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# **All-day hair manageability for textured hair types**

A revision of the current anti-frizz technologies and suggestions for the future

Master's thesis in Materials Chemistry

**MATILDE BENGTTSSON**

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Department of Chemistry and Chemical Engineering  
*Division of Applied Surface Chemistry*  
CHALMERS UNIVERSITY OF TECHNOLOGY  
Gothenburg, Sweden 2016



MASTER'S THESIS

# All-day hair manageability for textured hair types

A revision of the current anti-frizz technologies and suggestions for the future

MATILDE BENGTTSSON

SUPERVISOR:

Sylvain Lataste, AkzoNobel Surface Chemistry AB

EXAMINER:

Assoc. Prof. Martin Andersson, Chalmers University of Technology

Department of Chemistry and Chemical Engineering

*Division of Applied Surface Chemistry*

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Department of Chemistry and Chemical Engineering  
Division of Applied Surface Chemistry  
Chalmers University of Technology  
SE-412 96 Göteborg  
Sweden  
Telephone: + 46 (0)31-772 1000

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*Nothing in life is to be feared, it is only to be understood. Now is the time to understand more, so that we may fear less.*

-Marie Curie



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## Abstract

Today consumers have expectations on hair care products that stretch far beyond merely cleaning the hair. There is a significant manageability concern regarding frizziness, especially for curly hair people when exposed to high temperature and very humid environments. The currently most widely used anti-frizz technology provides a short-term solution. Thereby there remains a significant unserved market. It was hypothesized that there are other conditioning agents on the market that have a more significant impact on frizz reduction. The aim of this study was to identify current anti-frizz ingredients and examine their performance and limitations. A market investigation was performed and it was concluded that a number of surfactants, protein derivatives and silicones would be interesting to assess. Several representatives were selected within each group in order to gain an understanding of the correlation between molecular structure and manageability performance. The active ingredients were formulated in standardized formulas for rinse-off conditioners before the performance study began. Further a method development was done regarding the objective evaluation of frizziness. Frizz is caused by an imbalance in the moisture level of hair. This study conclude that the level up and test condition regarding time, temperature and relative humidity seem to be critical for the tendency of hair to frizz. Further studies would be needed to optimize the parameters. Finally a study of the manageability performance of the formulated conditioners was performed on human hair tresses. The widely used cationic surfactant docosyltrimethylammonium chloride was overall well performing, especially when it came to reduction of friction force and reduction of flyaway hair during combing. It was superior to the other cationic surfactant tested regarding reduction of frizz. This study suggests that the silicones and protein derivatives showed less promising results regarding the overall manageability. Preliminary data has implications that the efficiency of anti-frizz is correlated with cationic charge and high hydrophobicity of the conditioning agent.

**Key words:** Surface chemistry, polymer technology, surfactant, emulsion, conditioner, personal care, hair care, anti-frizz, anti-static, combing force reduction.

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## **Preface**

This master's thesis was conducted during five months in the spring of 2016 within the master program Materials Chemistry at Chalmers University of Technology. The thesis was performed within the Personal Care group at AkzoNobel Surface Chemistry AB. I would like to express my gratitude towards the Personal Care group for this fruitful working experience. It has provided me with valuable insights for my future career. Further I would like to take the opportunity to thank all interviewees in this study for taking time to share your experiences and market understanding. Working with this master's thesis has been an interesting experience, expanding my knowledge in polymer technology and surface chemistry related to new applications and exploring the dynamics of one of the strong players within the chemical industry. This version of the report covers method development and anti-frizz raw materials already in the public domain. All data on novel experimental materials, which represents a significant part of the work completed, remains confidential.

Gothenburg June 2016

Matilde Bengtsson



# 1 Introduction

The use of personal care products is currently expanding both regarding sales volume and geographically. In hair care the major product is shampoo, with conditioner close thereafter<sup>1</sup>. Other important market segments are hair treatments, hair colorants and hair styling. China, with its large population, is the biggest shampoo and conditioner market, with sales at US\$5.7 billion in 2013, closely followed by the US at US\$5.2 billion<sup>2</sup>. Today consumers have expectations on hair care products that stretch far beyond merely cleaning the hair<sup>1</sup>. Improving the appearance of hair with shampoo and conditioners has resulted in top claims globally such as brightening/illuminating, moisturising/hydrating and restoration of damaged hair. There is also a strong market trend towards natural ingredients such as botanical/herbal<sup>2</sup>.

This study will address the long term unmet consumer need and holy grail of the cosmetics industry regarding anti-frizz technologies. The most widely used technology today are silicones and deep conditioning agents such as docosyltrimethylammonium chloride, which provides an 2-4 hour solution. It is an unsatisfactory time range for frizz to be tamed only for a few hours. Therefore there remains a significant unserved market. It is crucial for the technology to function over a prolonged time in all weather conditions, while still leaving the hair looking and feeling natural to enable a wide consumer acceptance. It is especially problematic for people with curly hair that are exposed to high temperature and very humid environments. The hair type and texture affect the hair characteristics regarding appearance, manageability and response to treatment<sup>3</sup>.

It is hypothesized that there are other conditioning agents on the market that have a more significant impact on frizz reduction. The long-term aim would be towards a 24 h solution, which would serve as an all-day hair manageability technology. Manageability is defined as the ease of arranging hair in place and its temporary tendency to retain in place during grooming. Manageability can be strongly related to ease of combing and flyaway hair. For curly hair individuals also frizz is part of the manageability concern, which is strongly related to the balance of moisture in the hair. Frizz has been described as a lack of alignment of the curvature of neighboring hairs of an assembly, which cause the appearance of disorder. Further it is important to distinguish the consumer perception of moisturization, which is merely related to smoothness from the scientific meaning of water content<sup>4</sup>.

## 1.1 Objective

The purpose of the project is to define the ideal all-day anti-frizz technology for curly hair from both a consumer experience and raw material viewpoint. The aim is to gain an understanding of the performance and limitations of current anti-frizz raw materials. The project will investigate which types of molecules that are optimal and suggest possible modifications and combinations to improve efficiency. In collaboration with AkzoNobel scientists recommendations will be made to aid the intelligent design of a series of mass-market solutions for the future. The final step of the study would involve the transformation of the findings into an actionable format with any IP opportunities defined.

This thesis aims to answer the following three questions:

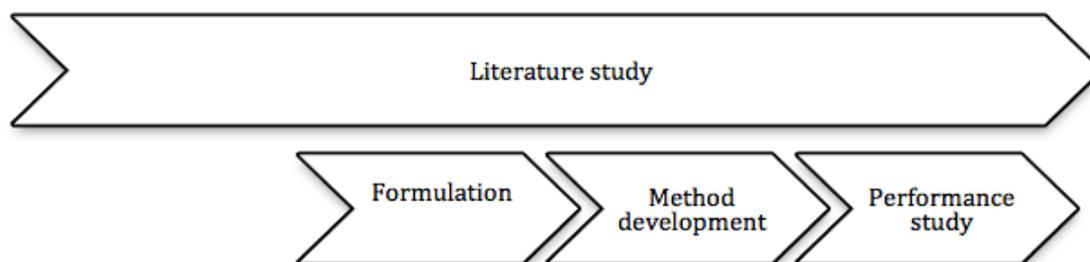
- ✦ How can anti-frizz performance be analyzed in a simple manner to enable screening of the present anti-frizz technologies on the market?
- ✦ What differences in performance can be seen between the conditioning technologies currently on the market?
- ✦ What implications are there on molecular structure in order to achieve anti-frizz benefits?

## 1.2 Scope

The methodology for the project will be shaped by the requirement regarding the hair, the test methods and the conditioning agents. Human hair will be used for this study in order to gain a realistic performance. The availability of hair types such as specific textures and colours will be a limitation in this project. A test method for anti-frizz performance will be developed according to the dependence of factors stated in literature, material availability and experimental findings to create appropriate test conditions. The number of ingredients in the standardized formulas will be held as low as possible in order to reduce the influence on the results from ingredients that are out of scope. When investigating conditioning technologies involving similar chemistries the same level of active content will be used when making comparisons. Rinse-off conditioners will be the major focus of this study, despite the trend towards multifunctional products such as 2-in-1 shampoos<sup>2</sup>. As these impose limitations for formulation regarding compatibility and efficiency due to conflicting mechanisms of action.<sup>4</sup> Focus will be on hair care, not styling products, as the aim is to develop a technology that can provide a natural feel and look. Further only the moisture dependent hydrogen bonding will be discussed here within. Thereby products affecting the cysteine bonds such as chemical treatments are not included.

## 1.3 Methodology

The project is in the feasibility phase of new product development, which creates a bridge between the initial idea and the design, realization and launch. The working process can be divided into stages according to **Figure 1**.



**Figure 1** The literature study will be performed continuously as to reach insights on the practical work. The first stage will be the literature study focusing on market understanding of high performing hair care products. The mapped active ingredients will be ordered before moving into the formulation stage. Further a method development will be needed regarding the objective evaluation of frizziness. Finally a study of the manageability performance of the formulated conditioners will be done.

## 2 Theory

In order to understand the chemical romance that is taking place between the conditioning agent and the hair, the biology and structure of hair together are presented before diving deeper into the chemistry of conditioners. These rather complicated emulsions gain their conditioning properties from a range of different technologies, which are described further under *Results from the market investigation*.

### 2.1 Human hair biology

Human hair can be described as a nanocomposite biological fiber. An understanding of these biological fibers is crucial to evaluate the existing hair care technologies and make suggestions for the development of improved solutions<sup>5</sup>. In general human scalp hair have a diameter between 45-100  $\mu\text{m}$ , which can be divided into four morphologically distinct structures: The cuticle, the cortex, the medulla and the cell membrane complex<sup>4</sup>.

#### 2.1.1 Morphologically distinct structures of hair

The main component of the outer layer of hair, the fatty acid 18-methyl eicosanoic acid (18-MEA), is covalently bound to the cross-linked sulfur proteins with thioester bonds. In between the 18-MEA molecules in the cell membrane complex of the cuticle there are free fatty acids. This layer act as a boundary lubricant and provides a continuous hydrophobic and conditioning layer on the surface<sup>4,6</sup>.

The protective external region at the surface of the hair shaft is made up of thin cells known as overlapping cuticle scales. Each cuticle cell is about 0,5 $\mu\text{m}$  thick and 60  $\mu\text{m}$  long with a scale interval of 6  $\mu\text{m}$ . The flat cells are attached at the proximal end of the hair and loose at the distal end - analogous with roofing tile - providing both flexibility and permeability to the outer morphology. The cuticle cells are bound to the cortical cells through complex interlocking structures formed by a mechanism that includes phagocytosis<sup>4</sup>.

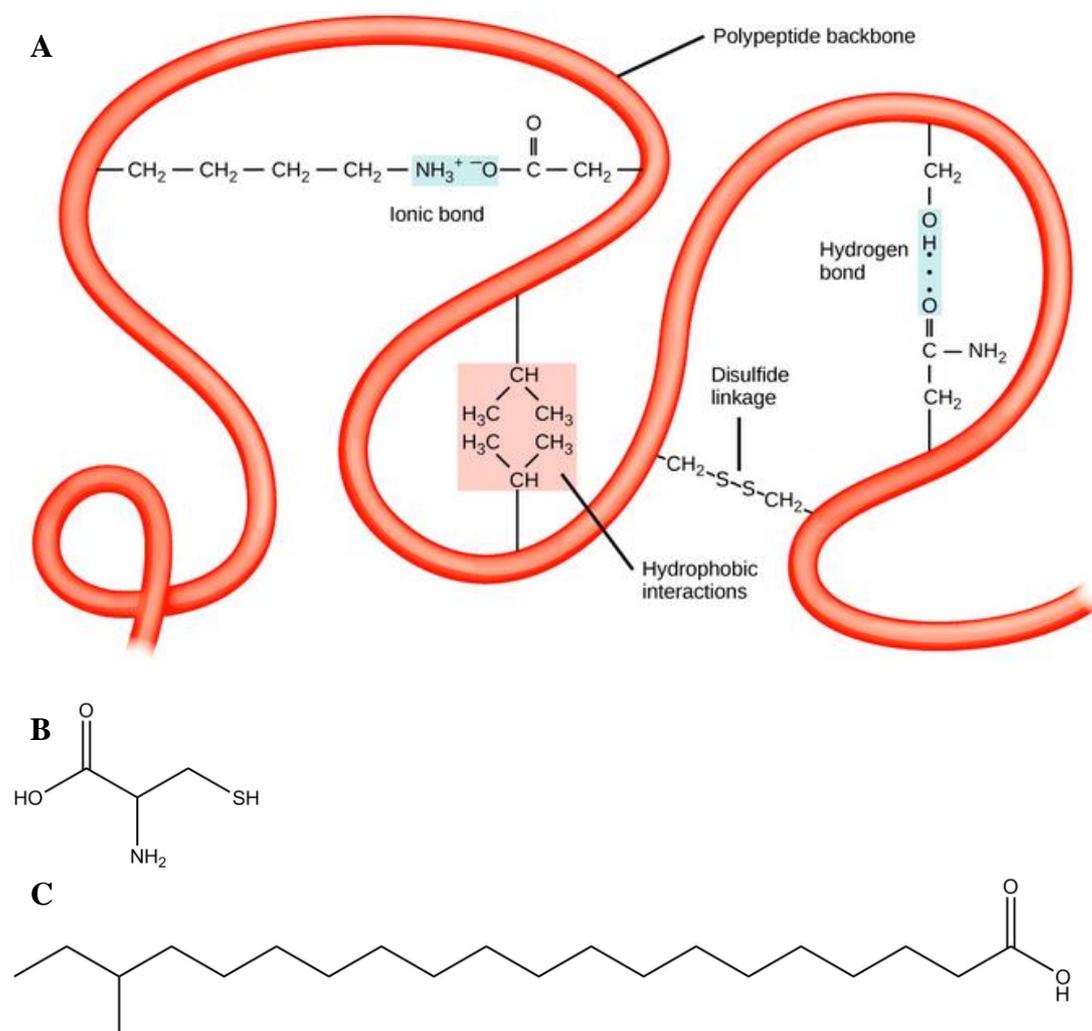
The cortex is the main structural component of hair fiber and constitutes about 80 % of the mass. The cortex can be divided into spindle shaped cells and intercellular binding material; these higher structures constitute the various domains of different cortical cell types. The cortical cells mainly contain spindle-shaped fibrous structures, macrofibrils. The macrofibrils are made up of highly organized structures, intermediate filaments (IFs), which are surrounded by a less ordered matrix. IFs consist of eight protofilaments, a core surrounded by seven filaments. The protofilaments are an assembly of  $\alpha$ -helical keratin chains that are shaped into coiled coil dimers containing equal parts of the acidic type I and the neutral or basic type II. These are staggered together to create tetramers<sup>7</sup>, see **Figure 2**. In hair fiber the helical proteins of the IFs are oriented along the axis of the fiber and thereby function to support the structural integrity of the fibers<sup>4</sup>.

The relatively amorphous matrix is the largest structural subunit and has the highest concentration of disulfide bonds of the cortex. The interactions are mainly intramolecular rather than intermolecular, as the matrix swell significantly when exposed to water. Therefor swelling occurs in the matrix between the IFs rather than



## 2.1.2 Molecular basis of hair fibers

Human hair is comprised of proteins, water, lipids, trace elements and pigments. The main component is protein, which vary between 65-95 %, highly depending on the level of hydration. Hair fibers can take up as much as 32 % of its weight in moisture. The main type of protein in hair is keratin. Cysteine is an important amino acid in keratin due to its ability to form disulphide bonds, forming cystine dimers. Hydroxyl-, amide-, basic- and carboxylic acid groups interact through hydrogen bonding. Hydrogen bonds are the most important non-ionic interactions in hair fibers due to their frequency and strength with bond energies generally in the order of  $30 \text{ kJ} \times \text{mol}^{-1}$ . In addition basic and carboxylic acid groups function through ionic bonding type interactions. These bonds are about an order of magnitude larger than hydrogen bonds<sup>4,10</sup>. The possible bonding types in keratins are shown in **Figure 3** together with the structures of the most important molecules for the surface chemistry of hair fibers.



**Figure 3** **A** Interactions in protein range from hydrophobic, hydrogen bonds and disulfide bridges to ionic bonds<sup>7,11</sup>. **B** Cysteine is the most important amino acid in hair. **C** 18-methyl eicosanoic acid is the main lipid of the outer layer of hair<sup>4</sup>.

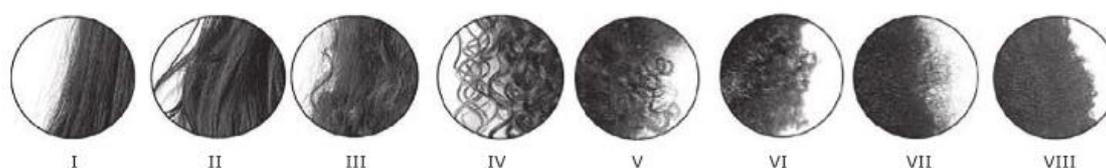
### 2.1.3 Origin of hair and its impact on texture

The majority of hair fibers have an oval shape that is twisted and indented with an irregular diameter. The size and shape of the hair follicles in the zone of keratinization is crucial for the shape of hair fibers<sup>4</sup>. Historically, hair has been roughly categorized in the three ethnical groups based on origin: African, Asian and European<sup>12</sup>. People of Asian descent have straight follicles and people with African roots have follicles that are best described as helical shaped. Caucasian people have follicles with an appearance ranging between the two mentioned<sup>4</sup>. The most important characteristic for the origin of hair fiber shape on a cellular basis is the occurrence of various cortical cells in the hair. The hair fibers of an Asian with straight hair contain only paracortical cells. A curly haired Caucasian has paracortical cells with a layer of orthocortical cells. In contrast, an African with very curly hair have equal amount of the two cells types in the hair fibers, see **Figure 2**. The paracortical cells are located on the inside of the curls, while the orthocortical cells are on the outside<sup>4</sup>. Orthocortex contain less cysteine and therefor show poor thermal stability and higher fragility<sup>3</sup>.

Curvature is strongly connected to the tendency to coil involving natural curls and curves. The curvature is defined as the inverse of the radius of curvature. In general the hair assembly volume is reduced with straighter hair. Curvature is the main fiber characteristic when it comes to aspects of hair assembly behavior such as styling and combing<sup>4</sup>. The key word seems to be manageability of the curls, as a more curly hair require more force during combing<sup>3</sup>. In contrast for straight hair friction and stiffness are determinant for the hair assembly behavior<sup>4</sup>.

There have been many attempts to create a reliable standard for classification of hair based on the curliness. In order to achieve this, a shape criteria had to be established based on easily accessible, objective measurements. A well-recognized method aims towards a worldwide robust classification of hair in eight categories (see **Figure 4**), which is based on the following measurements. The curve diameter (CD) is the smallest curve diameter of hair cut at the stretched length of 6 cm. The curve index (CI) is the ratio of the stretched length to the length of the hair at rest. The last measurement is the number of waves (w) of a hair fiber. This method would leave the oversimplified division based on ethnicity behind. A vivid example from research shows that Brazilian hair could range from class type I to VI. The classification based on ethnicity is problematic not least as the mixed origin is increasing<sup>12</sup>.

The hair color is classified separately not merely for convenience and clarity, but also for several other reasons. The absence of a strong correlation between the hair fiber shape and the hair color is one. Approximately 90 % of the humans of the world have hair colors in a narrow range from dark brown to black, which is another reason. This signifies that European hair colors ranging from red or blond to light brown constitute a low statistical weight considering the humans of the world<sup>12</sup>.

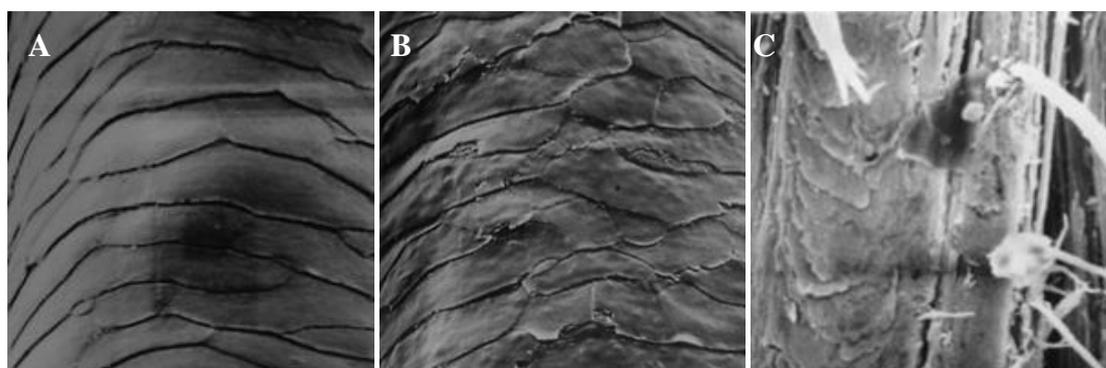


**Figure 4** A classification into eight different hair types based on curvature<sup>13</sup>.

### 2.1.4 History of hair affect the hair quality

Not merely the origin of hair but also the history of hair, how it has been treated, is crucial for its biophysical properties. Microscopy studies have shown that there is a difference even on individual hair fibers. The scales at the tip end are significantly more damaged than at the roots with broken scale edges due to the much longer history. This can be seen in the Scanning Electron Microscopy (SEM) pictures in **Figure 5**. Damage can arise from many sources such as chemical treatments (permanent waves, bleach, hair dyes), mechanical (combing), heat (blow-drying or straightening) and weathering (UV radiation, air pollutants). The damage caused by repeated washing, drying and mechanical wear result in changes in the surface layers where sulfur containing compounds and acids are formed. The wear also reduce both the free and bound lipid content of the surface, resulting in a more hydrophilic and negatively charged surface. On a macroscopic level this result in a dry sensory performance both concerning the appearance and the feel<sup>4</sup>.

In general, treatment combinations are more damaging to hair. For example, extensive sunlight exposure in combination with chemical bleaching or chemical bleaching combined with permanent waving pose a higher risk of severe damage or breakage of the entire hair fiber than chemical bleaching alone. More severe abrasive damage is expected from combing when also heat drying. The extent of alteration created by reduction and re-oxidation as a result from bleached hair has been evaluated by the degree of swelling, which is greater for treated than for untreated hair<sup>4</sup>.



**Figure 5** **A** Cuticles on a human hair shaft near the root end, where the scale edges are smooth. **B** Cuticles on another hair shaft near the tip end, where the scale edges are damaged. **C** An entire hair shaft that is damaged and split<sup>4</sup>.

### 2.1.5 Surface chemistry of chemically bleached hair

Generally bleaching treatments are applied with the aim to lighten the hair, which is usually achieved by oxidation. These treatments are alkaline with a pH ranging from 9 to 11, which promotes opening of the hair cuticle and facilitates penetration of the oxidizing agent into the hair fiber. Hydrogen peroxide is the main oxidizing agent used in bleaching products today, usually as a 6 % solution. Furthermore, fortunately for the application, hydrogen peroxide reacts faster with the pigment melanin than with the proteins in fibers. Despite this, it is inevitably that there are side reactions taking place simultaneously involving proteins. This is due to the severe reaction conditions needed in order to destroy the chromophoric groups of melanin combined with the proteinaceous nature of hair, consisting of many oxidizable groups<sup>4</sup>.

It should be taken into account that the amount of peptide bonds, the most recurrent structural unit of proteins, are almost an order of magnitude larger than that of the disulfide bonds in hair fibers. The main degradation of proteins in hair fibers done by hydrogen peroxide is at the disulfide bond of cystine. The oxidative cleavage of disulfide bonds in cystine during chemical bleaching occurs mainly through a sulfur to sulfur fission process and that a carbon to sulfur fission process is another possible mechanism. Cysteic acid is the main end product from the oxidation of cystine during bleaching. Studies have demonstrated that about 20 % of the disulfide bonds in hair fibers are affected under normal bleaching conditions. If severe bleaching is performed the equivalent value is 45 % and there are indications that some degree of peptide bond cleavage also occurs. Severe bleaching involves longer reaction times and higher concentrations of alkalinity and oxidizing agent in the applied product. After chemical bleaching there is a greater propensity for cuticle scale lifting due to cell membrane complex rupture. Further, friction increases with severity of bleach damage. The hair surface is altered from its native relatively neutral, hydrophobic state to have anionic character, higher surface energy and hydrophilic properties<sup>4</sup>.

## **2.2 The chemistry of conditioners**

In order to gain a better understanding of this system, an overview of the essentials in surface chemistry is needed before looking into the system on a molecular scale.

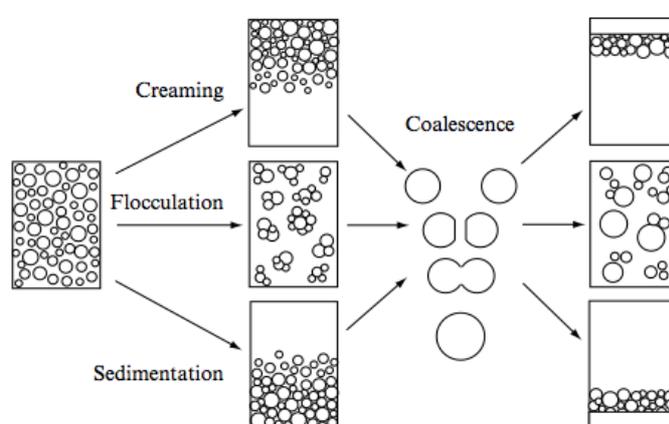
Some efforts will be made to present relevant classifications of chemicals, as identification of a compound of a certain class can efficiently provide information about its behaviour and gain an understanding of general concepts. Conditioners are often supplied as emulsions.

### **2.2.1 Chemistry of an emulsion**

A colloid can be described as a dispersion of particles ranging from 1nm to 1 $\mu$ m in diameter in a solvent. Colloids have optical properties between those of a homogenous solution and a heterogenous mixture. The dispersed particles are small enough to be homogenous, yet large enough to scatter light and provide a non-transparent appearance. A colloidal that is a suspension of one liquid in another is denoted an emulsion<sup>10</sup>. In general, one liquid is water and the other some kind of organic liquid, which is commonly termed as oil. The droplets in emulsions are the dispersed phase and the surrounding liquid is the continuous phase. The liquids are immiscible due to a large difference in polarity. Immiscible liquids tend to minimize their interfacial area, as there is a large surface tension between the phases<sup>14</sup>.

If surfactants are added to the system this results in a reduction in the free energy of the interface and the interfacial tension, which result in an increase in the interfacial area. The abbreviation surfactant stands for surface active agent, which reflects its tendency to absorb at surfaces and interfaces. A surfactant contains a hydrophilic head group and a long hydrophobic tail. The head group is used to classify surfactants based on their nonionic, anionic, cationic or zwitterionic character. Some important example of each class would be fatty alcohol ethoxylate, sodium lauryl ether sulphate (SLES), alkyl quaternary ammonium and betaine, respectively. The character of the polar head, chain length as well as chain branching is essential for their behavior<sup>14</sup>.

Despite the addition of surfactant, emulsions are to their very nature not stable. In contrast, microemulsions form without the addition of work and are thermodynamically stable containing dynamic aggregates that are several orders of magnitudes smaller than in emulsions. An emulsion is commonly created and upon destabilization regained by using high shear such as homogenisation. Emulsion destabilization involves creaming, sedimentation or flocculation. Creaming and sedimentation arise from the density difference between the phases. Oil-in-water emulsions have a tendency towards creaming as oil in general have a lower density than water. Flocculation, on the other hand, results from an energetically stable secondary minimum in which the droplets are in proximity to each other but their integrity is retained. Coalescence is another mechanism of emulsion destabilization where the droplets merge into each other<sup>14</sup>.



**Figure 6** Different mechanisms for destabilization of emulsions are described. Creaming, flocculation and sedimentation are reversible, while coalescence is an irreversible process. These processes can occur simultaneously<sup>14</sup>.

Even though emulsions are unstable from a thermodynamic viewpoint the major concern is rather on the kinetics. An emulsion droplet with a radius of 1  $\mu\text{m}$  in general has a very short half-life below 1 s. When some kind of potential energy barrier is present at the surface, the stability can be prolonged even to years. Electrostatic stabilization and steric stabilization are two important approaches, which may also be combined. Electrostatic stabilization arise from repulsive interaction when the diffuse double layer around the particles begin to overlap<sup>14</sup>. The diffuse double layer includes the strong electrical field that is generated at the actual interface together with the dissociated ions that are attracted to stay in the interface region<sup>15</sup>. Steric stabilization arise from the repulsive interaction, which comes from the loss in entropy when chains from different droplets begin to entangle<sup>14</sup>.

Surfactants are commonly used to stabilize emulsions, but amphiphilic polymers also fulfill this purpose. Low molecular weight surfactants are superior when it comes to forming an emulsion, as the surfactant can rapidly diffuse to and cover the created interface to reduce the interfacial tension. The stability will be related to the density difference between the water and the oil, the droplet size and the viscosity of the water phase. Due to this relationship the viscosity of the continuous phase is often increased by the addition of a polymer for emulsion stabilization<sup>14</sup>.

## 2.2.2 Molecular basis of conditioners

Conditioners can be described as oil-in-water emulsions with relatively high water content, about 85 %. Generally the oil phase is based on oily or waxy molecules such as long chain alcohols, triglycerides, fatty acids, mineral oil, true oils, waxes or silicones<sup>4,16</sup>. Oils are selected based on their melting point and polarity. Two oils with a significant difference in these two properties are preferably selected for stability regarding temperature changes and deterioration. The active ingredient is a surfactant, sometimes together with a polymer, both with a cationic character. The balance between cationic surfactants and higher alcohols (12-22C) is important for the viscosity and creaminess of the emulsion. Branched-chain higher alcohols can provide a stabilizing effect on the viscosity over time<sup>17</sup>. Further film-forming agents are included to coat the hair fiber and provide superior appearance and protection. Viscosity builders are added for the ease of application of the conditioner onto hair. pH adjustment is done for performance and combined with the preservative it protects from microbial growth and enable a shelf-life on the time scale of years<sup>16</sup>.

## 2.2.3 Interaction of conditioning agents with hair

In general surfactants used as conditioning agents are considered long chain, defined as chain length above 14 carbon atoms. Long chain surfactants form elongated micelles just above the critical micelle concentration (CMC). The molecular weight and charge of the surfactant affect the CMC and the surfactant polymer aggregation<sup>14</sup>. Conditioners usually have the morphology of multi-lamellar vesicles. It is important to realize the complexity of the emulsion in a final formula such as a commercial conditioner due to the influence of the many raw materials. As an example the morphology is also highly dependent on the salt concentration of the solution. Upon dilution the entropic effect of the counter ions cause the solution to phase separate. Therefor the conditioning species have a higher concentration when coating the hair<sup>1</sup>.

The mechanism for conditioning is deposition by coacervation, the precipitation of a polymer-surfactant aggregate onto the hair upon use as the conditioner is diluted. In this process silicone, which was previously entrapped in the aggregate, is also deposited onto the hair<sup>4</sup>. The interaction depends on the hydrophobicity of the conditioning agents as to its attraction to keratin relative to the attraction to the aqueous conditioner. Adsorption onto hair is of higher importance than absorption, due to low temperatures and high molecular weight of the conditioning agents. Adsorption to hair can be described as a continuum between charge driven and hydrophobically driven adsorption. A water-soluble cationic surfactant can be seen as mainly charge driven, while the adsorption of a hydrophobic silicone adsorbs onto hair mainly due to an entropic effect. Further, adsorption depends on diffusion of the active through the solution to reach the hair<sup>4</sup>.

The interaction occurs mainly at the surface within a few nanometers of the fiber periphery<sup>17</sup>. Cationic surfactant and polymers interact with hair by ionic bonds enhanced by van der Waals attractions. When cationic surfactants in conditioners interact with the hair surface their hydrophobic tails project out from the hair shaft. This increases the hydrophobic character of the surface, which is further strengthened by fatty alcohols and silicones from the conditioner formula<sup>4</sup>. Cationics are important to bridge the hydrophobic fatty alcohols and silicones<sup>17</sup>.

## 2.2.4 The function of conditioners

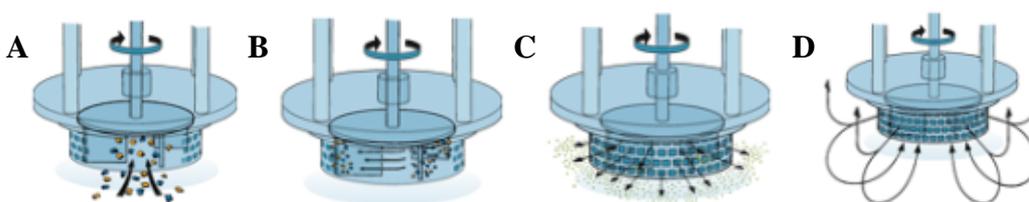
The fundamental function of conditioners is to reduce the friction between hair fibers to enable combing and other grooming activities<sup>1</sup>. For this purpose lubrication of the hair fiber surface is crucial, yet an appropriate balance have to be maintained to avoid greasy appearance<sup>16</sup>. Other important functions is to preventing flyaway hair, protect from further damage, provide glossiness and a pleasant feel in general<sup>4</sup>. Conditioners can be divided into three classes based on purpose, duration and timing of application. Rinse-out or instant conditioners are applied directly after shampooing and rinsed after a few minutes and they function to improve combability and also remove soap residues. Deep conditioners or repair treatments are applied either before or after shampooing for about half an hour and function to fill in the cracks in damaged hair. Leave-in conditioners are as the name suggests applied to towel dried hair before styling to improve combability and protect from heat damage. Possible product types include creams, rinses, balsams and hair masks<sup>16</sup>.

## 2.3 Performance study of conditioners

The performance study can be divided based on the characteristics of interest. Tendency to frizz can be derived from an imbalance of the moisture content in the hair. Static behaviour of hair is related to flyaway hair. The force reduction from wet combing is commonly used to gain an understanding of the friction. First when the formulation is stable for the time frames relevant for the application it is feasible to analyse its properties. As described previously, it is vital to use shear force to enable an emulsion to form and maintain stability.

### 2.3.1 Emulsification during formulation

Common formulation devices related to emulsification are propeller mixer, paddle mixer, disperser and homomixer. The propeller mixer is suitable merely for dissolving substances, while the disperser rather create a strong shear that is useful when incorporating polymers. The paddle device emulsifies without shear, while the most efficient device probably is the homomixer. The homomixer is suitable for the initial phase, where the emulsion is enable. Except the timespan other important factors are the temperature and stirring speed<sup>17</sup>. The Silverson's high shear rotor batch mixer function through four-steps of mixing and shearing actions<sup>18</sup>. The circulatory manner in which the solution passes through the workhead is described in detail in **Figure 7**.



**Figure 7** **A** In the first step the high speed of the rotorblades within the workhead creates a strong suction, causing the solution to flow from the bottom of the beaker into the center of the workhead. **B** In the second step the centrifugal force causes the solution to flow towards the periphery of the workhead where it is milled in the clearance between the rotor blades and the inner wall of the stator. **C** In the third step

a strong hydraulic shear is created when the solution is forced outwards through the perforations in the stator wall leaving the workhead. **D** In the forth and last step the solution leave the workhead horizontally towards the sides of the beaker<sup>18</sup>.

### **2.3.2 Stability testing of a formulation**

Various approaches are undertaken to ensure that the formula will resist common stresses related to temperature, light and mechanical shocks. Typically the stability testing is tailored towards the vulnerability of the particular product and its expected use conditions, storage and mode of transportation. The most frequently carried out tests concern stability at stress temperatures. A cycle stress test is a rapid analysis to gain an idea of the chances of a formula to be stable. It is executed in three cycles alternating 24 h at stress temperature with 24 h in room temperature. At the end of each cycle the samples appearance is examined. Long-term stability tests are made to ensure that the appearance (uniformity and color), odor, viscosity and pH are the same over the time scale of years. It is performed at elevated temperature as this is known to accelerate the reaction rates<sup>4</sup>. This accelerated storage testing over 2-3 months provides a prediction of the long-term stability at room temperature. It should be noted that at high temperatures such as 50°C certain changes take place, which are not possible at room temperature irrespectively of the storage time<sup>19</sup>.

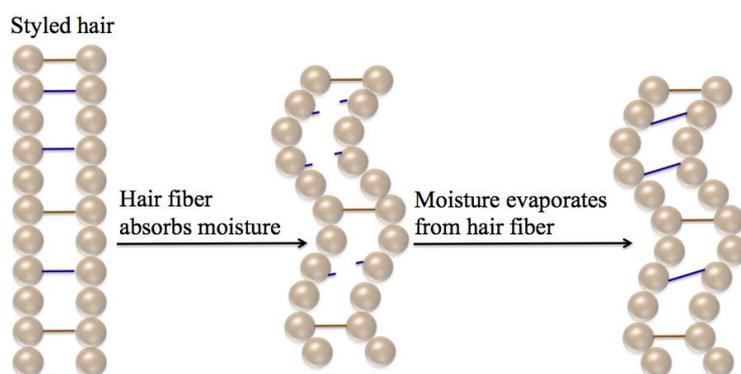
### **2.3.3 Moisture content of hair**

The moisture content is relevant due to its importance when it comes to the physical properties of hair and therefor also the efficiency of personal care products. It is important to realize that the moisture content of hair fibers depend on the chosen reference set as the state of dryness and on the present environment in terms of relative humidity (RH). Under normal conditions, which is considered 50 % RH, hair has a moisture content of roughly 10 %. The protons of water in hair fibers are interacting with hydrogen bonds and are more fixed than in the bulk liquid. Under conditions of low RH (<25 %) water molecules are mainly interacting with hydrogen bonds at hydrophilic sites of the fiber. If the humidity rises, additional water is sorbed, which reduces the binding energy of water already associated with the fiber. Under conditions of high RH (>80 %) the importance of water on water sorption increases<sup>4</sup>.

Blow-dried hair has reduced moisture content in contrast to air-dried hair. Despite the absorption of water that takes place when the blow-drying is finished, the hair fiber still has a deficit in comparison to air-dried hair fiber. This deficit is maintained until the hair is rewet and a new condition is set. Studies have implied that this type of hysteresis arises from the variation in the ratio of bound to free water in the hair fibers. The additional bound water featured on desorption than on absorption results from the additional available water binding sites that are available from the wet state than the dry state. There is a range of hydrophilic side chains (amino, carboxyl and hydroxyl) as well as peptide bonds of protein fibers that contribute to water sorption<sup>4</sup>.

### 2.3.4 Underlying causes of frizziness

The appearance of frizz, loss of shine and smoothness creates a perception of an unhealthy hair. Frizziness causes an appearance of unmanageable fibers at the top of the scalp and at the tips of the hair combined with an increased volume throughout the hair. The mechanism for frizz induction includes absorption of moisture by the hair fiber from the surrounding environment<sup>20</sup>. Both the cuticles and the cortex will tend to absorb moisture at high humidity levels, which result in weakened hydrogen between the protein molecules within each hair shaft. This effect has been seen to be stronger in chemically damaged hair<sup>5</sup>. The water molecules more specifically replace hydrogen bonding sites in the proteins within the fiber, that have been formed during styling operations to retain a desired hair shape. When this occur the hair return to its natural conformation, which often signify undesired loss of alignment known as frizz. Further the water absorption swells the fiber, which results in an increase in volume<sup>20</sup>.



**Figure 8** Schematic diagram showing the mechanism for the formation of frizz due to higher humidity levels. In the first step water diffuse into the fiber and break the hydrogen bonds, which enable the disulphide and salt bridges to pull back the hair fiber into its natural configuration. In the second step the hydrogen bonds reform in the hair fibers natural configuration upon evaporation of water<sup>21</sup>.

### 2.3.5 Static build-up on hair during dry combing

Static flyaway is considered to reduce hair manageability and results from build-up of electrical charge on the hair fiber surface. The build-up is generated mainly by rubbing forces created during combing and the difference in electrochemical potentials between the fiber surface and the grooming object such as a comb. The hair fibers physically move apart due to the repellation caused by having the same charge. When the object is no longer in contact with the hair the dissipation is driven by the electrical conductivity of hair fibers. Therefore static flyaway can be avoided by increasing the conductivity of the hair surface and by reducing hair fiber friction<sup>21</sup>. In a previous study it was implied that electrostatic charge dissipate quickly from hair that had a continuous, uniform layer of conditioning agents or natural layer of lipids. Untreated chemically damaged hair, which lack a lipid layer, seemed to have worse dissipation of charge than virgin hair, either untreated and treated. Interestingly relative humidity was shown to be significant for the mobility of surface charge on the hair shaft. A higher relative humidity improved the mobility and charge dissipation<sup>5</sup>.

### **2.3.6 Friction forces on hair during wet combing**

In order to achieve the desired smooth feel of the hair, the friction must be minimized both in wet and dry conditions. This concerns both the friction between hair shafts and between hair and another object such as a comb or a hand. Further, to reduce entanglements it is also desirable to minimize the adhesive forces. On the other hand adhesive forces enable certain hairstyles such as hair alignment, especially regarding curly hair. Studies have shown that the friction force was reduced on all length scales for treated chemically damaged hair in contrast to the untreated equivalent. A reduction in friction force was also seen for virgin treated hair on a macro- and microscale. On these length scales the conditioning agents function as lubricants over the hair shaft across several cuticles. The difference in behaviour on a nanoscale was implied to arise from the hydrophobicity of virgin hair, which affects the deposition and consequently the adhesive force contribution largely to the friction force. Adhesive force mapping imply a higher deposition of conditioner by the scale edges. In contrast, the behaviour for the damaged hair can be derived from its higher negative charge and hydrophilic surface, which generate a uniform deposition and improved lubrication of the conditioning agents<sup>5</sup>.

### 3 Results from the market investigation

The literature study is comprised of searches in databases containing published articles of relevance for the subject. Searches were performed in more general databases such as Google Scholar and also in subject specific databases such as Journal of Cosmetic Science. Information about the content of commercial products was found in Mintel's Global New Product Database - the industry gold standard for new product trends and innovation. Further market understanding was gained from interviews with hair stylists where a trend analysis was performed.

#### 3.1 Interviews with curly haired hair care consumers

In order to gain a first overview I asked for advice of some curly haired people that are dealing with the hair assembly of their own curls on a daily basis. Soon it became evident that it is problematic to determine trends due to a division into two groups. The first group has reached an acceptance for their frizzy curls that appear during certain conditions. The other group is devoted to solving the problem by combining many different products both regarding hair care and styling, often together with excessive straightening. The use of flattening irons affects the choice of products that shifts towards a focus not merely on products with anti-frizz claims but also on heat protection as a preventive measurement and products for already damaged hair.

#### 3.2 Interviews with hair stylists

In conversation with a hair stylist at *Victor Noblesse* it became evident that not only efficiency but also convenience of application of a product was highly important. As an example one of the products recommended was a leave-in conditioner to use between washes to tame frizz whenever needed. Both a hair stylist at *Björn Axén* and a salesman at *Åhlens City's* hair care section pointed out the importance of choosing different products for coarse hair and thin hair for maximum efficiency. Heavy conditioners were advised to be used carefully when applied to thin hair to avoid weighting it down. The hair stylist insinuated that the problem with build-up was limited to oil-based silicones in contrast to water-soluble silicones and by using a deep cleansing shampoo problems were rapidly solved. A hair stylist at *Tid* stated from professional experience that silicones are in fact needed to gain a strong conditioning but also emphasised that careful consideration about differences between various types should be taken. Both staff at *Tid* and *Klippotek Dandy* emphasised that except from effectiveness, natural ingredients and natural-looking simple packaging solutions such as a see-through plastic jars had a strong customer appeal.

In summary, a clear market demand was implied concerning a long lasting anti-frizz product for textured hair types. Consequently, products specifically for curly hair with this claim could be found from numerous brands, see **Table 1**. Further, there are predominant trends with products marketed as natural combined with a resistance towards the use of parabens as preservatives and sulphate containing surfactants. These market concerns affected which products that were recommended.

**Table 1** An overview of the hair products with anti-frizz benefits that were recommended by professionals within hair care.

Participant	Product recommended	Ingredients of interest
Victor Noblesse	Whipped crème	Cetrimonium Chloride Hydrolyzed Keratin
	Goldwell DualSenses Curly Twist	Behentrimonium Chloride Steatrimonium Chloride Quaternium-80
	Alterna Bamboo Smooth Après-Shampooing Anti-Frizz	Cyclopentasiloxane Dimethiconol, Dimethicone Amodimethicone Guar Hydroxypropyltrimonium Chloride
Åhléns City	Frizz Ease by John Frieda (Shampoo & conditioner)	Behentrimonium Chloride Polyquaternium-7 Polyquaternium-10 Polyquaternium-39
	Redken Curvaceous	Amodimethicone Behentrimonium Chloride Cetrimonium Chloride Hydrolyzed Soy Protein
Björn Axén	Kevin.Murphy Hydrate-Me	Behentrimonium Chloride Cetrimonium Chloride Steatrimonium Chloride Amodimethicone Polyquaternium-7
	Moroccan oil (only for coarse hair)	Cyclomethicone Dimethicone
Tid		Behentrimonium Chloride
Klippotek Dandy	Davines Love Lovely Smoothing Conditioner	Dimethicone, Amodimethicone Cetrimonium Chloride Polyquaternium-10

### 3.3 Mapped conditioning technologies

Conditioning technologies were mapped from commercial products with anti-frizz claims based on the market investigation. The active ingredients were grouped based on their molecular structures into the following groups: surfactants, protein derivatives and silicones. Representatives from each group were chosen based on the companies branding and advice as well as claims in Mintel's Global New Product Database, see **Table 2**. Oils, vitamins, extracts and amino acids were excluded even if a conditioning effect was stated. This as the effect is assumed to be small, both due to the small content and based on the general market trend towards natural ingredients, also described as story ingredients<sup>4</sup>.

Cationic surfactants are the third largest surfactant class with applications related to their adsorption to surfaces and thereby in situ surface modification, such as to hair in conditioners<sup>14</sup>. In general, it is a nitrogen atom carrying the cationic charge. Surfactant depends on the number of alkyl chains, which give rise to primary-, secondary- or tertiary amines or even quaternary ammonium. Dialkyl surfactants should preferably be combined with monoalkyl surfactants for an efficient emulsification. Amides are also common as the ester linkage increase degradability and thereby reduce the aquatic toxicity. The main cationic surfactant is often either behentrimonium chloride (22C) or cetrimonium chloride (16C), which provide desired sensory performance and also act as emulsifiers. Behentrimonium chloride has shown to be superior but is not suitable for leave-on products as they provide too heavy conditioning, weighting down the hair. The length of the hydrophobic tail affects sensory benefits, solution behavior and viscosity. The moisturization increases with an increase of the chain length<sup>17</sup>.

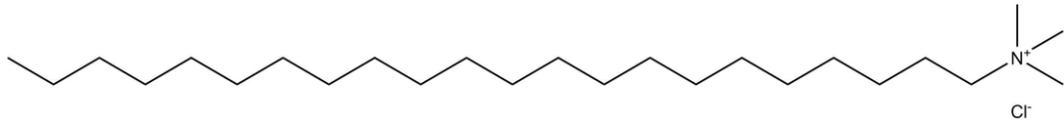
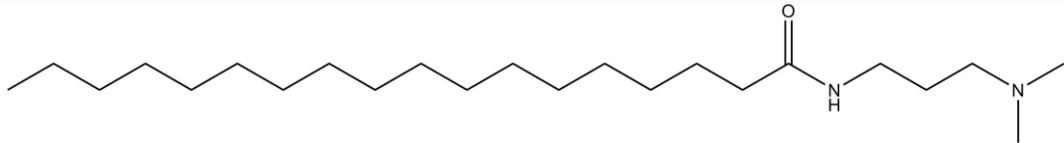
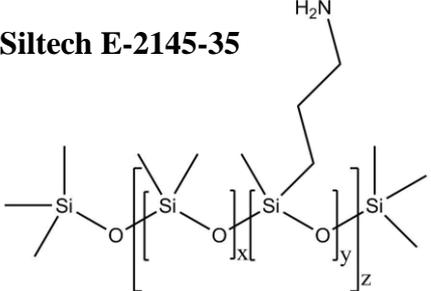
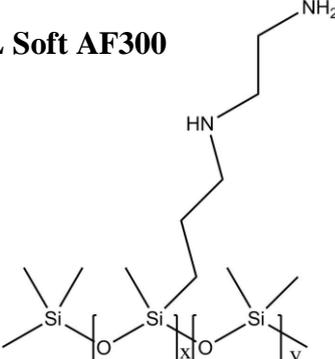
Polymers are macromolecules, which constitutes of repeat units, monomers. Polymers can be classified as biological and non-biological macromolecules<sup>10</sup>. Proteins are important biological macromolecules<sup>14</sup>, which are both commonly used in modified forms for hair care ingredients<sup>17</sup>. The solution behavior of a polymer is highly dependent on the structure, which can be divided into linear, branched or cross-linked<sup>14</sup>. The advantages for surface active polymers over surfactants are their tendency to accumulate at interfaces at low concentration and insensitivity of change in physical variables such as salt and temperature<sup>14</sup>.

Proteins are the only monodisperse polymers and as molecular weight is an important factor for adsorption it provides unique possibilities<sup>7</sup>. Hydrolyzed proteins function to give a healthier appearance. Commonly hydrolyzed collagen, keratin, placenta proteins or soy and wheat polypeptides are used for this function. These ingredients have shown to penetrate through damaged hair fiber via cracks in the cuticle and cortex and increase tensile strength and temporary restore split ends. More specifically the hydrolyzed proteins are found in short-contact, instant and leave-on conditioners marketed for fine or damaged hair<sup>16</sup>.

Silicones function to improve shine, lubrication and at the same time reduce flyaway hair<sup>16</sup>. The typical strategy to prevent frizz is to formulate leave-on products with silicone, which result in a hydrophobic surface modification and thereby decreasing the interactions between hair fibers. When high amounts of silicones are used it can provide increased cohesive forces, which holds fibers together. On the downside the coating may give the hair a highly undesired greasy look and feel. Increasing the hydrophilic character, for example with pegylation, can reduce this effect. Silicones have a basic framework consisting of dimethylsiloxane, which is either circular or a straight chain. Often highly polymerized dimethicone are combined with intermediately polymerized dimethicone and an amino-modified silicone. Almost all rinse-off conditioners contain a large amount of dimethicone. Amodimethicone is the most frequently used amino-modified silicone. Silicone content can be up to 10 %<sup>20</sup>. Silicone quats have shown to provide long-lasting conditioning benefits that are retained through several shampoo cycles. The key to achieve long-term substantivity to hair is for the conditioning agent to have some cationic character, which has been done by grafting cationic polymers to silicone backbones. Another approach involves emulsified silicones in combination with cationic conditioning agent<sup>1</sup>.

### 3.4 Summary of the conditioning technologies currently on the market

**Table 2** An overview of the selected ingredients with potential anti-frizz benefits that were mapped from the recommended products.

Product	INCI name	Chemical name
<b>Surfactants</b>		
<b>Varisoft BT 85</b>	Behentrimonium Chloride	Docosyltrimethylammonium chloride
		
<b>Mackine 301</b>	Stearamidopropyl Dimethylamine	N-[3-(dimethylamino)propyl] stearamide
		
<b>Protein derivatives</b>		
<b>Gludin WQT P</b>	Hydroxypropyltrimonium Hydrolyzed Wheat Protein	-
<b>Soy Tein NPNF</b>	Hydrolyzed Soy Protein	-
<b>Kera Quat NPNF</b>	Cocodimonium Hydroxypropyl Hydrolyzed Keratin	-
<b>Silicones</b>		
<b>Siltech E-2145-35</b>	Amodimethicone	Amino modified polydimethylsiloxane emulsion
<b>ABIL Soft AF 300</b>	Aminopropyl Dimethicone	Amino functional siloxane
<b>Siltech E-2145-35</b>		
<b>ABIL Soft AF300</b>		

### **3.5 Interview with hair distributor regarding hair quality**

In e-mail conversation with Jeffrey Grupp, the origin and quality of the hair used for this study was assessed. The hair had the following specifications, natural European wavy brown (colour 7/0) human hair. The hair came from all over Europe; Norway Spain, Italy, Great Britain, Ukraine. There are different hair suppliers depending on the country. The normal length provided for laboratory use is about 25cm. In general human scalp hair grows 14cm per year<sup>4</sup>, which would mean that the tips of the hair provided has a lifetime of about two years.

It was not possible to get detailed information about the hair. The people who cut their hair and sell it to the hair suppliers are common people without any previous contact with the suppliers. Thereby the hair suppliers have no influence over the growing of hair. Consequently the hair has experienced normal damage as no recommendations were given to the individuals before growing their hair. Jeffery states that it could be problematic to get virgin hair in the future due to the increased use of hair products, especially European and Brazilian hair. In the near future there is not the same problem with the distribution of virgin Indian and Chinese hair as there are economic and cultural barriers for excessive usage of hair products.

When the Jeffrey Grupp receives hair it is washed with a neutral shampoo, which does not contain silicones or perfumes. It is subsequently analysed with Fourier transform infrared (FTIR) spectroscopy to assure that the hair is virgin before sorting and mixing. The hair is sorted based on colour and texture. In this case the texture does not follow the previously mentioned classification, but rather an internal grading of wavy, curly, very curly and kinky. The internal classification is used in combinations with pictures or samples to have well-informed customers. After the sorting in classes the hair is mixed by hand with a hackle to enable a homogenous set of tresses. In general, batches are created in the range from 5-15kg depending on the customer request. A plait from an individual weight 30-60g, consequently for a 5000g batch about 100-150 plaits from different individuals are used.

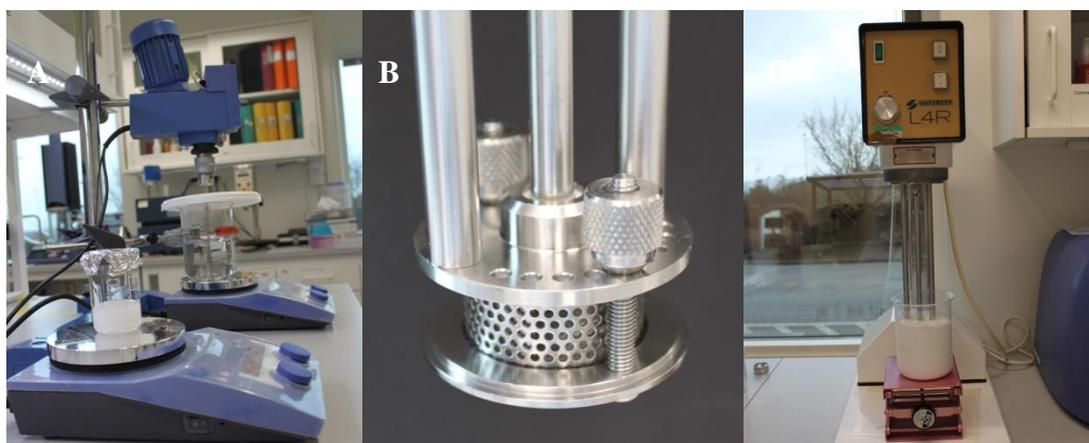
The hair was delivered in tresses from:  
Kerling International Haarfabrik GmbH  
Postfach 13 30  
D – 71522 Backnang, Germany

## 4 Experimental procedure

Materials will be specified related to their application in each method. In each performance study, natural, wavy, brown (colour 7/0), European human hair was used. The procedure of the performance study is introduced and it is specified how the biophysical analysis methods were applied. The conditioners were prepared and applied onto hair tresses in the same manner in order to obtain comparable results.

### 4.1 Formulation of simple hair conditioners

1. The water-phase was prepared by mixing deionized water and the chelating agent Dissolvine GL47S in a beaker with a U-shaped propeller and heating with a hot plate to 75°C.
2. The oil-phase was prepared in a separate beaker by blending Lanette O, Brij CS20 and Crodamol IPM together, melting them and subsequently heat to 75°C on the hotplate, see **Table 5** for precise fractions.
3. The oil-phase was added to the water-phase at the Silverson homogeniser. The solution was homogenized to ensure the emulsion to form, see **Figure 9**.
4. The batch was brought back to the propeller mixer and cooled down during stirring. The active species were in general added when the temperature was below 60°C. Note that 60°C was set as the standard, but if the manufacturer gave any other recommendation the procedure was changed accordingly. Some actives required higher temperature for incorporation, while others had to be added at a lower temperature to avoid structural damage. Further the active species that had the physical appearance of a powder or pellets were premixed with deionized water as a separate phase and heated to 60°C prior to addition. This affected the ease of incorporation into the formula.
5. Subsequently the rheology modifier and emulsion stabilizer Structure XL was slowly added to the main batch during mixing.
6. When the emulsion had a temperature below 45°C the preservative Glydant Plus Liquid was added and pH was adjusted to target (pH 5) with lactic acid.
7. The formula was stirred until it reached 25°C and then transferred to a glass jar for storage. The viscosity was measure with a Brookfield viscometer.



**Figure 9** A The simultaneous heating of the aqueous- and the oil phase. B The workhead of the homogenizer. C Homogenization performed for 5 min at 5000rpm.

**Table 5** An overview of the standardized conditioner formula, where 1,5 % of surfactant or protein or 0,5 % of any other active ingredient was added (X). The formula contained nearly 90% deionized water (Y=remainder).

Trade name	INCI name	Chemical name	(%)
Deionized Water	Aqua	Deionized Water	Y
Dissolvine GL47S	Tetrasodium Glutamate Diacetate	Tetrasodium N,N- bis(carboxymethyl)-L glutamate	0,2
Lanette O	Cetearyl Alcohol	Cetyl stearyl alcohol	5
Brij CS20	Ceteareth-20	PEG-20 cetyl/stearyl ether	1
Crodamol IPM	Isopropyl Myristate	Isopropyl tetradecanoate	2
Active	-	-	X
Structure XL	Hydroxypropyl Starch Phosphate	Hydroxypropyl Starch Phosphate	2
Glydant Plus Liquid	DMDM hydantoin	1,3-Bis(hydroxymethyl)-5,5- dimethylimidazolidine-2,4-dione	0,5
Lactic Acid	Lactic Acid	Lactic Acid	qsp

## 4.2 Damaging hair by bleaching

In order to distinguish conditioners with good performance, the hair have to be damaged prior to the testing. This rather severe damage will result in a levelling of the previous damage of the hair that is caused by daily wear. The damage was done by hair bleaching according to a standard operating procedure (SOP) at AkzoNobel Surface Chemistry AB<sup>22</sup>.

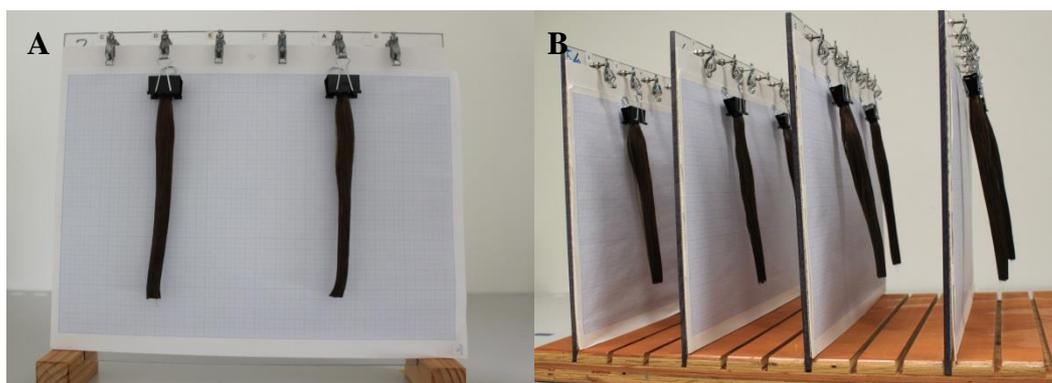
1. 1200 ml of 6 % hydrogen peroxide solution was prepared.
2. The pH was adjusted to pH 10 with a 10 % ammonium hydroxide solution.
3. 18 tresses were bleached in three separate batches.
4. 6 tresses were placed in a dish with 400 ml of the hydrogen peroxide solution.
5. Glass plates were placed on top of the tresses in order to keep the tresses submerged in solution despite the fierce reactions that were taking place.
6. After 40 min of bleaching each tress was rinsed separately under tap water.
7. Each tress was soaked in a 10 % SLES solution for an hour.
8. The tresses were combed in order to distribute the SLES throughout the hair.
9. The tresses were rinsed under running tap water during combing.
10. Steps 7 to 9 of the washing procedure were repeated.

## 4.3 Anti-frizz analysis

The method development will be further specified in the section *Method development for anti-frizz analysis*. The final procedure that was established will be presented here within. Two hair tresses of 20 g with 19,5 cm is free hair were used for each product tested. The preparation of the hair tresses before analysis was done according to a SOP at AkzoNobel Surface Chemistry AB<sup>23</sup>.

1. The tresses were kept in the humidity chamber at 21°C and 55% RH overnight.
2. Hydration in tap water for a minimum of five minutes in a Pyrex baking dish.

3. 0,5 gram of the desired conditioner was applied to each tress.
4. The conditioner was worked into each tress for 30 s in a downward motion.
5. Each tress was rinsed for under running tap water, 30 s 2 L x min<sup>-1</sup> 30°C.
6. Each tress was then combed through at least 6 times to remove entanglements and subsequently squeezed together by running your thumb and forefinger in a loop in a downward motion in an attempt to eliminate 'initial frizz'.
7. Two tresses with the same product were hanged per board.
8. 4 boards were placed in the humidity chamber at 32°C and 30 % RH for 2 h.
9. Initial pictures were taken after the level up, see **Figure 10**.
10. Experiments were performed at 32°C and 90% RH.
11. The evaluation of performance was done based on the photos at 4 and 6 h.



**Figure 10** **A** Demonstration of the set up for the anti-frizz analysis when the pictures are taken at 0, 4 and 6 h. **B** The set up for the anti-frizz analysis during the experiment when kept in the humidity chamber is shown.

#### 4.4 Anti-static analysis

The tresses were prepared in a similar manner as for the anti-frizz measurements, but with damaged hair tresses of 4,25 g bleached hair, 18 cm free hair for each product tested. The preparation of the hair tresses before analysis was done according to a SOP at AkzoNobel Surface Chemistry AB<sup>23</sup>.

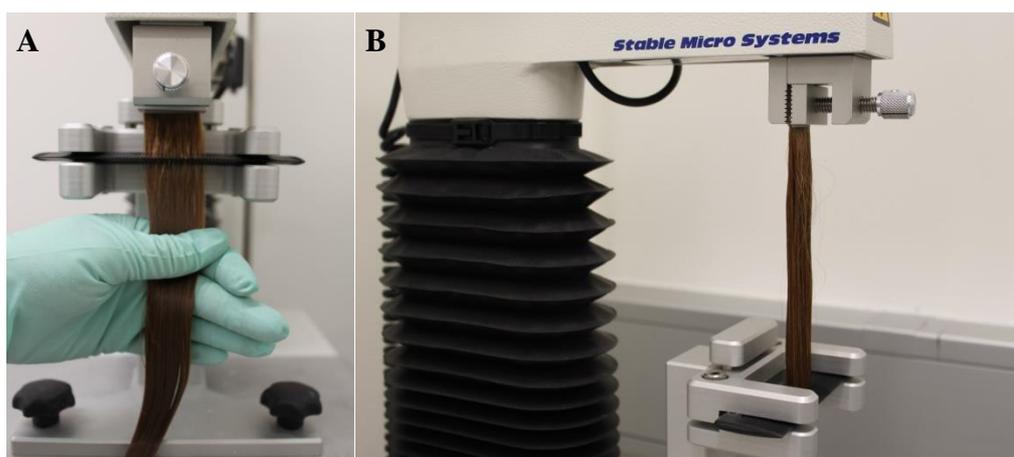
1. Hydration in tap water for a minimum of five minutes in a Pyrex baking dish.
2. 0,25 gram of the desired conditioner was applied to each tress.
3. The conditioner was worked into each tress for 30 s in a downward motion.
4. Each tress was rinsed for under running tap water, 30 s 2 L x min<sup>-1</sup> 30°C.
5. Each tress was then combed at least 6 times with an ACE comb.
6. The tresses were dried at 50°C for 2 hours prior testing.
7. Each tress was combed rapidly 10 times directly followed by photography.

#### 4.5 Wet combing analysis

The tresses were prepared similar as for the anti-frizz measurements, but with damaged hair tresses of 4,25 g bleached hair, 18 cm free hair for each product tested. The analysis was done according to a SOP at AkzoNobel Surface Chemistry AB<sup>23</sup>.

1. Hydration in tap water for a minimum of five minutes in a Pyrex baking dish.
2. 0,25 gram of the desired conditioner was applied to each tress.
3. The conditioner was worked into each tress for 30 s in a downward motion.
4. Each tress was rinsed for under running tap water, 30 s  $2 \text{ L} \times \text{min}^{-1}$   $30^{\circ}\text{C}$ .
5. Each tress was then combed at least 6 times with an ACE comb.

The blanks were measured after each wash as the washing in SLES in combination with the mechanical forces during combing contributes to increasingly damaged hair. All measurements were performed with the TA.XT. plus Texture Analyzer by Stable Micro Systems, see **Figure 11**. The instrument software Exponent Software TE32 continuously recorded combing forces. The values between 20-150 mm are used. Six hair tresses for each product were used to determine the combing force properties. In general eight tresses were prepared per product, as outliers occurred due to difference in damage. Pantene Classic Clean Daily Conditioner was used as control, which was tested prior to the evaluation of the products of interest to gain a better idea of the quality of the hair after bleaching. Six combing force values were used to gain the average combing force. Every second run the tress was flipped to the other side in order to avoid tracking, which would artificially reduce the average comb force. Outliers with unusually higher values were due to the presence of entanglements. Data was reported as percentage of reduced combing force for the treated hair.



**Figure 11** **A** The comb was mounted in the TTC Hair Combing Rig with quick release TA-412 with an extra long post for hair combing. Consequently, the tress was attached to the A/MTG Mini Tensile Grip at 20 mm distance from the comb and softly fixed at the starting position into the teeth of the mounted comb. **B** The force was measured as the tress was pulled through the teeth of the mounted comb at a test speed of  $16.67 \text{ mm} \times \text{s}^{-1}$ .

## 5 Experimental results and discussion

The overall performance including anti-frizz, anti-static and wet comb provided insights of different aspect of hair manageability. First when the formulation is stable for the time frames relevant for the application it is feasible to analyse its properties.

### 5.1 Stability testing of a formula

The results from the stability tests performed on a formulation according to *Formulation of simple hair conditioners* with Product P can be seen in **Table 6**. Often the toughest test is at 50°C and even though it appear to be stable indeed there seem to be a loss in viscosity. Interestingly there is a strong increase in viscosity at 40°C after 2 weeks, which then reduces again. Furthermore, all formulations with different actives were stabile at room temperature for the time frame of the project, which was sufficient for the purpose of the performance study.

**Table 6** The stability of conditioner formula with Product P was evaluated, where appearance, pH and viscosity (RV6, 10 rpm) were assessed during six weeks.

Long term stability				
Condition	Time	Appearance	pH	Viscosity (cP)
<b>Room temperature</b>	Day 1	White cream	5,17	36500
	Week 2	White cream	5,03	38500
	Week 3	White cream	4,99	37600
	Week 6	White cream	4,87	36000
<b>8°C</b>	Week 2	White cream	5,09	38400
	Week 3	White cream, grainy bulk	5,18	42400
	Week 6	White cream, grainy bulk	5,21	41200
<b>40°C</b>	Week 2	White cream	4,65	46000
	Week 3	White cream	4,62	44000
	Week 6	White cream	4,54	41500
<b>50°C</b>	Week 2	White cream	4,55	37000
	Week 3	White cream	4,56	32400
	Week 6	White cream	4,80	27300

### 5.2 Method development for anti-frizz analysis

Initially a method development was performed and therefor test conditions were changed. On the way I also encountered several problems concerning the set up and the humidity chamber used. The amount of product applied and the number of boards in the set up varied. The test conditions will be specified whenever changing. The level up condition regarding time, temperature and relative humidity seem to be critical for the test results. These were adjusted with the aim to establish a robust and efficient screening procedure, see **Table 7**.

**Table 7** An overview of the changes regarding set up and level up that were made in order to create a feasible method for screening purposes.

Test conditions	Performance	Modification
1 g of product 1 h level up at 50°C and 55 % RH 6 test boards 0 h, 4 h and 24 h test photos.	The 4 h photo implied that products on the same board in general performed equal.	A suspicion arose that there might be an interaction between the two tresses on the same board. This was taken under investigation.
-	The previous suspicion was confirmed, there was in fact a contamination between the two tresses on the same board, see <b>Figure 12 A-C</b> .	The procedure was adjusted accordingly so that only one product was present per test board.
-	All products tested are performing the same after 24 h, which induce a question of the gain from this long test time.	A 6 h test photo was added.
1 g of product 1 h level up at 50°C and 55 % RH 6 test boards 0 h, 4 h, 6 h and 24 h test photos.	No clear difference could be seen after 24 h and the photographs at 4 h and 6 h seem to provide more information about the performance, see <b>Figure 13 B, D</b> .	Test photos should instead be taken at 0 h, 4 h and 6 h. This enables a more efficient screening procedure.
-	A previously excellent performing product was now underperforming, which could be deduced from the fierce agitation from the fan located in the middle of the humidity chamber. One of the hair tresses was found to be stuck in the fan, see <b>Figure 13 A</b> .	The set up was modified so that the rack contained 4 test boards to avoid placing any board next to the fan. Further, a plexiglas was placed in front of the fan, perpendicular to the test boards, to achieve a homogenous airflow throughout the chamber.
1 g of product 1 h level up at 50°C and 55 % RH 4 test boards 0 h, 4 h and 6 h test photos.	All the products had a good anti-frizz performance after 6 h, except from one of the tresses.	The experiment conditions need to be even harsher for an efficient screening. Further more a realistic levelling temperature was desired.
0,5 g/1 g of product 1 h level up at 32°C and 30 % RH 4 test boards	There was a significant difference between the products after 22 h. No clear dependence on the amount product applied	As the lower amount (0,5 g) seemed to be sufficient it was applied in the rest of the experiments. This was

0 h, 4 h, 6 h, 22 h test photos. (6-22 h in a non-controlled environment)	for the anti-frizz benefits could be seen, see <b>Figure 12 E</b> .	an approach to make the test conditions harsher.
-	One of the tresses had a split end after the level up, which resulted in higher frizziness, see <b>Figure 13 C</b> . The moisture could more efficiently reach the core of the tress.	It indicates a dependence on tress thickness as it can be seen as divided into two parts. This demonstrates the sensitivity of the method for precise preparation.
0,5 g of product 1 h level up at 21°C and 30 % RH 4 test boards 0 h and 4 h test photo, before experiment was discontinued.	Tresses still wet after level up, which means that 21°C is a too low temperature for the hair to dry even at low relative humidity. It is suspected to be important that the hair is relatively dry as it is the imbalance in moisture that is believed to cause frizz.	Longer time or higher levelling temperature would be possible changes.
-	One of the blank tresses did not frizz after 4 h of testing, which indicated a polymer build up on the hair, see <b>Figure 12 D</b> . The conclusion was that the washing was insufficient. It had been performed in 3 % SLES solution during 2 h with initial combing to spread the anionic surfactants and final combing while rinsing to minimize residues.	A new procedure was established were the dry hair was also combed to break the polymeric film. Thereafter it was combed in 15 % SLES and kept in solution during 2 h of which 30 min at 45°C in an ultrasonification bath.
0,5 g of product 1 h level up at 32°C and 30 % RH 4 test boards 0 h, 4 h and 6 h test photo.	Tresses still wet inside at the end of the experiment as they were not allowed to dry when levelled up at 32°C 30% RH for only an hour.	This created a sticky chunk of hair in the middle that did not come apart during the experiment. Consequently the level up was prolonged.
0,5 g of product 2 h level up at 32°C and 30 % RH 4 test boards 0 h, 4 h and 6 h test photo.	There was a difference in the performance between all products tested and a replicate experiment showed a similar trend. Further the blanks showed no signs of polymer residues.	Screening could proceed.



**Figure 12** A Product X. B Product X and Product Y. C Product Y. D Blank tresses. E 22h overview of 0,5g Product X, 1g Product X, 0,5g Product Z and 1g Product Z.



**Figure 13** A Effect of fan. B Product W. C Effect of split hair end. D Product Q.

### 5.3 Anti-frizz performance

Test conditions during screening was as follows: 0,5g of product were applied to the tresses and the level up was performed at 32°C and 30% RH for two hours for all products here within. The rack contained 4 test boards. Test photos were taken initially, after 4 h and 6 h.

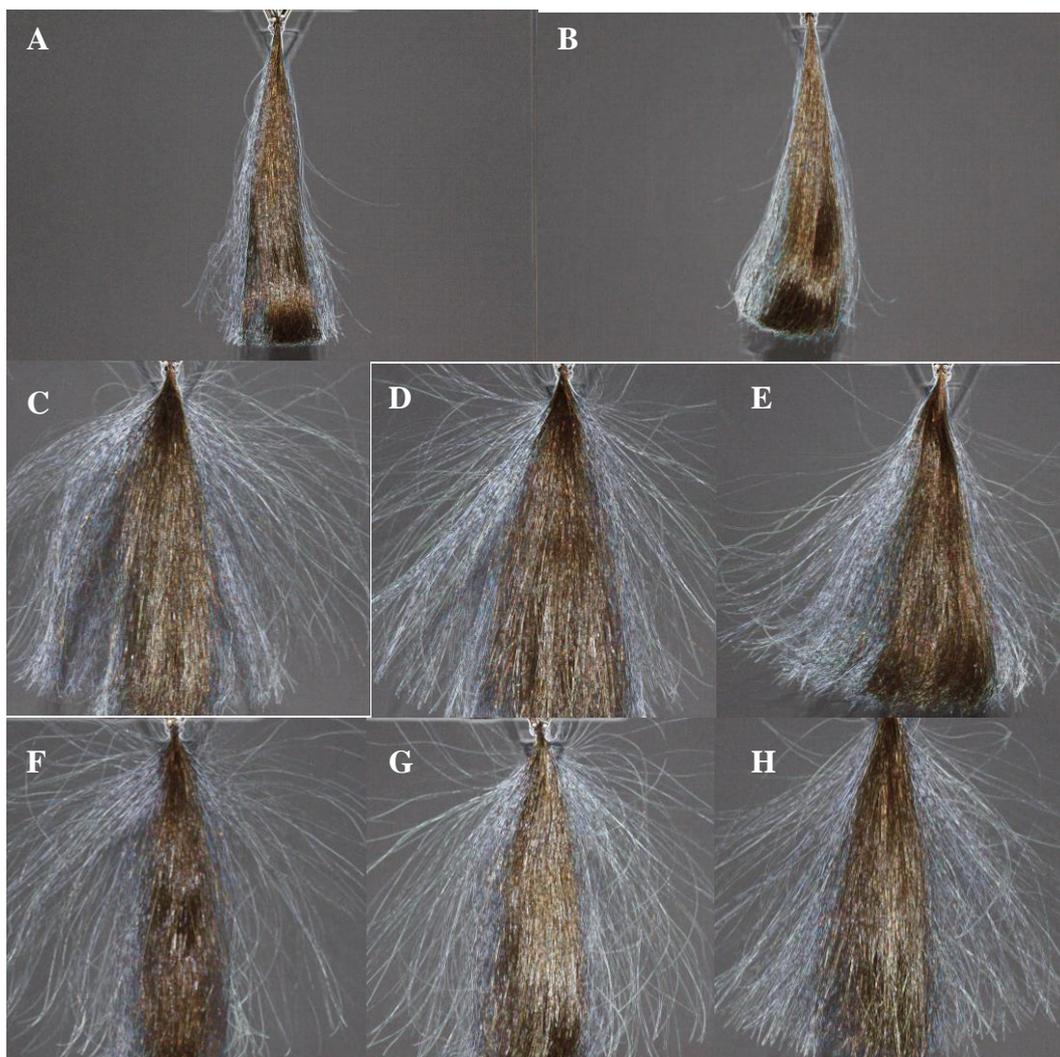
**Figure 14** shows the results regarding anti-frizz performance. Varisoft BT 85 had the most promising anti frizz performance. Preliminary results for ABIL Soft AF300 and SoyTein NPNF showed various performances during the method development and screening, thereby further testing is advised for a precise ranking. There is no significant difference between Siltech 2145-35, Keraquat NPNF, Gluadin WQT P and Mackine 301U. Further these are not demonstrating any frizz reduction as their performance is similar to the blank, which is prepared with tap water. This provides proof that the conditioner formula is simple enough and it is suggested that any benefit seen during testing can be assigned to the conditioning agent.



**Figure 14** A Varisoft BT 85. B ABIL Soft AF 300. C SoyTein NPNF. D Siltech 2145-35. E Keraquat NPNF. F Mackine 301U. G Gluadin WQT P. H Blank.

## 5.4 Anti-static performance

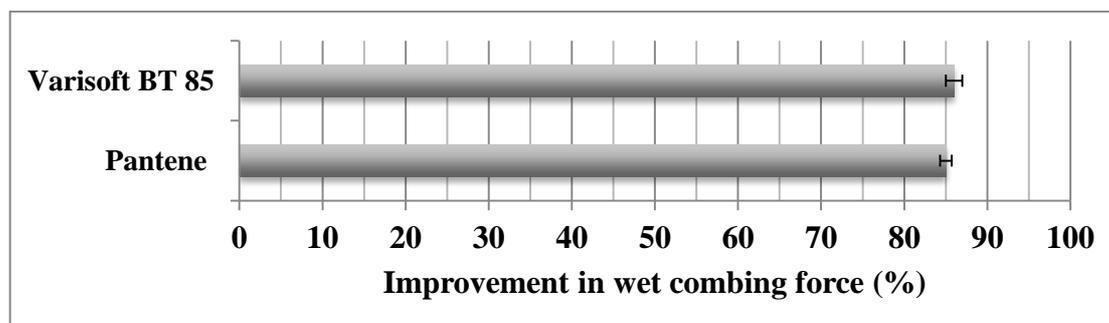
Both tested surfactants, Varisoft BT 85 and Mackine 301U, showed excellent anti-static benefits, see **Figure 15**. No significant reductions were seen for the silicones or protein derivatives compared to the blank, which was prepared with tap water. This implies inefficiency in dissipating the charge build up. Gluadin WQT P shows slightly reduced static behavior, which can be deduced from difficulties in combing this tress.



**Figure 15** A Varisoft BT 85. B Mackine 301U. C Keraquat NPNF. D SoyTein NPNF. E Gluadin WQT P. F ABIL Soft AF 300. G Siltech E2145-35. H Blank.

## 5.5 Wet combing performance

Commercial Pantene Classic Clean Daily Conditioner was used as a control and showed an improvement of  $85\pm 0,7$  %. There was no significant difference to the widely used benchmark Varisoft BT 85, which showed an improvement of  $86\pm 1$  %. It can be concluded that Varisoft BT 85 demonstrated an excellent wet combing performance. The improvement in wet combing force in contrast to a bleached blank hair tress can be seen in **Figure 16**.



**Figure 16** The standard error for the six tresses measured for each product is shown, whereas each measurement on the same tress was treated as a technical replicate.

## 5.6 Summary of the overall performance

**Table 9** A comparison of the performance between the selected products is shown. The anti-frizz and anti-static performances have been qualitatively graded based on weak performance (+), promising performance (++) and excellent performance (+++). Wet combing is defined as above 80 % improvement (+++). When no measurement was performed this is marked with (NM). If further testing is needed for precise ranking this is marked (\*).

Product	Anti-frizz	Anti-static	Wet comb
<b>Surfactants</b>			
Varisoft BT 85	++	+++	+++
Mackine 301U	+	+++	NM
<b>Protein derivatives</b>			
Gluadin WQT P	+	+	NM
Kera Quat NPNF	+	+	NM
Soy Tein NPNF	++*	+	NM
<b>Silicones</b>			
Siltech E-2145-35	+	+	NM
ABIL Soft AF 300	++*	+	NM

The overall performance for all of the selected technologies can be seen in **Table 9**. Both surfactants showed excellent anti-static performance. As expected, the heavy conditioning agent Varisoft BT 85 demonstrated excellent wet combing benefits. These results are related to the ability of surfactants to efficiently attach to the hair and provide a hydrophobic modification of the hair fiber surface. In the anti-frizz analysis Varisoft BT 85 vastly outperformed Mackine 301U who seemed to lack any anti-frizz ability. It was suspected that the performance depended on the lack of charge. A high total charge density could be provided with many Varisoft BT 85, which could efficiently neutralize the original anionic charge on the hair fiber surface.

The three protein derivatives were showing relatively weak performance regarding anti-frizz and anti-static. As anti-frizz was the major focus of this manageability study, these were not screened for wet combing benefits. The molecular structures were company secrets, which were another reason for focusing on other chemistries. Further protein derivatives are seen as story ingredients. Therefore the use in hair care products can be derived from a customer appeal towards natural ingredients.

Silicones are frequently used in conditioners for their many benefits. The reason that this cannot be seen within this study can be deduced from the fact that silicones are highly dependent on deposition agents. It was expected that amino-modified silicone technology should demonstrate a promising performance, but rather various anti-frizz results were gained combined with a weak anti-static performance. It might be due to an insufficient charge density. As anti-frizz was the major focus of this manageability study, these were not screened for wet combing benefits. Further it has been proposed that a high level would be needed for efficiency. As mentioned, there is an important market trend is towards multifunctional products. The driving force would be the customer appeal of having one product that could potentially replace several others on the bathroom shelf. This could have implications regarding convenience, time-efficiency and economics. It serves as a motivation to gain several benefits from a single ingredient in a conditioner. This also insinuates a significant economical advantage for Varisoft BT 85, as alone, at a very low level seems to be sufficient for promising manageability performance, in contrast to silicones and protein derivatives.

Curvature is the main fiber characteristic determining manageability for curly hair in contrast to friction for straight hair. Therefore it is important to realize that the results presented here within are limited to hold true for hair of a somewhat similar texture. Further it is important to assess all aspects of the hair that are affected in order to market the product in a truthful way towards consumers. The active ingredient in conditioners might have an impact on the appearance and feel, which could affect the customer appeal. An example is change in curvature, which can be seen in **Figure 18**.



**Figure 18** **A** Appearance of blank wavy hair tresses. **B** The formula containing Product S had a straightening effect on the wavy hair tresses.

## **6 Conclusions**

The level up and test condition regarding time, temperature and relative humidity seem to be critical for the frizziness. Therefore these should be chosen wisely and kept under control to gain robust results. Further studies would be needed to optimize the parameters. The widely used cationic surfactant docosyltrimethylammonium chloride was overall well performing, especially when it came to reduction of friction force and reduction of static during combing. It was superior to the other cationic surfactant tested regarding reduction of frizz. This study suggests that the silicones and protein derivatives showed less promising results regarding the overall manageability. Preliminary data has implications that the efficiency of anti-frizz is correlated with cationic charge and high hydrophobicity of the conditioning agent.

## 7 Recommendations for future research

It would be interesting to study a more realistic conditioner formula that contains both cationic surfactants and silicones, which would affect the morphology of the conditioner and a synergistic effect could be expected. An optimal technological solution, at least for a mass-market non-premium product, would only require one conditioning agent, which in this study would point toward a cationic surfactant.

The study has implications that the efficiency of anti-frizz performance is correlated with cationic charge and high hydrophobicity. Therefore a suggestion for future research regarding improving the manageability performance, more specifically anti-frizz, should focus on these properties. More thorough studies with a greater number of candidates with fine tuned molecular characteristics around the most promising candidate Varisoft BT 85 would be suitable to further understand the relationship. It would also be interesting to explore the manageability performance of other molecular groups than the selection presented here within.

A more complex set up of the experiments would be required in order to proceed with the new product development and distinguish between highly performing products. As there was a problem with contamination between the products, the optimal situation might be to only test one product at the time and wash the tresses separately in order to avoid a mixture of residues. A quantitative analysis would be required rather than qualitative. Therefore I would also recommend the development of appropriate algorithms for a robust determination of the anti-frizz performance. One approach could be to apply convolutional neural networks and deep learning algorithms for an efficient and accurate image analysis.

In addition, it would be interesting to further look into the mechanisms behind anti-frizz. Further studies would be needed to fully exploit the dependence on time, temperature and relative humidity as well as regarding the hair surface modification. Microscopy studies (AFM) could provide valuable insights about the film formed on the hair fiber upon conditioning, which is believed to be crucial for the moisture balance. I would advice to test how this film is affected by various conditions. It is of high priority to determine how this film is affected by washing, in order to understand the optimal conditions for washing the hair during laboratory tests. The cleaning procedure should be developed to cause minimal damage on the hair and ensure that build up can be avoided. In order to establish claims towards long-lasting products it would be relevant to determine if the film can survive several washing cycles.

As mentioned, it is important to realize that the results presented here within are limited to hold true for hair of a somewhat similar texture. The problem with manageability regarding frizziness is larger for more curly hair. Therefore it would be of high importance to test hair of a higher degree of curliness. The quality of hair is another obstacle mentioned. An improvement would be to require for the hair suppliers to provide detailed information about the history of the hair. This is becoming increasingly important with the increased amount of hair products on the market, which result in a limited availability of untreated hair. It might be an improvement to bleach the hair tresses also for the anti-frizz analysis. On long term it would be relevant with research regarding the development of synthetic hair.

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