquaternium-24 is the reaction product of hydroxyethyl cellulose with CHPDLAC (Figure 7).

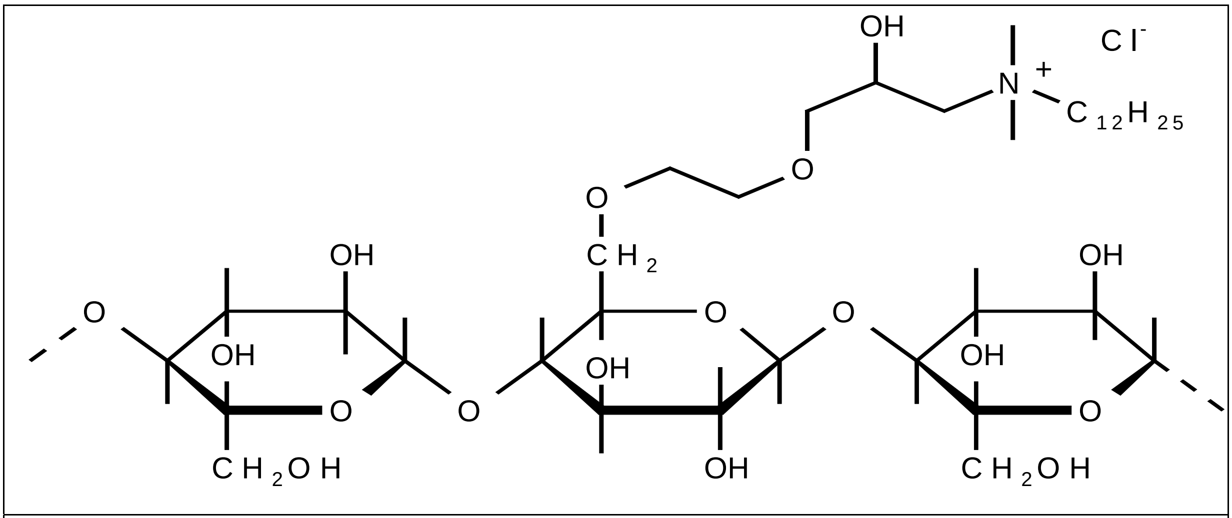


Figure 7. Polyquaternium-24

The following table provides an overview of various quaternary derivatives used in personal care formulations, as well as their INCI or chemical name:

Table 2. **Examples of Quaternary Derivatives Used in Personal Care Formulations**	
Starting Material	INCI or Chemical Name of Cationic Derivataive
Guar	Guar Hydroxypropyltrimonium Chloride Hydroxypropyl Guar Hydroxypropyltrimonium Chloride
Cellulose	Polyquaternium-10 Polyquaternium-24 Cocodimonium Hydroxypropyloxyethyl Cellulose Lauryldimonium Hydroxypropyloxyethyl Cellulose Stearyldimonium Hydroxyethyl Cellulose Stearyldimonium Hydroxypropyl Oxyethyl Cellulose
Protein (animal based)	Hydroxypropyltrimonium Hydrolyzed Collagen Lauryldimonium Hydroxypropyl Hydrolyzed Collagen Cocodimonium Hydroxypropyl Hydrolyzed Collagen Steartyltrimonium Hydroxyethyl Hydrolyzed Collagen Stearyldimonium Hydroxypropyl Hydrolyzed Collagen Hydroxypropyltrimonium Hydrolyzed Keratin Cocodimonium Hydroxypropyl Hydrolyzed Hair Keratin Cocodimonium Hydroxypropyl Hydrolyzed Keratin Hydroxypropyltrimonium Gelatin Hydroxypropyltrimonium Hydrolyzed Casein
Protein (vegetable based)	Hydroxypropyltrimonium Hydrolyzed Wheat Protein Cocodimonium Hydroxypropyl Hydrolyzed Wheat Protein Lauryldimonium Hydroxypropyl Hydrolyzed Wheat Protein Stearyldimonium Hydroxypropyl Hydrolyzed Wheat Protein Hydroxypropyltrimonium Hydrolyzed Soy Protein Cocodimonium Hydroxypropyl Hydrolyzed Soy Protein Lauryldimonium Hydroxypropyl Hydrolyzed Soy Protein Hydroxypropyltrimonium Hydrolyzed Conchiolin Protein Hydroxypropyltrimonium Hydrolyzed Rice Bran Protein Ginseng Hydroxypropyltrimonium Chloride Hydroxypropyltrimonium Hydrolyzed Silk Protein Hydroxypropyltrimonium Hydrolyzed Whey Protein Hydroxypropyltrimonium Jojoba Protein Cassia Hydroxypropyltrimonium Chloride Locust Bean Hydroxypropyltrimonium Chloride
Lanolin	Quaternium-33
Chitosan	Polyquaternium-29
Sugars	Hydroxypropyltrimonium honey Lauryl Methyl Gluceth-10 Hydroxypropyldimonium Chloride Dextran Hydroxypropyltrimonimum Chloride
Starches	Hydroxypropyltrimonium Hydrolyzed Wheat Starch Hydroxypropyltrimonium Hydrolyzed Corn (Maize) Starch Hydroxypropyltrimonium Hydrolyzed Potato Starch Hydroxypropyltrimonium Hydrolyzed Amylopectin
Silicone	Polyquaternium-42

Summary

Cationic polymer and oligomers derived from guar gum, cellulose, animal and plant derived proteins, oligosaccharides, honey, starch, chitosan, lanolin and silicones are indispensable ingredients in today's hair and skin care formulations. The cationizing reagents that are used for their production are commercially available. Various reagents with different alkyl chains at the quaternary ammonium group can be used to achieve unique properties of the conditioner.

References:

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2. *Principles of Polymer Science and Technology in Cosmetics and Personal Care*: Marcel Dekker, Inc. (1999)
3. US Patent Number 4,663,159, *Hydrophobe substituted, water-soluble cationic polysaccharides*, GL Brode, RL Kreeger, ED Goddard and FM Merrit assigned to Union Carbide Corporation (1985)
4. US Patent Number 4,940,785, *Method for preparing cellulose ethers containing tertiary or quaternary nitrogen,* R Stober, D Bischoff and M Huss assigned to Degussa AG (1988)

Footnotes:

a) QUAB® 188 (“CHPTAC”) is a product of SKW QUAB Chemicals, Inc.
b) QUAB® 151 (“EPTAC”) is a product of SKW QUAB Chemicals, Inc.
c) QUAB® 342 (“CHPDLAC”) is a product of SKW QUAB Chemicals, Inc.
d) QUAB® 360 (“CHPCDAC”) is a product of SKW QUAB Chemicals, Inc.
e) QUAB® 426 (“CHPDSAC”) is a product of SKW QUAB Chemicals, Inc.

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