ISTANBUL TECHNICAL UNIVERSITY * GRADUATE SCHOOL OF SCIENCE, ENGINEERING AND TECHNOLOGY

EVALUATION OF SILICONE POLYMERS IN SHAMPOOS

M. Sc. THESIS

Pınar TAŞKIN

Department of Polymer Science and Technology

Polymer Science and Technology Programme

Thesis Advisor: Prof. Dr. İ. Ersin Serhatlı

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SİLİKON POLİMERLERİN ŞAMPUANLARDAKİ ETKİSİNİN DEĞERLENDİRİLMESİ

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Pınar TAŞKIN
515041037

Polimer Bilim ve Teknolojisi Anabilim Dalı

Polimer Bilim ve Teknolojisi Programı

Tez Danışmanı: Prof. Dr. İ. Ersin Serhatlı

KASIM 2016

Pınar Taşkın, a M.Sc. student of ITU Graduate School of Science Engineering and Technology student ID 515041037, successfully defended the thesis entitled "Evaluation of Silicone Polymers in Shampoos" which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor: **Prof. Dr. İ. Ersin SERHATLI** ………………
İstanbul Technical University

Jury Members: **Prof. Dr. İ. Ersin SERHATLI** ………………
İstanbul Technical University

Prof. Dr. Oya ATICI ……………....
İstanbul Technical University

Prof. Tarık EREN ………………
Yıldız Technical University

Date of Submission : 27 November 2016
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FOREWORD

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Chemist

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ABBREVIATIONS

CAPB **:** Cocamidopropyl Betaine (35%)
EO **:** Ethylene Oxide
PDMS **:** Polydimethylsiloxane
PO **:** Propylene Oxide
SLES **:** Sodium Laureth Sulfate (70%)
SLS **:** Sodium Lauryl Sulfate

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EVALUATION OF SILICONE POLYMERS IN SHAMPOOS

SUMMARY

Being one of the industries which is least effected by various economic crisis in the world, personal care industry is known with its wide range of products and dynamic consumers. Among all personal care products, shampoos are known to be of interest by all consumers of all age groups since shampoos are perceived by the consumer as the “must-have” items. Silicones are used in a number of personal care products, providing their unique sensory benefits from shampoos and skin creams to cosmetics and antiperspirants. Silicones are fast becoming an essential ingredient in the cosmetics and personal care market as producers continue to provide more customized and specialized silicone ingredients to meet consumer demand for innovative, multifunctional and sensory-appealing products. Clear shampoos are perceived as being pure and less harmful to both hair and skin by consumers, as they do not weigh down hair, provide volumizing and contain less amount of ingredients. Thus, main aim of this study was to formulate a clear and conditioning shampoo while investigating the behaviors of silicones in shampoo base.

Moreover, the shampoo industry is moving towards using less amount of ingredients and obtaining optimum results. Functional silicones play a critical role on the overall effect of such shampoos because functional silicones can provide ease of combing, shine, volume and enhanced foam.

In this study, different types of silicones were investigated in shampoo systems. These silicones are graft silicone copolymers, trisiloxane polyethers and finally polyetheramine silicone copolymers.

The aim of the study was to see which silicone system can be thickened by salt, what kind of effect the stable formulations provide on hair, the solubility profile of the silicones in shampoo system, to see clarity and uniformity of the finished products.

The most successful formulations were obtained in Experiment 5 and 6. The results of experiment 6 were by far the optimum results in terms of conditioning both for hair and skin. Sodium Laureth Sulfate and Cocamidopropyl Betaine are selected as the surfactants.

Methyl Gluceth-20 and C12-15 Alkyl Lactate are used as thickeners in selected formulations. Shampoos were evaluated for clarity, viscosity, salt (NaCl) content/efficacy and via combing force, conditioning effect, shine and conditioning properties of the applied hair.

Emulsion silicones were found to provide conditioning, ease of combing and softness to both wet and dry hair and as well as skin. The final formulations with the emulsion silicones can also be used in facial washes, body washes, shower gels and hand washes by doing slight changes in formulations. These formulations can also be opacified by using glycol distearate and/or acrylates copolymer based opacifiers/thickeners.

SİLİKON POLİMERLERİN ŞAMPUANLAR ÜZERİNDEKİ ETKİSİNİN DEĞERLENDİRİLMESİ

ÖZET

Dünya üzerindeki ekonomik krizlerden en az etkilenen sektörlerden biri olan kozmetik sektörü, yenilikçi ürünleri ve sürekli dinamik kalan tüketici tarzı ile bilinmektedir. Tüm kozmetik ürünlerin içerisinde, şampuanlar, tüm tüketiciler tarafından en çok kullanılan ürünler arasında yer alır zira şampuanlar herkesin “kullanması şart” olan ürünlerdendir. Silikonlar, başta şampuan ve saç kremleri olmak üzere cilt kremleri ve anti-perspiranlar gibi pek çok farklı kozmetik üründe kullanılır. Silikonlar, kozmetik ürünlerde giderek daha fazla oranda kullanılmaktadır ve yenilikçi, multi-fonksiyonel ürünlerin bir kısmında silikonların kullanımı şarttır çünkü formülün temel özelliğini kullanılan özel silikonlar sağlar.

Şeffaf şampuanlar, çoğu tüketici tarafından cilde ve saça daha az zararlı ürünler olarak algılanır çünkü çoğu şeffaf şampuan saçı ağırlaştırmaz, aksine hacim sağlar, opak şampuanlara kıyasla daha az bileşen içerir. Bu çalışmanın amaçlarından birisi de şeffaf, sade içerikli ve saçı nemlendirme özelliğine sahip bir şampuan formüle ekmektir.

Bununla beraber, şampuan formülleri giderek daha sadeleşmekte ve az bileşenle optimum etki alınması hedeflenmektedir. Fonksiyonel silikonlar bu anlamda çok etkili olmaktadır çünkü tek bir fonksiyonel silikon kullanarak ıslak-kuru taranabilirliği kolaylaştırmak, saça hacim ve parlaklık vermek ve köpüğü zenginleştirmek mümkündür.

Silikonlar, ilk sentezlendikleri zamandan bu yana kozmetik sektörü için son derece ilgi çekici bileşenler olagelmiştir. Örneğin, en temel silikon polimeri olan poldimetilsiloksanın kozmetikte çok fazla kullanım yeri vardır. Polidimetilsiloksan saç serumlarında hem saç yumuşatıcı hem de diğer silikonlar için taşıyıcı olarak kullanılır. Polidimetilsiloksanın düşük viskoziteli tipleri bazı şampuanlarda nemlendirici olarak kullanılır. Poldimetilsiloksan cilt için de çok iyi bir bariyer oluşturucu ve koruyucudur. Cildin üst tabakasını koruyarak cildin alt tabakalarındaki suyun (nemin) muhafaza edilmesine yardımcı olur. Polidimetilsiloksanın bir diğer kullanım yeri de renkli kozmetik olarak da bilinen makyaj ürünleridir. Bu silikon polimeri makyaj ürünlerinde taşıyıcı ve pigment sabitleyici olarak kullanılır.

Poldimetilsiloksanın türevlendirilmesi sayesinde değişik silikonlar sentezlenmiş olur. Bu sayede farklı özellikte silikon polimerleri elde edilir ve bu polimerler kozmetik alanında farklı amaçlarla kullanılabilir.

Polidimetilsiloksan suda çözünmez. Suda çözünmeyen bu polimerin türevlendirilmesi ile suda çözünür özelliğe sahip yeni silikonların sentezi mümkün olmuştur. Bu özel silikon polimerler hem sulu sistemlerde – ki kozmetik ürünlerin pek çoğu su bazlıdır, hem de fonksiyonellik aranan sistemlerde rahatlıkla kullanılabilir durumdadır.

Bu tez çalışmasında, farklı tipte silikon polimerler en sık kullanılan türde bir şampuan bazında denenmiştir ve silikonların etkileri araştırılmıştır. Kullanılan silikonlar graft silikon polimerleri, trisiloksan polieterler ve son olarak polieteramin tipi silikonlardır. Farklı tipte silikonların aynı şampuan bazında denenmesi silikonlar arasındaki farkların daha rahat anlaşılmasını sağlamıştır.

Çalışmada kullanılan silikonların hepsi suda çözünen silikonlardır. Bir silikon polimerin suda çözünmesi onun şampuan bazında da etkili olacağını garanti etmez dolayısı ile çalışmanın bir diğer amacı da silikonun bitmiş üründe yani şampuanda olduğu kadar, şampuan bazında nasıl davrandığını da görmektir. Bu davranışı sonucu silikonun sisteme uygun olup olmadığı, silikonun sonraki türevlendirilmesinde nasıl bir yolun takip edilip edilemeyeceği de kestirilebilir.

Çalışmanın amacı, hangi silikonlu sistemin tuz ile kalınlaştırılabildiğini tayin etmek, bu silikonların saç üzerinde verdiği etkiyi görmek, silikonların şampuan bazının şeffaflığı ve homojenliği üzerindeki etkisini araştırmaktır.

Bu çalışmada toplam altı deney gerçekleştirilmiştir. En olumlu sonuçlar beş ve altı numaralı çalışmaların sonucunda elde edilmiştir. Beş ve altı numaralı çalışmalardaki formüllerin bir kısmı hem saç hem de cilt üzerinde belirgin bir nemlendirme ve yumuşatma etkisi sağlamıştır. Olumlu sonuçtan kasıt, silikonun şampuan sisteminde iyi çözünmüş olması, sisteme dahil edilen tuz (sodyum klorür) miktarının optimum bir seviyede olması, bitmiş ürünün yani şampuanın stabil bir viskoziteye sahip olması ve nihayetinde deneklerin duyusal analiz sonuçları ile birlikte saç tutamları üzerinde de ürünün iyi etki vermis olmasıdır.

Çalışmalardaki formüllerde, sürfaktanlar olarak Sodium Laureth Sulfate ve Cocamidopropyl Betaine seçilmiştir. Bu sürfaktanlar, şampuanlarda ve benzeri tüm surfaktan sistemlerde (duş jeli, sıvı el sabunu vb.) kullanılan geleneksel sürfaktan tipleridir ve ticari olarak da en çok kullanılan surfaktanlardır. Anyonik Sodium Laureth Sulfate saç ve saç derisi temizliğini gerçekleştirirken, amfoterik olan Cocamidopropyl Betaine temizliğe yardımcı olur, ayrıca köpüğü zenginleştirir ve şampuanın viskozitesini arttırır. Bir şampuanın viskozitesini ayarlamak için en çok sodyum klorür kullanılır. Çoğu ticari üründe çok fazla kullanılan sodyum klorür aslında saçı ve saç derisini kurutur, dolayısı ile optimum bir formülde oranı mümkün mertebe düşük tutulması tercih edilir. Bu yüzden bu çalışmanın bazı formüllerinde viskozite arttırmaya yardımcı ajan olarak Methyl Gluceth-20 ve C12-15 Alkyl Lactate kalınlaştırıcı olarak kullanılmıştır. En ideali %1 civarında sodyum klorür ve %1 civarında da viskozite ajanı içeren bir şampuan yapabilmektir. Şampuanlar, şeffaflık, viskozite, tuz (NaCl) içeriği, ıslak ve kuru taranabilirlik, parlaklık ve nemlendirme açısından değerlendirilmiştir.

Beşinci ve altıncı deneyler, ticari olarak bilinen Silsoft isimli bir kopolimer silikonun muadili olan silikonların türevleri ile gerçekleştirilmiştir. Beşinci deney bu muadil silikonun direkt yağ formu ile gerçekleştirilmiştir. Yağ formu silikonlar, emülsiyon versiyonlarına kıyasla formülde daha zor çözünmüştür ve saç üzerindeki etkisi biraz daha ağır olmuştur. Silikon polimerin formülde daha rahat çözünmesi, üretim aşamasında tercih edilecek bir durumdur dolayısı ile altıncı çalışma bu yağ silikonların emülsiyon versiyonları ile yapılmıştır.

Altıncı çalışmada, emulsiyon silikonların saçta nemlendirme ve yumuşaklık sağladığı tespit edilmiştir. Emulsiyon silikonlar kullanılarak yapılmış şampuan formülleri hem kullanılan sodyum klorür miktarı, hem elde edilen ürünlerin şeffaflığı, hem de saç ve saç derisi üzerindeki nemlendirme etkisi sayesinde tüm çalışmalar içinde en iyi sonucu vermiştir. Silikon polimer nemlendirme/conditioning etkisini kuatlaştırılma seviyesi sayesinde sağlamaktadır. Hiç kuatlaştırılmamış bir silikon polimeri, %100 kuatlaştırılmış bir silikon polimerine nazaran daha az nemlendirme sağlayacaktır. Bu çalışmada, kuatlaştırma seviyesinin de saç ve cilt nemlendirme üzerindeki etkisi duyusal analizde açık bir şekilde görülmüştür. %100 kuatlaştırılmış silikonlar fazla nemlendirme özelliğinde ötürü saçta ağırlık ve ciltte yoğun bir tabakaya sebebiyet vermiştir. Bununla birlikte, en iyi nemlendirmeyi %50 kuatlaştırılmış emülsiyon silikonlar sağlamıştır. Kuat formüllerin, saçın ve cildin anyonik yapısından ötürü saça tutunduğu bilinmektedir. Ancak kuat oranı yüksek olduğunda bu tutunma fazlalaşır ve bu da ağırlık, yağlanmaya meyilli olmak gibi şekillerde kendini gösterir. Bu durum, tüketici açısından tercih edilir bir durum değildir dolayısı ile optimum bir kuat seviyesi yakalanmalıdır.

Bazı deneylerde, bazı silikonların şampuan bazında hiç çözünmediği gözlemlenmiştir. Bu durum silikon polimerin sistemle uyumsuz olduğunu göstermiştir. Bazı deneylerde ise silikonlu şampuan bazının sodyum klorür ile viskozite kazanmadığı görülmüştür. Nitekim bazı silikonlar sürfaktan sistemler ile uyumsuzdur dolayısı ile bu gibi silikonları formüle dahil edebilmek için proses değiştirilmeli ya da farklı kalınlaştırıcı ürünler kullanılmalıdır. Bazı bitmiş formüller (şampuanlar) ise, formülün tamamlanmasından bir kaç hafta sonra faz ayrışmasına uğramıştır. Bu formüllerin ise stabilitesi geliştirilebilir, bu formüllere süspanse edici ya da disperse edici ajanlar eklenebilir.

Bu çalışma, silikon polimerlerin şampuan bazında nasıl davrandığının çok yönlü bir analizi olarak görülebilir. Bu çalışma aynı zamanda ticari bir şampuan ürününün formüle edilmesinin bir ön çalışmasıdır. Kendi içinde kıyas edilen silikonlarla yapılan bu çalışma sonrası emülsiyon tip kopolimer silikonun %50 kuatlaştırılmış versiyonunun en iyi sonucu verdiği gözlemlenmiştir. Bu silikon, ideal kullanım oranı, ideal proses ve ko-bileşenleri bulmak amacıyla daha ileri bir çalışmada denenebilir ve enstrümental analiz ile duyusal analiz sonuçları teyit edilebilir. Bu çalışmadan kullanılan bazı şampuan formülleri aynı zamanda duş jelleri, yüz yıkama ürünleri, el yıkama sabunları gibi formüllerinde de kullanılabilir. Bu formüller aynı zamanda glikol distearat ya da akrilat kopolimer gibi opaklaştırıcı ajanlar kullanılarak opaklaştırılabilir.

1. INTRODUCTION

Personal care includes products as diverse as cleansing pads, colognes, cotton swabs, cotton pads, deodorant, eye liner, facial tissue, hair clippers, lip gloss, lipstick, lotion, makeup, nail files, pomade, perfumes, razors, shaving cream, moisturizer, talcum powder, toilet paper, toothpaste, and wet wipes. The personal care product industry boasts roughly 750 companies that produce a combined annual revenue of more than $40 billion. The 50 largest companies generate almost 70% of the entire revenue. Still, the market will bear competition from small companies that can offer a specialized product or cater to a particular niche market. Industry leaders include companies like Kimberly-Clark, Johnson & Johnson, Estee Lauder, Unilever, Avon, Colgate-Palmolive, L'Oreal, Proctor & Gamble and Revlon. Companies within the industry formulate, manufacture, market and sell a huge array of beauty and personal care products which are:

Makeup, deodorant and nail products comprise 33% of health and beauty care industry revenue.

Hair care products generate 25% of personal care product revenue, while and creams/lotions create 21%.

Perfumes, mouthwashes, shaving preparations and other products make up the remaining revenue for beauty skin care product revenues [1].

Shampoos today are the mainstay of the hair-care and cleansing market. They represent 50% of the total units sold in the hair products sector, which demonstrates their considerable importance in terms of the market and of social and individual habits [2]. Consumption of silicones increases yearly with their ever-widening application in cosmetics and personal care products. More than fifty percent of new cosmetics and personal care products launched in 2000s contained silicones, according to industry observers [3]. Aside from their aesthetic benefits, silicones also offer functional benefits such as skin protection, cleansing, actives-enhancement, resistance to wash-off, conditioning benefits in hair care products; the list goes on and on and there are more benefits being discovered. Its multi-functionality and value-added benefits are what makes it an ideal ingredient in almost all cosmetics and personal care products. Specialty silicones that have value-added benefits to end consumer will continue to be the key trend in this fiercely competitive market. There are various commercial silicones in the market currently which can be used for shampoos and as well as conditioners. On the other hand, a formulator's aim is to use one silicone which can provide all properties at once. Usage of a single silicone is favored for production scale. Not every silicone is clearly soluble in shampoo systems. Thus, incorporating a silicone into a shampoo system and obtaining a clear solution is a crucial step in formulating a functional shampoo.

2. THEORETICAL PART

2.1 Shampoos

2.1.1 Ingredients of shampoos

Water, detergents and preservatives are the main ingredients in all shampoos. Deionized water makes up from 70 to 80 percent of the shampoo formula. Detergents are the cleansing ingredient in shampoo and help to remove oil from hair. Preservatives prevent the growth of bacteria and other microbes in shampoo. Thickeners, foam boosters and conditioning agents are the secondary ingredients in shampoo. Foam boosters help increase the amount of foam and bubbles. Conditioning agents are added to offset the effect of harsher ingredients on hair. These agents reduce static electricity and improve the softness and feel of hair. Ingredients that modify the color and scent of shampoo are special additives. Other special additives include botanical extracts, natural oils, proteins and vitamins. Depending on the type of shampoo, other ingredients are sometimes added. All-natural shampoos use plant extracts and other all-natural ingredients. Alternative shampoos use fewer harsh chemicals. Cosmetic chemists develop shampoo formulas in the lab. After defining the characteristics of the shampoo, decisions are made regarding smell, color and thickness. Irritation and performance of the shampoo are also considered during formula development. Shampoo is made by combining a surfactant with a co-surfactant. These are the two main components in Shampoo. A surfactant is a substance that reduces the surface tension of a liquid in which it is dissolved. In shampoo, a surfactant works as a detergent to clean the hair, although it can also act as a wetting agent, foaming agent, and an emulsifier. The other component in shampoo is a co-surfactant. Co-surfactant is a substance that is used to increasing the oil solubilizing capacity. Sodium laureth sulfate, which is also called sodium lauryl ether sulfate, and sodium lauryl sulfate are the cleaning agents in shampoos. Both substances are used not only in shampoos, but in a range of household cleaning products too. This is due to their ability to produce foam, cut through grease and suspend soil particles so that they can easily be washed away.

Sodium laureth sulfate is referred to as SLES (sodium lauryl ether sulfate), while sodium lauryl sulfate is called SLS [5].

Most commonly used surfactants in cleansing systems are given Table 2.1 [8].

Table 2.1 : Anionic surfactants used in cleansing systems.

Surfactant name	Chemical Formula
Sodium carboxylate (soap)	RCOONa
Sodium alkyl sulfate	ROSO3Na
Disodium alkyl sulfosuccinate	ROCOCH(SO3Na)CH2COONa
Disodium amido sulfosuccinate	RNHCOCH(SO3Na)CH2COONa
Sodium acyl taurate	RCON(CH3)CH2CH2SO3Na
Sodium acyl isethionate	RCOOCH2CH2SO3Na
Sodium alkyl sulfoacetate	ROCOCH2SO3Na
Sodium alkyl sarcosinate	RCON(CH3)CH2COONa
Disodium acyl glutamate	RCONHCH(COONa)CH2CH2 COONa
Sodium monoglyceride sulfate	RCOOCH2CHOHCH2OSO3Na
α-sulfo fatty acid esters	RCH(SO3Na)COOCH3
Sodium dodecyl benzene sulfonate	RC6H5SO3Na
Sodium alkyl ether sulfate	RO(CH2CH2O)nSO3Na
α-olefin sulfonate	RCHCHCH2SO3Na

2.1.2 Invention of shampoo

Shampoo was invented by Hans Schwarzkopf in 1898. He created a water-soluble powder shampoo that was easier to use than the oils and soaps traditionally used to clean hair at the end of the 19th century. Schwarzkopf was a Berlin chemist who developed a number of perfume and hair-care products. His water-soluble powder shampoo was an immediate success and soon reached a wider market. Figure 2.1 is the advertisement of this first commercial shampoo. However, his shampoo dulled the hair, as it caused unwanted alkaline reactions. More hair-care innovations came in the 1920s and 1930s. Schwarzkopf continued to work on his line of hair-care products, launching a liquid shampoo in 1927. In America, Dr. John Breck developed a pH-balanced shampoo, which he introduced to New England in 1930 [6].

Figure 2.1 : First commercial shampoo’s advertisement, adapted from Gray (2001).

2.1.3 Differences between shampoo and soap

Shampoo differs from soap in that it is designed to cleanse the hair, can be formulated for specific hair types, is non-toxic, biodegradable and able to wash off with a clean finish.

When people try to wash their hair with soap, the hair can get damaged and dried out. This is because bar soaps and body soaps don't contain the same ingredients as shampoos. Shampoos are also varied in their formulas because hair has many different characteristics. There are shampoos for oily hair, dry hair, itchy scalps, frizzy hair, thick hair, thin hair, blonde hair. If shampoo is used as a soap, it usually doesn't work well, either. This is because soap is designed to be washed in the hair. It naturally forms a sudsy texture with lots of bubbles and washes off easily. When shampoo is applied to the skin, there is no hair there to naturally produce the suds. This can lead to the shampoo forming a slimy feeling on the skin. Because of this, it's recommended that people use soap for washing their body and shampoo for washing their hair, as this is what these types of products are intended for [18].

2.1.4 Working mechanism of shampoos

The act of shampooing involves the following steps: hair and scalp are wetted and the liquid shampoo distributed; shampoo is foamed and massaged into the scalp; shampoo foam is distributed throughout the hair; water is used to thoroughly rinse the hair and scalp; hair is towel dried to absorb excess water; wet hair is combed [7].

The target of cleansing is the outermost layer of tissue of our body, the keratinizing epithelium. It is composed of a cornified cell envelope, which is an extremely tough protein/lipid polymer structure. Akin to a wall built from bricks and mortar, the cornified layer also consists of hard building blocks (the individual corneocytes) stuck together with space-filling mortar (intercorneocyte lipids). This hard and lipophilic layer of the epidermis would not easily retain dirt without the intervention of an outer hidrolipid film that covers it and picks up particles of soil. This outer natural film of lipids entraps and glues environmental dust, pollutants, smoke, greases, keratinous debris, organic and inorganic compounds of the sweat, cosmetics, and other substances that come in contact with it. The process of washing consists of the removal of the outer layer of grease in which the soil (no matter what kind) is embedded. Figure 2.2 is showing the anionic surfactant molecule structure and the activity of the surfactant molecule on hair fiber. This is a complex physicochemical phenomenon that involves the following steps: Weakening the binding forces between the keratin and the grease by reducing the surface tension between the water and the water-resistant oil/grease. Because of reduced surface tension, water and, with it, the molecules of the surfactants can penetrate into the finest wrinkles of the skin. In this way, more and more interface is occupied by surfactants, and the adhesiveness of the soil is weakened, a process that is facilitated by mechanical rubbing.

Transferring the oil into the aqueous vehicle. This process is facilitated by the fact that the micelles that had been created when the soil was emulsified have a negatively charged surface and are rejected by the negative charge of the keratin of the skin surface.

Dispersing/suspending the oil and dirt particles in the foam and preventing it from being redeposited on the surface preparing for being washed off. Thus, cleansing will always remove fat from the skin, simply because the soil to be removed is embedded in the sebum of the skin. As a result, the methods for measuring the cleansing capacity of cleansing systems are based mainly on testing their ability to remove fat [8].

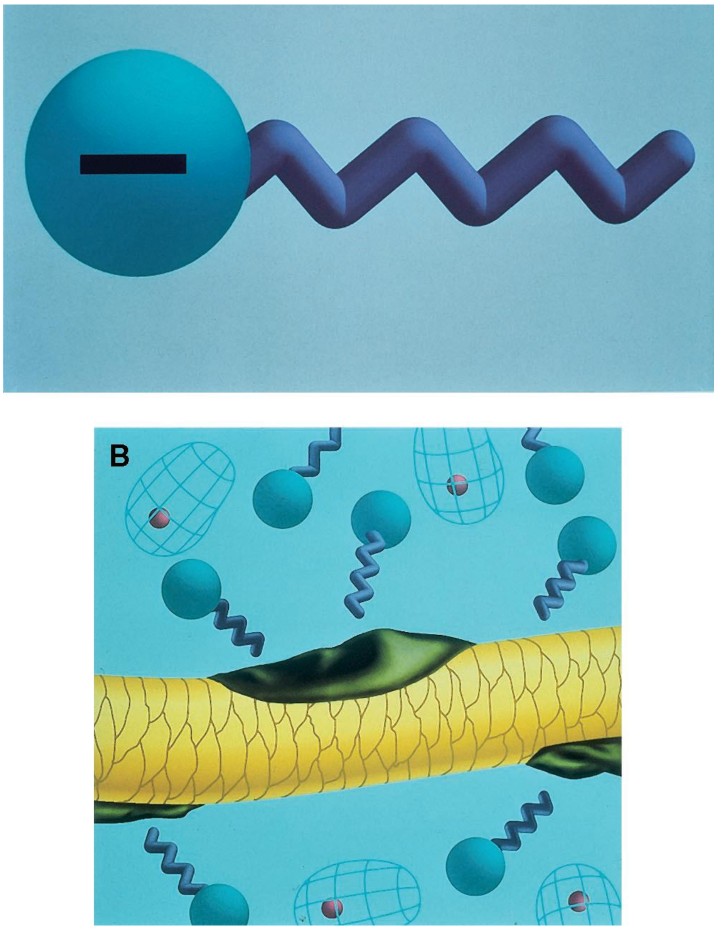

Figure 2.2 : Anionic surfactant molecule structure and activity of the surfactant molecule on hair fiber, adapted from Draelos.

2.1.5 Shampoo formulations

2.1.5.1 Clear shampoo formulation

A clear shampoo consists of one main anionic surfactant and a co-surfactant which is usually non-ionic. A thickener can be used to provide viscosity with sodium chloride. Sodium chloride is the most commonly used thickener for basic and cost-effective formulations. Acrylates copolymer is a typically used thickener and suspension agent for both clear and opaque systems. All shampoos have to contain a suitable preservative. A light conditioner can be used in a clear shampoo for slight conditioning, like clear silicone emulsions. Polyquaternium-10 (Quaternized hydroxyethyl cellulose) and polyquaternium-7 (Copolymer of acrylamide and diallyldimethylammonium chloride) are other commonly used conditioners. Figure 2.3 is showing the chemical structure of Polyquaternium-10 and Figure 2.4 is showing the chemical structure of Polyquaternium-7.

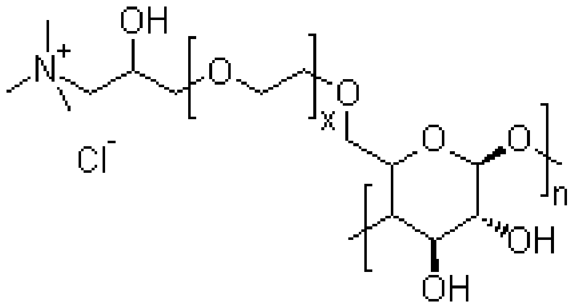

Figure 2.3 : Chemical structure of Polyquaternium-10.

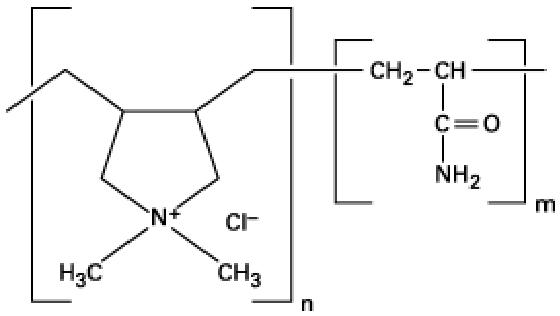

Figure 2.4 : Chemical structure of Polyquaternium-7.

Clear shampoos are mostly based on the formulation which is given by Table 2.2.

Table 2.2 : Clear shampoo base formulation.

Ingredient	%
SLES (70%)	10-15
CAPB (35%)	4-7
Thickener	0.5-2
Conditioner / Silicone	0.2-2
Preservative	0.1 – 1

2.1.5.2 Opaque conditioning shampoo formulation

Conditioning agents are added to provide softness and gloss, to reduce flyaway, and to enhance disentangling facility. They are particularly useful in shampoos for dry and damaged hair. Their role in a shampoo is not as effective as that of a separate conditioner or a rinse, because of the many functions a shampoo has to fulfill, the likelihood of incompatibility, or even conflicts resulting in a compromise. They do, however, have a major effect on the feel, appearance, manageability, and esthetic and cosmetic qualities of hair after shampooing. A great number of ingredients may be introduced, depending on the type of cleansing base and formulation and the objectives. They are mostly fatty ingredients-fatty alcohols, lanolin derivatives, vegetable or mineral oils or waxes, lecithins, essential fatty acid and derivatives, hydrolyzed proteins (keratin, collagen, silk, wheat, soya), and quaternized (cationic) derivatives, silicones, and cationic polymers. Antioxidants, sun screens, vitamins, and panthenol are also used. Special mention should be made here of cationic polymers and silicones, both of which have brought about a breakthrough in the approach to conditioning hair. As explained above, cationic surfactants are the preferred agents for smoothing and softening the hair shaft, for reducing friction when combing hair, and for neutralizing static electricity. But they are not compatible with anionic surfactants, which are the major cleansing agents used in shampoos [2]. Table 2.3 and Table 2.4 are demonstrating the typical ingredients of an opaque shampoo.

Table 2.3 : Prototype conditioning shampoo base formula using silicone gum blend.

Ingredient	%
Water	57.40
PEG-120 methylglucose dioleate	3.00
Sodium laureth sulfate (28%)	30.00
Cocoamidopropyl betaines (45%)	3.00
Cyclomethicone (and) dimethiconol	2.60
Cocamide Monoethanolamine	4.00
Preservative	q.s.
Citric acid 50%	

Table 2.4 : Prototype conditioning shampoo base formula using aminofunctional silicone.

Ingredient	%
Water	63.25
Polyol alkoxy ester	1.50
Trimethylsilylamodimethicone	2.00
Ammonium lauryl sulfate	30.00
Cocamide DEA	3.00
DMDM hydantoin	0.25
50% citric acid	q.s. to pH 6

2.2 Hair and Hair Conditioning

2.2.1 Structure of hair

The main part of the keratinized hair fiber is the cortex, which is made up of closely packed elongated cells whose axis is parallel to that of the hair. Covering this is the cuticle, composed of six to eight layers of flattened cells that overlap each other from root to tip (Fig 1 A, B, C). In humans, a third component may be present in terminal hairs, the central medulla; this consists of specialized cells containing air spaces. Hair structure is very stable and resists breakdown even for thousands of years after death, as the discovery of the bog bodies has shown [9].

The hair fibre structure is shown in the figure 2.5, from outside surface towards the inner structure.

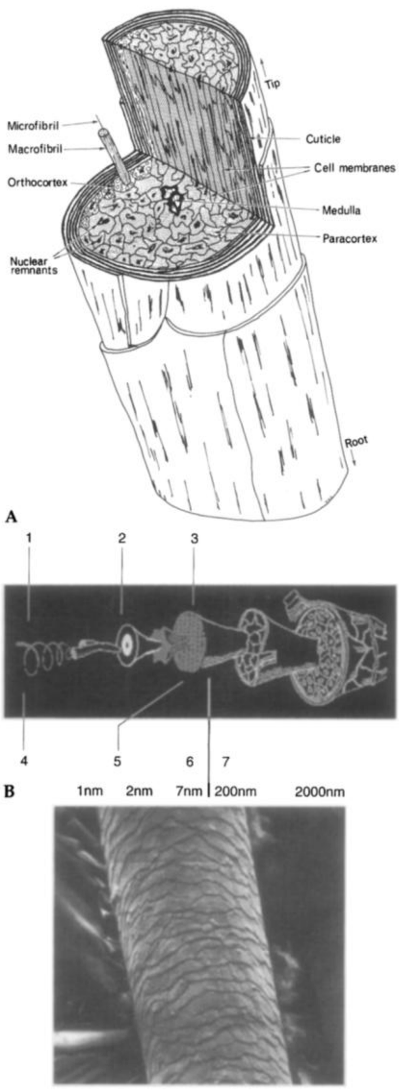

Figure 2.5 : Hair fibre structure, adapted from Gray (2001).

A. Hair fiber structure

B. Hairsubunit structure:

(I) right-handed alpha helix; (2) low-S;

(3) high-S; (4) left-handed coiled-coil rope; (5) matrix; (6)

Surface structure-closely apposed overlapping cuticufar cells

(scanning electron micrograph)

2.2.2 Chemical composition of hair

Human hair is a very complex fiber made up of various morphologic components and several different chemical species. For convenience and simplicity, the different chemical components are described separately in the text. Human hair is an "integrated" system, with the chemical components acting together. The chemical composition of hair varies somewhat with its water content. The main component is protein, which is 65-95% of the hair weight, keratinous, and a condensation polymer of amino acids. Other constituents are water, lipids, pigment, and trace elements [9].

2.2.3 Cleansing the hair

The substrate (hair) to be cleansed amounts to a large surface area – 100,000 to 150,000 individual hairs which adds up to 4 to 8 sqm for an average female head of hair, representing 50 to 100 times the surface area of the scalp underneath. Cleansing is not a small endeavor: mass of water employed in rinsing is enough to realize what a huge task is performed by a dose of shampoo. The substrate to be cleansed is a hard hydrophobic protein that would not easily retain dust were it not for the presence of sebum, which is the sticking point. Secreted by the sebaceous appendage and flowing into the hair follicle, sebum is a natural lubricating oil. It contributes to luster but has one major drawback: it entraps and glues all that comes near it-environmental dust, pollutants, smoke, grease, keratinous debris off the scalp, organic or inorganic compounds carried by sweat, or cosmetics, such as hair sprays, styling aids, and tonics. What is more, the sebum's chemical composition evolves over time as a result of incubation and microbial enzymatic activity, leading to partial transformation of entrapped material [2].

2.2.4 Conditioning the hair via rinse-off systems

The functions of a rinse off hair conditioning system is to make hair easier to comb by lubrication of the fiber surface, prevent flyaway and is to make hair shine [10].

Rinse off hair conditioning can occur via either the use of a conditioning shampoo or a separate hair conditioner. In both ways, hair conditioning provides the hair soft and pleasant touch in the end. Hair is anionic and damaged hair is even more anionic due to protein structure of hair. Thus, conditioners are cationic compounds which can attach to the anionic hair. These attached molecules can stay on the hair even after washing. The most popular case of cationic surfactants incorporated in conditioners are the quaternary ammonium compounds which comply to the general formula of: $(R_4N)^+X^-$, where R is fatty chain and X is halide, commonly chloride. The quaternary ammonium salt is normally formulated into a high water content, oil-in-water emulsion, which is stabilized using external thickeners, secondary emulsifiers. pH of conditioning shampoos are slightly below 6 and those of conditioners is around 3.0-5.0 [11]. Figure 2.6 is a schema of the virgin or damaged hair versus the conditioner treated hair and the attaching mechanism of the cationic conditioner molecules on them.

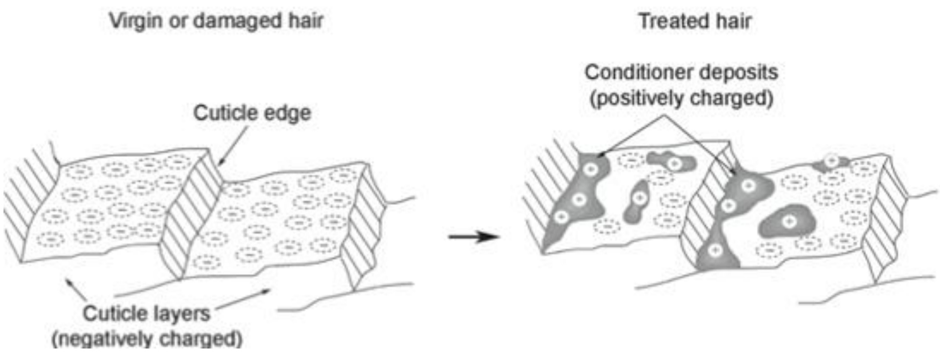

Figure 2.6 : Structure of virgin hair vs. conditioner-treated hair.

2.3 Silicones

Silicones are organic-inorganic polymers consisting of silicon, carbon, oxygen and hydrogen and they are derived from silica. The unique fluid properties of silicone give it a great deal of slip, and in its various forms it can feel like silk on the skin, impart emolliency and be a water-binding agent that holds up well, even when skin becomes wet. In other forms, it is also used extensively for wound healing and for improving the appearance of scars [13].

Silicone is the pure element Si, which makes up of 28% of earth's crust. Silica is the sand which is naturally occurring SiO2. Silicate is the chemically bonded Si, O and other metals. Silicone is also the general name which is given to silicone polymers.

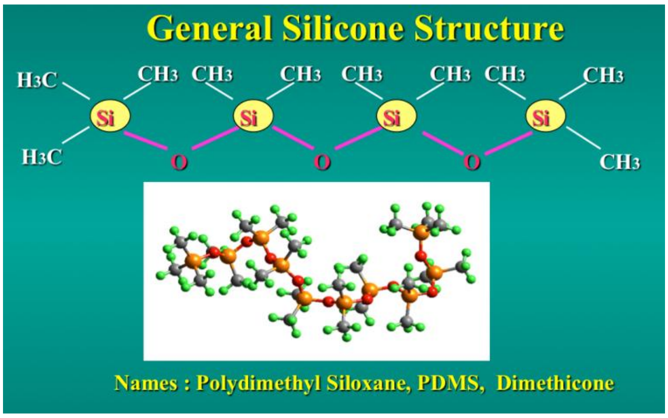

Figure 2.7 : Silicone polymer structure.

2.3.1 Silicone polymers

Silicone polymers exist as: linear or branched fluids, cyclics, gums, resins, elastomers. Main silicone molecule can be derivatized by adding functional groups to the main chain, where each group creates a different polymer with unique properties. Figure 2.7 shows the molecular structure of the basic silicone polymer – polydimethylsiloxane.

2.3.1.1 Polydimethylsiloxane (Dimethicone)

PDMS consists of fully methylated linear siloxane polymers containing repeating units of the formula (CH3)2SiO, with trimethylsiloxy end-blocking units of the formula (CH3)3SiO. It has inorganic backbone and has pendant organic (methyl) groups. Inorganic backbone has higher surface energies whereas the methyl groups provide low surface energies [14]. Figure 2.8 is the basic structure of the simplest silicone polymer.

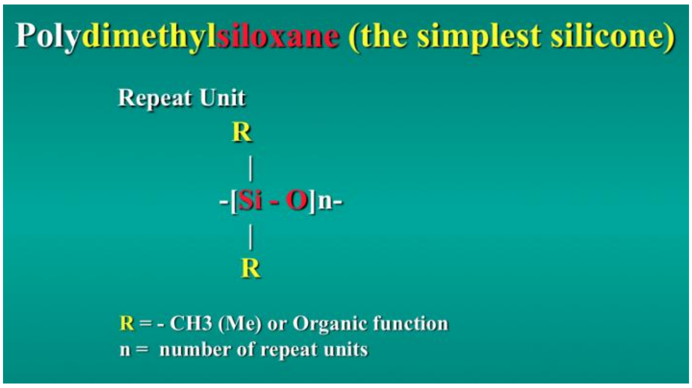

Figure 2.8 : The simplest silicone polymer.

The backbone presents the organic groups at the interface and organic groups provide the surface active properties. Figure 2.9 is a demonstration of the properties of the polydimethylsiloxane.

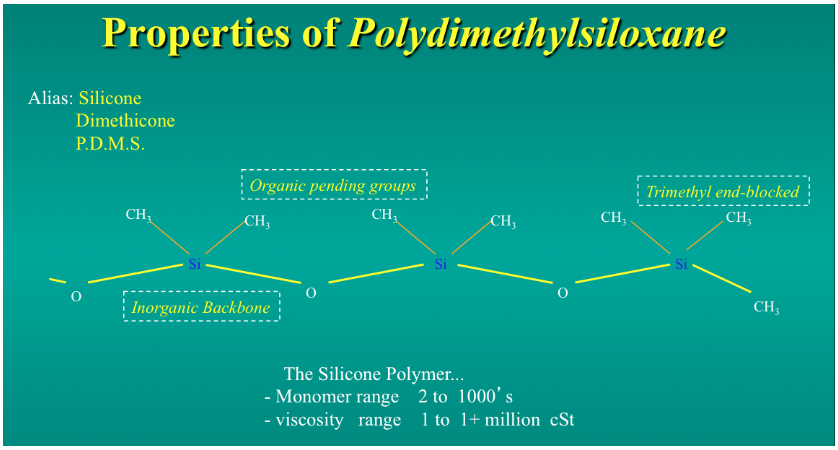

Figure 2.9 : Properties of PDMS.

Figure 2.10 is showing the properties of the flexible backbone of a silicone polymer.

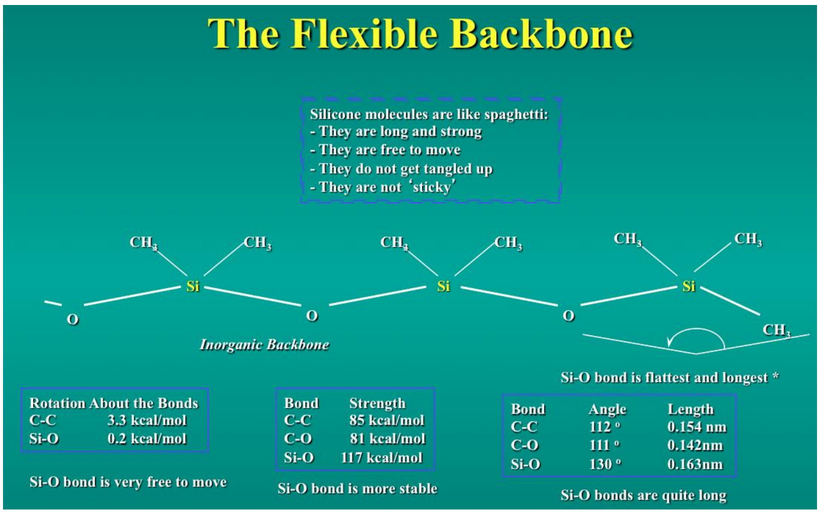

Figure 2.10 : The flexible backbone of silicone polymer.

As the molecular weight of the silicone increases, the end material stars to become gummy. It is possible to add various functionalities to the silicone backbone. The polymer can be cyclic or linear. In addition to that, it is possible to have resinous or cross-linked silicones.

PDMS is insoluble in water and in ethanol; soluble in carbon tetrachloride, benzene, chloroform, diethyl ether, toluene and other organic solvents. The average value for n is 90 to 410. PDMS is viscoelastic, meaning that at long flow times (or high temperatures), it acts like a viscous liquid, similar to honey. However, at short flow times (or low temperatures), it acts like an elastic solid, similar to rubber.

PDMS is used variously in the cosmetic and consumer product industry as well. For example, PDMS can be used in the treatment of head lice on the scalp and dimethicone is used widely in skin-moisturizing lotions where it is listed as an active ingredient whose purpose is "skin protection." Some cosmetic formulations use dimethicone and related siloxane polymers in concentrations of use up to 15%. The Cosmetic Ingredient Review's (CIR) Expert Panel, has concluded that dimethicone and related polymers are "safe as used in cosmetic formulations [14].

PDMS compounds such as amodimethicone, are effective conditioners when formulated to consist of small particles and be soluble in water or alcohol/act as surfactants (especially for damaged hair), and are even more conditioning to the hair than common Dimethicone and/or Dimethicone copolyols [16].

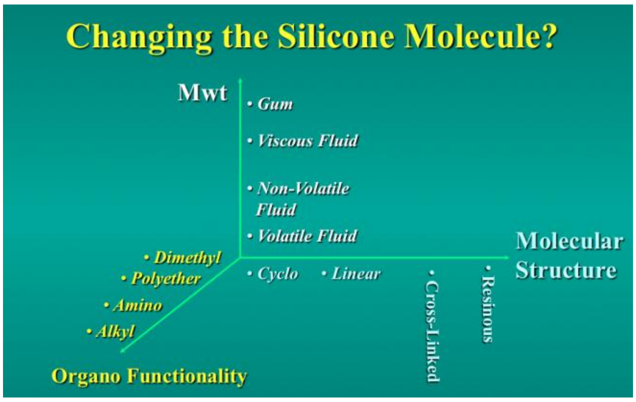

Figure 2.11 : Changing the silicone molecule.

Silicone polymer can vary from a very gummy gel to a fluid as seen in Figure 2.12.

Figure 2.12 : Gummy silicone gel vs. viscous silicone fluid.

If the silicone polymer is linearly structured, then the end product is likely to have less viscosity compared to a cross-linked polymer which behaves more like gel and rubber. Figure 2.13 is the structure of linear silicone polymer and Figure 2.14 is the structure of a crosslinked silicone polymer.

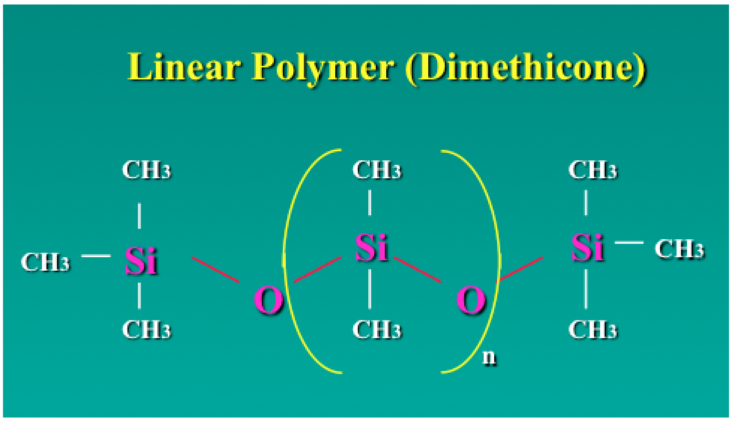

Figure 2.13 : Linear PDMS structure.

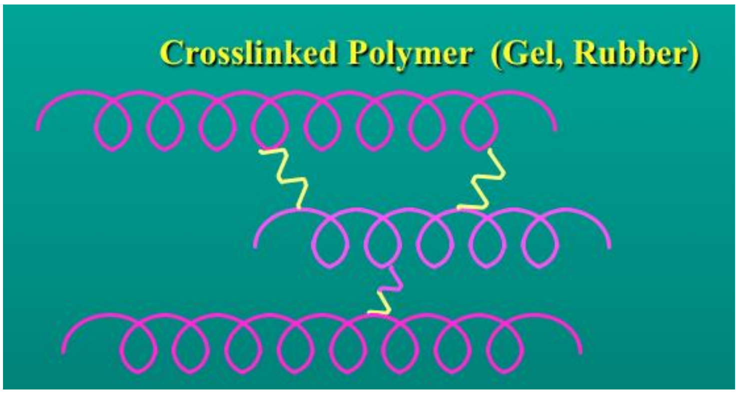

Figure 2.14 : Cross-linked silicone polymer structure.

2.3.1.2 Dimethiconol

The main feature of dimethicone copolyols is that they are soluble in water and ethanol. In hair care products they improve wetting and reduce the stickiness of fixative resins. In skin care, they provide soft and subtle feel on skin.

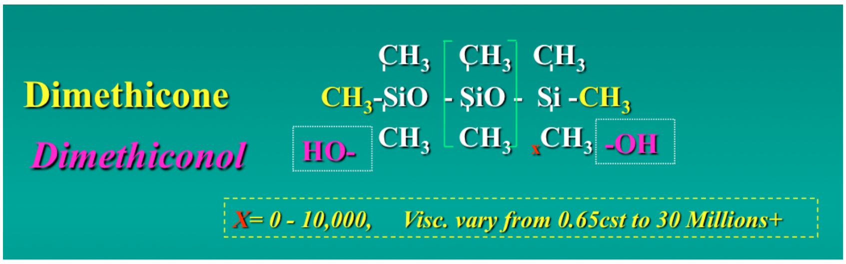

Figure 2.15 : Dimethicone and dimethiconol.

It is possible to add functional groups to a linear PDMS polymer. Figure 2.16 is summarizing the possible additions to the linear PDMS polymer chain.

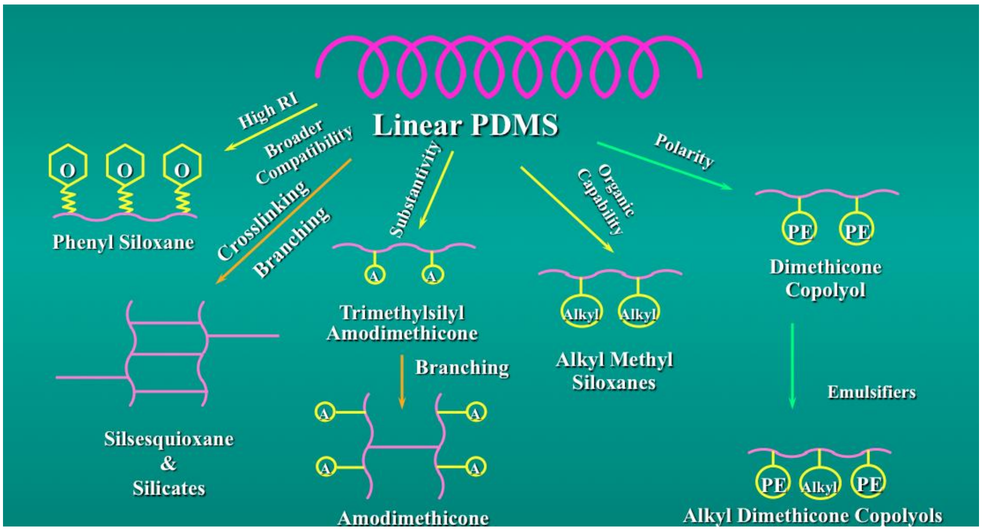

Figure 2.16 : Adding organo-functionality to linear PDMS.

High viscosity fluids can perform a protective film, while low viscosity fluids are able to be emulsified and have better solubility with other ingredients.

2.3.1.3 Cyclomethicone / Cyclopentasiloxane

Among all cyclomethciones, cyclopentasiloxane is the most commonly used silicone in cosmetics. Cyclopentasiloxane is especially a critical ingredient in skin lotions and makeup products. Cyclomethicones are very good solvents. They are non-stinging, non-staining, colorless, odorless, with high volatility. Cyclomethicones improve manageability of wet hair in hair care products, suppress the stickiness of organic materials in skin care products and act as delivery vehicle for active ingredients. Due to their low heat of vaporization, they do not feel cold on skin. Figure 2.17 is the chemical structure of cyclic silicone polymer.

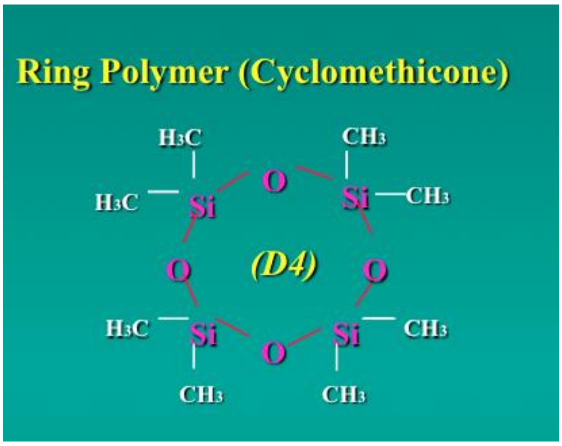

Figure 2.17 : Cyclopentasiloxane structure.

2.3.1.4 Phenyl Trimethicone

Phenyl trimethicones bring the different properties of a phenolic substituent to the PDMS chain. Phenyltrimethicones are easy to emulsify. Their main property in hair care is that they provide shine on hair and water repellent properties. They also have solvent properties. They can be used as plasticizier of polymer films, in aerosol sprays. Phenyl trimethicone chemical structure is given in Figure 2.18.

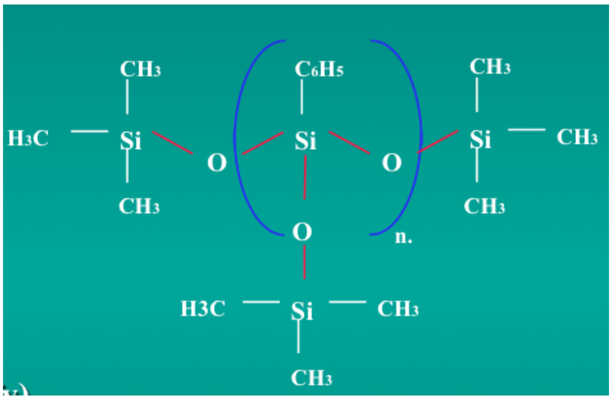

Figure 2.18 : Phenyltrimethicone structure.

2.3.1.5 Amodimethicone

Amodimethicone is typically an emulsion-polymerized polymer. Amodimethicone polymers undergo a condensation cure reaction during drying to form a a durable elastomeric film on hair, providing wet and dry combing benefits, lowering triboelectric charging effects, increasing softness of the dry hair. They are excellent conditioners for all types of hair care products [17].

A reactive polymer with –OH functionality forms a high molecular weight polymer through crosslinking which results in silicone gum like silky soft, non-oily feel, after blow drying. The chemical structure of the amodimethicone polymer is given in Figure 2.19.

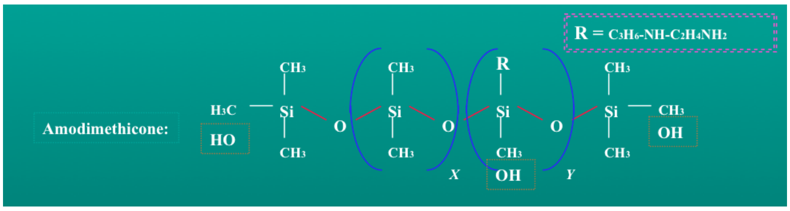

Figure 2.19 : Amodimethicone.

2.3.1.6 Amodimethicone blends

Most amodimethicone blends are emulsions of amodimethicone with Tridecyl Alcohols (Trideceths) and a conditioner and emulsifier molecule such as cetrimonium chloride. These blends are easier to dissolve in water and brings the conditioning effect of both amodimethicones and cetrimonium chloride. They vary from almost clear solutions to white mixtures depending on the type of the ingredients [19].

2.3.2 Volatility of silicones

Silicone Fluids can be distinguished as volatile and non-volatile silicones fluids. Most consumers prefer non-greasy, oil-free personal care products over heavy and greasy, old fashioned ones. Mineral oil is usually replaced by silicone fluids. Oil-free claims are wide-spread in the product categories: foundations, makeups, blushers, face cleansers, sun care products, body lotions, moisturizing creams and shampoo/conditioners.

The reasons that consumers like the light silicone feel compared to other greasy products are that they penetrate rapidly into the skin, there remains no greasy, sticky film on the skin, they do not leave glossy shine on the skin, they are perceived to be light, they do not clog pores and they allow the instant application of makeup [14].

2.3.2.1 Volatility of cyclic silicone fluids

The cyclic silicone fluids known under the CTFA/INCI designation cyclomethicones are totally volatile but their speed of evaporation is lower than that of water or ethanol. Because of their low heat of vaporization, they do not produce a cooling sensation on skin, as do water or alcohol. For a comparison, the respectives heats of vaporization are: 540 cal/g for water, 210 cal/g for ethanol and 32 cal/g for cyclomethicones tetramer and 28 cal/g for cyclomethicones pentamer. Due to their very low surface tension, they spread easily on skin (good for antiperspirants). Water in silicone emulsions can easily be prepared with the silicone emulsifier: Cyclomethicone (and) Dimethicone Copolyol. in the form of two commercial specialties with superior spreading characteristics, they become miscible in all proportions with polar oils such as Isopropyl myristate or non-polar oils such as mineral oil. (PPG-15 Stearyl Ether and Cyclomethicone [14].

2.3.2.2 Volatility of linear polysiloxanes

This group comprises a volatile and a series of non-volatile silicones. These are linear polymers with a silicone-oxygen backbone, as explained earlier. Volatile linear silicone is the low viscosity PDMS and the remaining linear silicones are known to be non-volatile [14]. One typical linear and volatile silicone is disiloxane, which is used in some hair care serums where a light effect is needed. Such volatile linear silicones are usually combined with heavy feeling silicones because they form a stable film on hair.

3. EXPERIMENTAL

Six experiments were made to evaluate the solubility and behaviour of selected silicone polymers in shampoos. Shampoos were evaluated for their clarity, viscosity, conditioning effect and combing forces on hair. These formulations are all pre-studies of possible commercial products and main aim has been to investigate silicone properties while formulating an optimized shampoo system.

3.1 Experiment 1

Experiment 1 investigates and evaluates selected silicones in shampoo base.

3.1.1 Materials

Sodium Laureth Sulfate which is of 70% active material is the main anionic surfactant used in all experiments, from 1 to 6. SLES is supplied by BASF under trade name of Texapon. Cocamidopropyl Betaine which is of 35% active material is the non-ionic surfactant used in all experiments. It is supplied by Zimmer&Schwarz under trade name of Amphotensid. Trelin B30 is a preservative with the INCI name of Methylisothiazolinone, Chloromethyisothiazolinone and Formaldehyde. The silicones used in experiment 1 are listed below table. These silicones are obtained from Denge Kimya except BYK. Table 3.1 is the list of all silicones used in this experiment.

Table 3.1 : Chemical properties of the silicones used in experiment 1.

Ingredient	Structure	Property
SC-SA 10032	Trisiloxane Polieter	60EO/40 Silicone
SC-SA D33	Graft EO Silicon copolymer	EO/PO
SC-SA D40	Graft EO Silicon copolymer	EO/PO
SC-SA D 60	Graft EO Silicon copolymer	EO/PO
SC 81000-37	Cyclic dimethicone	0 EO/ 30 silicone
SC 81000-39	Poliether terminated disiloxane	80 EO/ 20 silicone
SC-SA L 7602	Poliether graft silicone	60 EO / 40 Silicone
SC-SA L 7001	Poliether graft silicone	20 EO/60 PO/40 silicon
BYK 037	Silicone blend with mineral oil	

Figures from 3.1 to Figure 3.6 are showing the chemical structures of silicones used in Experiment 1.

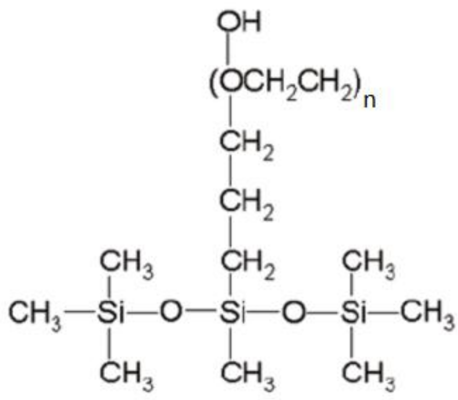

Figure 3.1 : Chemical structure of SC-SA 10032.

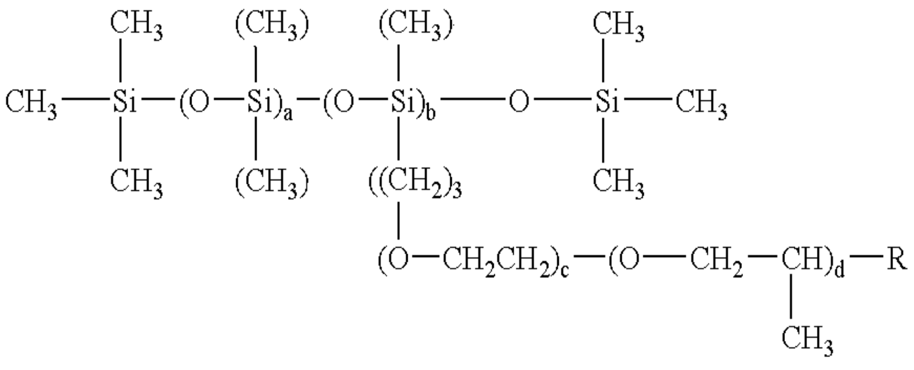

Figure 3.2 : Structure of graft silicone copolymers (SD-SA D33, 40 and 60).

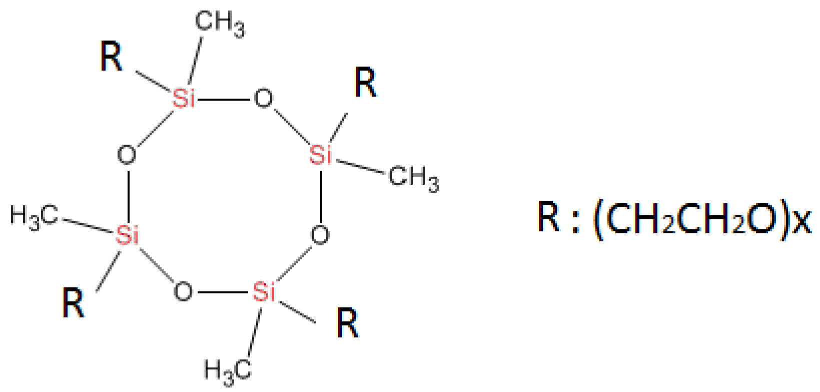

Figure 3.3 : Structure of cyclic dimethicone – SC8100037.

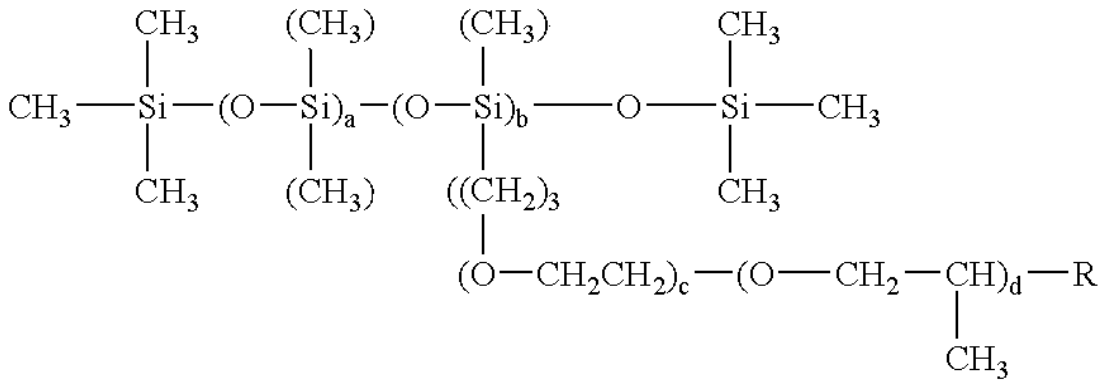

Figure 3.4 : Structure of SC 81000-39.

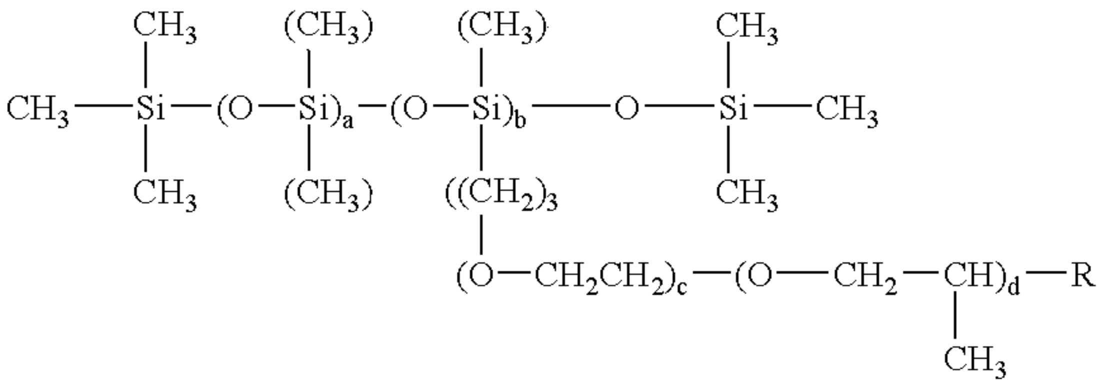

Figure 3.5 : Structure of SC SA L-7602.

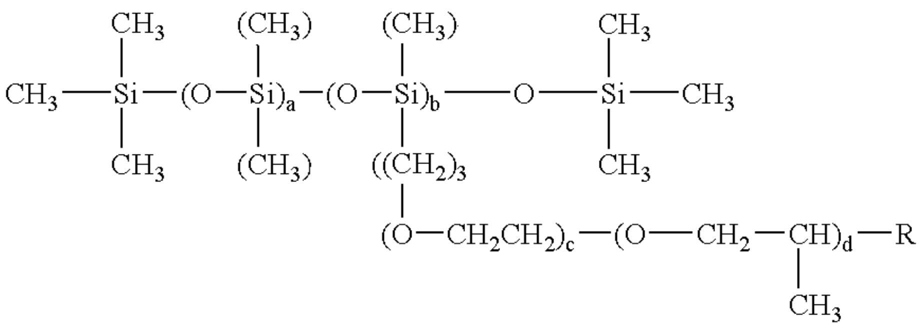

Figure 3.6 : Structure of SC SA L 7001.

3.1.2 Formulations and process

Shampoo formulations of experiment 1 are given in Table 3.2.

Table 3.2 : Shampoo formulations of experiment 1.

Formula no:	1	2	3	4	5	6	7	8	9
<u>Ingredient</u>									
Deionized water	77	77	77	77	77	77	77	77	77
SLES 70%	12	12	12	12	12	12	12	12	12
CAPB 34.5%	6	6	6	6	6	6	6	6	6
Trelin P30	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
SCSA 10032	2	-	-	-	-	-	-	-	-
SC-SA D33	-	2	-	-	-	-	-	-	-
SC-SA D40	-	-	2	-	-	-	-	-	-
SC SA D63	-	-	-	2	-	-	-	-	-
SC 8100037	-	-	-	-	2	-	-	-	-
SC 8100039	-	-	-	-	-	2	-	-	-
SC-SAL 7602	-	-	-	-	-	-	2	-	-
SC-SA L 7001	-	-	-	-	-	-	-	2	-
BYK 037	-	-	-	-	-	-	-	-	2

All formulations are prepared in 100 gr batches. SLES is added on water, mixed with magnetic mixer with slight heating to around 60°C. When the SLES is completely dissolved, CAPB is added and mixed. Silicone is added and its behavior is evaluated while dissolving. Trelin B30 is added and mixed. Finally salt is added and it is evaluated whether it is increasing the viscosity and effecting the clarity.

3.2 Experiment 2

This study consists of the evaluation of selected cationic silicones in shampoo base. The silicones used in experiment 2 are listed in Table 3.3. These silicones are from Denge Kimya.

Table 3.3 : Silicones used in experiment 2.

Ingredient	silicone %
ARGE ST Microemulsion	30
ARGE EC Microemulsion	30
ARGE MR Macroemulsion	50

The chemical structure of the silicones used in Experiment 2 are given in Figure 3.7.

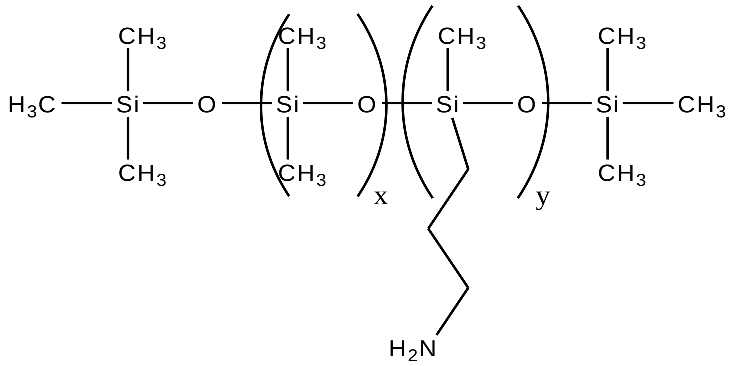

Figure 3.7 Structure of silicones used in Experiment 2.

ST type silicone contains twice as many amine groups as EC product. Since these are commercial products, more information could not be disclosed at this stage.

3.2.1 Formulations and process

Shampoo formulations of experiment 2 are given in Table 3.4.

Table 3.4 : Shampoo formulations of experiment 2.

Formula no	1	2	3
Deionized Water	77	77	77
SLES 70%	12	12	12
CAPB 34.5%	6	6	6
Trelin P30	0.1	0.1	0.1
ARGE ST Microemulsion	2	-	-
ARGE EC Microemulsion	-	2	-
ARGE MR Macroemulsion	-	-	2

All formulations are prepared in 100 gr batches. SLES is added on water, mixed with magnetic mixer with slight heating to around 60 C. When the SLES is completely dissolved, CAPB is added and mixed. Silicone is added and its behavior is evaluated while dissolving. Trelin B30 is added and mixed. Finally salt is added and it is evaluated whether it is increasing the viscosity and effecting the clarity.

3.3 Experiment 3

This study consists of the addition of a non-ionic thickener to the shampoo formulations of Experiment 1. The aim is to see whether the addition of non-ionic thickener can help the viscosity of the system. PEG-120 Methyl Glucose Dioleate is the non-ionic thickener which is under the trade name of MGDOE120 KC, supplied by KCI company. Salt level is kept constant at 1.5%

Chemical structure of PEG-120 Methyl Glucose Dioleate is given in Figure 3.8.

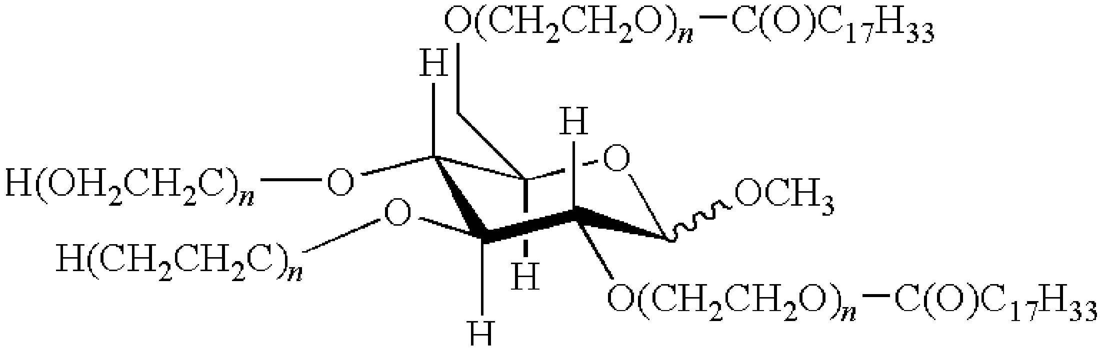

Figure 3.8 Chemical structure of PEG-120 Methyl Glucose Dioleate.

3.3.1 Formulations and process

Shampoo formulations of experiment 3 are given in table 3.5. Formulation process is kept same as Experiment 1 except that PEG-120 Methyl Glucose Dioleate is added after silicone is dissolved. Shampoo is heated mildly to dissolve PEG-120 Methyl Glucose Dioleate.

Table 3.5 : Shampoo formulations of experiment 3.

Formula no:	1	2	3	4	5	6	7	8	9
Ingredient	use level as %								
Deionized Water	77	77	77	77	77	77	77	77	77
SLES 70%	12	12	12	12	12	12	12	12	12
CAPB 34.5%	6	6	6	6	6	6	6	6	6
Trelin P30	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
SCSA 10032	2	-	-	-	-	-	-	-	-
SC-SA D33	-	2	-	-	-	-	-	-	-
SC-SA D40	-	-	2	-	-	-	-	-	-
SC SA D63	-	-	-	2	-	-	-	-	-
SC 8100037	-	-	-	-	2	-	-	-	-
SC 8100039	-	-	-	-	-	2	-	-	-
SC-SAL 7602	-	-	-	-	-	-	2	-	-
SC-SA L 7001	-	-	-	-	-	-	-	2	-
BYK 037	-	-	-	-	-	-	-	-	2
MGDOE 120KC	1	1	1	1	1	1	1	1	1
NaCl amount is 1.5% for all formulations.									

3.4 Experiment 4

This study consists of the addition of a non-ionic thickener to the shampoo formulations of Experiment 2. The aim is to see whether the addition of non-ionic thickener can help the viscosity of the system. PEG-120 Methyl Glucose Dioleate is the non-ionic thickener which is under the trade name of MGDOE120 KC, supplied by KCI company. Salt level is kept constant at 1%.

3.4.1 Formulations and process

Shampoo formulations of Experiment 4 are given in table below. Formulation process is kept same as Experiment 2 except that PEG-120 Methyl Glucose Dioleate is added after silicone is dissolved. Shampoo is heated mildly to dissolve PEG-120 Methyl Glucose Dioleate.

Table 3.6 : Formulations of experiment 4.

Formula no:	1	2	3
Ingredient	Use level as %		
Deionized Water	77	77	77
SLES 70%	12	12	12
CAPB 35%	6	6	6
Trelin P30	0.1	0.1	0.1
ARGE ST Microemulsion	2	-	-
ARGE EC Microemulsion	-	2	-
ARGE MR Macroemulsion	-	-	-
MGDOE 120KC	1	1	1

3.5 Experiment 5

3.5.1 Materials

Six types of silicones are tested within the shampoo formulations. The properties of these silicones are given in table 3.7. Solids level of all silicones is 78-82%. Viscosity of silicones oils vary from 2000 to 10000 cPs. These silicones are obtained from Denge Kimya. Figure 3.5 is the general structure of the silicones used in Experiment 5. Figure 3.9 is the appearance of the silicones oils used in Experiment 5.

Table 3.7 : Properties of silicone oils used in experiment 5.

Product	Polyether (%)	Quat (%)
Denge 1	10	0
Denge 2	10	50
Denge 3	10	100
Denge 4	20	0
Denge 5	20	50
Denge 6	20	10

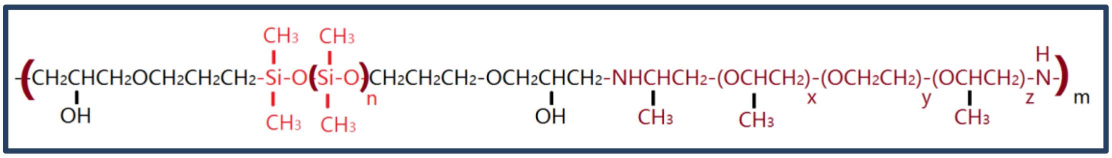

Figure 3.9 : General chemical structure of silicones used in experiment 5.

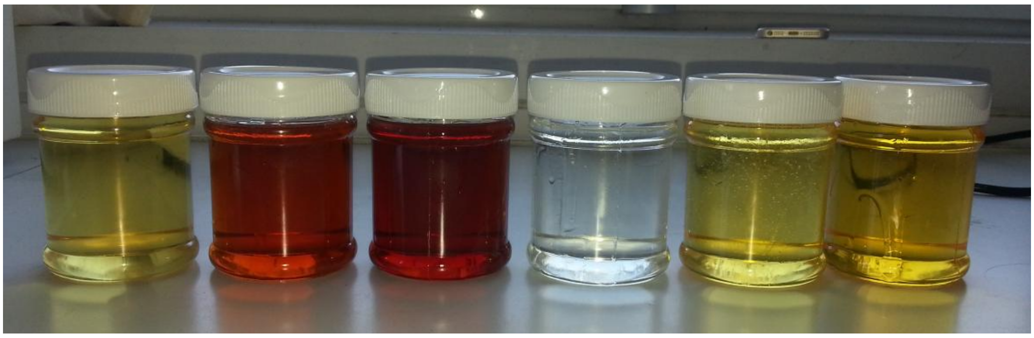

Figure 3.10 : Appearance of the silicones used in experiment 6, from 1 to 6, from left to right.

Advance II is used as the preservative, which is a mixture of Chloromethylisothiazolinone and Methylisothiazolinone. Advance II is supplied by Eigenman & Veronelli. Ceraphyl 41 is the liquid emollient which has shampoo thickening properties. INCI name of Ceraphyl 41 is C12-15 Alkyl Lactate and is supplied by Ashland Specialty Ingredients. Ceraphyl 41 is chosen because of ease of use as it is a liquid material and does not require heating while processing. Silicones oils number 2 and 3 are more reddish than the others due to the slightly longer time which passed during their synthesis at Denge Kimya.

The aim of this experiment is to see how the silicones effect the shampoo formulation, to see whether formulation can be thickened properly by sodium chloride, to see their conditioning effect on hair by sensory analysis, to see their solubility behaviours and effect on clarity of shampoo base, to compare shampoo properties with Silsoft A+. INCI of Silsoft A+ is PEG-40/PPG-8 Methylaminopropyl/Hydroxypropyl Dimethicone Copolymer. Figure 3.10 shows the silicones which are used in Experiment 5.

3.5.2 Formulations and process

Shampoo formulations of Experiment 5 is given in Table 3.8.

Table 3.8 : Shampoo formulations of experiment 5.

Formula no	1	2	3	4	5	6	7
Surfactant mixture **	94	94	94	94	94	94	94
Silsoft A+	2	-	-	-	-	-	-
Denge 1	-	2	-	-	-	-	-
Denge 2	-	-	2	-	-	-	-
Denge 3	-	-	-	2	-	-	-
Denge 4	-	-	-	-	2	-	-
Denge 5	-	-	-	-	-	2	-
Denge 6	-	-	-	-	-	-	2
Advance II	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Ceraphyl 41	0.6	0.6	0.6	0.6	0.6	0.6	0.6

NaCl percentages that is used in each formulation is given as below, from formulation 1 to 7, respectively.

Sodium chloride percentages: 1,32; 5,15; 4,12; 7,93; 4,09; 4,17; 4,02

Contents of surfactant mixture** is given below:

Deionized water 75%

Sodium Laureth Sulfate (70% - Texapon N70) 13%

Cocamidopropyl Betaine (35% - Amphotensid) 6%

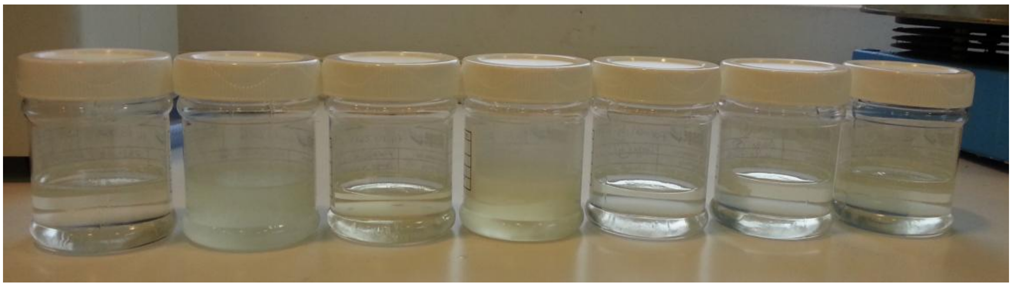

Figure 3.11 : Finished formulations – Shampoos from left to right as 1, 2, 3, 4, 5, 6,7.

The shampoos are prepared by following the steps: Surfactant mixture is prepared by heating the water mildly, adding SLES and mixing slowly. CAPB is added after

SLES is completely dissolved. A uniform and slightly yellowish solution is obtained. All shampoos are 100 gr trial batches. 94 gr of surfactant solution is weighed, silicone is added on top. Figure 3.11 is the finished formulations of Experiment 5.

Formula no 1: Silsoft A+ makes the solution hazy. Dissolved well, then Ceraphyl 41 is added. No change in color is observed. Sodium chloride could increase the viscosity gradually and properly.

Formula no 2: Silicone is added in half portions in surfactant solution and dissolved with heat. Heat is preferred for the solution of this silicone. Ceraphyl 41 gets the solution hazy, the solution becomes clear upon mild heating and good mixing. Sodium chloride is added gradually to improve viscosity.

Formula no 3: Similar process and results to formula 2 were obtained. The formula gains back its clarity much easier than Formula 2 when Ceraphyl 41 is added. The final pH is found to be around 9. Citric acid is added to adjust pH to around 6. Similar process and results to formula 3 were obtained.

Formula no 5: Similar process and results to formula 3 were obtained.

Formula no 6: Similar process and results to formula 3 were obtained.

Formula no 7: Similar process and results to formula 3 were obtained.

Shampoos are then applied on hair tresses and evaluated for various aspects.

3.6 Experiment 6

6 types of silicone emulsions are tested within the shampoo formulations.

These products are the emulsion grade of the silicones which are used in experiment 5. Figure 3.12 is showing the appearance of the silicone emulsions used in Experiment 6.

Figure 3.12 : Silicone emulsions used in experiment 6.

The aim of this experiment is to see how the silicones effect the shampoo formulation, whether formulation can be thickened properly by sodium chloride, their conditioning effect on hair by sensory analysis, their solubility behaviours and effect on clarity of shampoo base. The emulsion silicones used in experiment 6 are obtained from Denge Kimya.

The properties of these silicones are given in table 3.9.

Table 3.9 : Shampoo formulations of experiment 6.

Formula no	1	2	3	4	5	6
Surfactant mixture **	94	94	94	94	94	94
Denge emulsion 1	2	-	-	-	-	-
Denge emulsion 2	-	2	-	-	-	-
Denge emulsion 3	-	-	2	-	-	-
Denge emulsion 4	-	-	-	2	-	-
Denge emulsion 5	-	-	-	-	2	-
Denge emulsion 6	-	-	-	-	-	2
Advance II	0.1	0.1	0.1	0.1	0.1	0.1
Ceraphyl 41	0.6	0.6	0.6	0.6	0.6	0.6

Emulsion properties of silicones which are used in Experiment 6 are given in Table 3.10.

Table 3.10 : Properties of silicone emulsions used in experiment 6.

	Silicone oil (%)	Hexylene Glycol (%)
Denge emulsion 1	30	5
Denge emulsion 2	30	5
Denge emulsion 3	30	5
Denge emulsion 4	30	5
Denge emulsion 5	30	5
Denge emulsion 6	30	5

4. RESULTS AND DISCUSSIONS

4.1 Experiment 1

Silicone addition is investigated in experiment 1. Addition of silicone resulted in the following changes in the SLES/CAPB mixture:

Formula 1, 2, 5, 6 and 8: Silicone is dissolved easily and clear solution is obtained. For formula 3 and 4, silicone is dissolved easily, got hazy first, then clear solution is obtained finally.

For formula 7, silicone is dissolved upon mixing for 30 minutes, then dissolved and clear solution is obtained.

Salt (NaCl) is the viscosity builder in surfactant systems. Most silicone polymers and derivatives tend to break viscosity of surfactant systems which require much salt addition. This is an unwanted issue because too much salt dries the skin and hair. Here, it is investigated whether these systems can be thickened by salt and if yes, the amount of salt is evaluated. As a result, it is evaluated what type of silicone is appropriate for surfactant system.

The results of each formulation in terms of salt content is summarized in the table 4.1. Salt is added in 4 or 5 parts so that the salt curve is not passed. Salt curve is the maximum amount of salt that the surfactant system can stand, because after that level, the viscosity is suddenly lost. pH of all viscous shampoos are 6.

Table 4.1 : Effect of salt addition in shampoos of experiment 1.

Formula	Salt %	Observation
Formula 1	3,6	gains viscosity
Formula 2	8	stays liquid
Formula 3	8	stays liquid
Formula 4	8	stays liquid
Formula 5	8	stays liquid
Formula 6	4	gains viscosity
Formula 7	5,2	gains viscosity
Formula 8	8	stays liquid
Formula 9	8	stays liquid

Formulas 1, 6 and 7 are successfully thickened by salt and sensory tests are done with these formulations.

4.1.1 Sensory analysis results

The analysis was done on real human-beings. Each person gives points to the shampoo to evaluate the foam during washing, wet combability, dry combability, anti-frizz and dry hair conditioning; 5 points being the best, 1 point being the worst. All test objects are female and with non-dyed hair. Each test object tries the shampoo twice during washing and follows their own rinsing off regime.

Test object 1

Shampoo 1: Foam 4, wet combability 3, dry combability 3, hair conditioning 3, anti-frizz 2.

Shampoo 6: Foam 4, wet combability 4, dry combability 4, hair conditioning 3, anti-frizz 3.

Shampoo 7: Foam 4, wet combability 4, dry combability 4, hair conditioning 4, anti-frizz 4

Test object 2

Shampoo 1: Foam 5, wet combability 3, dry combability 3, hair conditioning 3, anti-frizz 2.

Shampoo 6: Foam 5, wet combability 3, dry combability 4, hair conditioning 3, anti-frizz 3.

Shampoo 7: Foam 4, wet combability 4, dry combability 5, hair conditioning 4, anti-frizz 4

Test object 3

Shampoo 1: Foam 4, wet combability 3, dry combability 3, hair conditioning 2, anti-frizz 3.

Shampoo 6: Foam 4, wet combability 4, dry combability 3, hair conditioning 3, anti-frizz 4.

Shampoo 7: Foam 4, wet combability 4, dry combability 5, hair conditioning 5, anti-frizz 4

4.1.2 Sensory analysis comments

According to the results of the sensory analysis done by 3 test objects, the foam of each shampoo is found the same. Silicones do not differ much in terms of foam stability and structure. Shampoo 7 was found to have better wet combability of all. Polyether terminated polidisiloxane could enhance the wet combability. Shampoos 6 and 7 showed better performance than shampoo 1, so there is no major difference among all silicones. Shampoo 7 showed better hair conditioning performance which corresponded to the better deposition property of SC-SA L7602 (graft silicone of 60 EO/40 silicone). The same silicone performed the best in terms of anti-frizz effect.

4.2 Experiment 2

The results of salt addition is shown in Table 4.2 for experiment 2.

Table 4.2 : Effect of salt addition in experiment 2.

Formula no	Salt %	Observation	pH
1	2,4	good viscosity	6
2	8	viscous but less than formula 1	6
3	7	viscous but less than formula 1	6

4.2.1 Sensory analysis results

The analysis was done on real human-beings. Each person gives points to the shampoo to evaluate the foam during washing, wet combability, dry combability, anti-frizz and dry hair conditioning, 5 points being the best, 1 point being the worst. All test objects are female and with non-dyed hair.

Test object 1

Shampoo 1: Foam 5, wet combability 4, dry combability 3, hair conditioning 4, anti-frizz 4.

Shampoo 2: Foam 5, wet combability 4, dry combability 3, hair conditioning 4, anti-frizz 4

Shampoo 3: Foam 5, wet combability 2, dry combability 3, hair conditioning 4, anti-frizz 4

Test object 2

Shampoo 1: Foam 5, wet combability 3, dry combability 3, hair conditioning 4, anti-frizz 4

Shampoo 2: Foam 5, wet combability 4, dry combability 4, hair conditioning 4, anti-frizz 4

Shampoo 3: Foam 5, wet combability 2, dry combability 3, hair conditioning 4, anti-frizz 4

Test object 3

Shampoo 1: Foam 5, wet combability 4, dry combability 4, hair conditioning 4, anti-frizz 4

Shampoo 2: Foam 5, wet combability 4, dry combability 4, hair conditioning 4, anti-frizz 4

Shampoo 1: Foam 5, wet combability 3, dry combability 3, hair conditioning 3, anti-frizz 4

4.2.2 Sensory analysis comments

The silicones used in Experiment 2 have major influence on the foam of shampoos compared to the shampoos of Experiment 1.

Comparing the formulations of experiment 2, formula no 2 and 3 are ideally not to be commercialized because of high salt content which would have drying effect both for skin and hair in long term use. Formula no 2 showed the best wet combability which corresponds to the ST EC Microemulsion (with higher amount of amine groups).

4.3 Experiment 3

The results of salt addition is shown in Table 4.3 for experiment 3.

Table 4.3 : Effect of salt addition in experiment 2.

Formula no	Salt %	Observation	pH
1	0,4	good viscosity	6
6	1,6	viscous but less than formula 1	6

Addition of PEG-120 DOE resulted in much less salt addition as expected.

Two stable shampoos were obtained and sensory test was done on each.

The analysis was done on real humanbeings. Each person gives points to the shampoo to evaluate the foam during washing, wet combability, dry combability, anti-frizz and dry hair conditioning, 5 points being the best, 1 point being the worst. All test objects are female and with non-dyed hair.

4.3.1 Sensory analysis results

The analysis was done on real human-beings. Each person gives points to the shampoo to evaluate the foam during washing, wet combability, dry combability, anti-frizz and dry hair conditioning, 5 points being the best, 1 point being the worst. All test objects are female and with non-dyed hair.

Test object 1

Shampoo 1: Foam 5, wet combability 3, dry combability 4, hair conditioning 4, anti-frizz 5

Shampoo 6: Foam 4, wet combability 3, dry combability 4, hair conditioning 5, anti-frizz 4

Test object 2

Shampoo 1: Foam 5, wet combability 4, dry combability 4, hair conditioning 4, anti-frizz 4

Shampoo 6: Foam 5, wet combability 3, dry combability 5, hair conditioning 4, anti-frizz 5

Test object 3

Shampoo 1: Foam 5, wet combability 3, dry combability 5, hair conditioning 4, anti-frizz 4

Shampoo 6: Foam 5, wet combability 3, dry combability 3, hair conditioning 4, anti-frizz 4.

4.3.2 Sensory analysis comments

Two shampoos were evaluated. Two formulations did not show major difference in wet combing, dry combability and hair conditioning, as well as anti-frizz properties. This could suggest that when salt level is at optimum, difference that the silicones make in final formulations become less.

4.4 Experiment 4

Table 4.4 shows the results of shampoos which are prepared for Experiment 4.

Table 4.4 : Effect of salt addition in experiment 4.

Formula no	Salt %	observation	pH
1	1,2	good viscosity, semi-transparent	6
2	1,1	good viscosity, clear	6
3	0,8	good viscosity, clear1	6

4.4.1 Sensory analysis results

The analysis was done on real human-beings. Each person gives points to the shampoo to evaluate the foam during washing, wet combability, dry combability, anti-frizz and dry hair conditioning, 5 points being the best, 1 point being the worst. All test objects are female and with non-dyed hair.

Test object 1

Shampoo 1: Foam; 5, wet combability 4, dry combability 3, hair conditioning 4, anti-frizz 4.

Shampoo 2: Foam 5, wet combability 4, dry combability 4, hair conditioning 4, anti-frizz 4

Shampoo 3: Foam 5, wet combability 2, dry combability 3, hair conditioning 4, anti-frizz 4

Test object 2

Shampoo 1: Foam 5, wet combability 3, dry combability 3, hair conditioning 4, anti-frizz 4

Shampoo 2: Foam 5, wet combability 3, dry combability 4, hair conditioning 4, anti-frizz 4

Shampoo 3: Foam 5, wet combability 2, dry combability 3, hair conditioning 4, anti-frizz 4

Test object 3

Shampoo 1: Foam 5, wet combability 3, dry combability 4, hair conditioning 4, anti-frizz 4

Shampoo 2: Foam 5, wet combability 4, dry combability 4, hair conditioning 4, anti-frizz 4

Shampoo 1: Foam 5, wet combability 3, dry combability 3, hair conditioning 3, anti-frizz 4

4.4.2 Sensory analysis comments

The results of Experiment 4 are in line with the results of Experiment 2 which show that addition of thickener agent does not effect the impact of silicone in these formulations. Usage of less salt is possible in these formulations as expected.

4.5. Experiment 5

Silsoft A+ shampoo can thicken more easily with sodium chloride compared to other silicone oils. That means, less amount of salt is needed to thicken Silsoft A+ shampoo compared to other silicones. Formula 3 and 4 provide very good skin conditioning effect during rinse-off. 2 weeks after making the shampoos, their condition at room temperature has been evaluated and their conditions are summarized in Table 4.5.

Table 4.5 : Conditions of shampoos 2 weeks after production.

Formula no	Condition
1	Clear and uniform
2	Hazy and there is white phase on top
3	Clear, uniform and good rheology
4	Hazy and there is white phase on top
5	Clear and good rheology
6	Clear, uniform and good rheology
7	Clear, uniform and good rheology

4.5.1 Sensory analysis results on hair tresses

Since the formula no 2 and 4 are not stable, sensory analysis was done on the remaining formulations.

Shampoos are evaluated on hair tresses with the following method: Hair tresses are washed with plain water, at room temperature. Excess water is removed with towel, then 1 gr of shampoo is added and hair is foamed for 30 seconds. Foam quality and structure is evaluated, then hair is rinsed-off. During rinse off, hair is combed first by the large tooth of comb, then by the fine tooth part. After hair tress is completely rinsed off, excess water is removed and it is left for 5 minutes, then hair is combed first by the large tooth of comb, then by the fine tooth part. This is the wet combing evaluation. Hair is dried naturally, then combed the same way. This is the dry combing evaluation. The hair is evaluated by hands for its softness and conditioning and also shine.

Formula 1

Foam 5, wet combability 3, dry combability 4, hair conditioning 4, anti-frizz 4

Formula 3

Foam 5, wet combability 4, dry combability 4, hair conditioning 4, anti-frizz 4

Formula 4

Foam 5, wet combability 3, dry combability 4, hair conditioning 4, anti-frizz 4

Formula 5

Foam 5, wet combability 5, dry combability 4, hair conditioning 5, anti-frizz 4

Formula 6

Foam 5, wet combability 3, dry combability 5, hair conditioning 5, anti-frizz 5

Formula 7

Foam 5, wet combability 3, dry combability 4, hair conditioning 4, anti-frizz 4

All silicones help enhance the foam of the shampoo. Among all trials, formula 6 which corresponds to Denge silicone 5 (20% Polyether, 50% quat level) is found to provide best effects on hair.

4.6 Experiment 6 Results

4.6.1 Sensory analysis on hair tresses

Shampoos are evaluated on hair tresses with the following method: Hair tresses are washed with plain water, at room temperature. Excess water is removed with towel, then 1 gr of shampoo is added and hair is foamed for 30 seconds. Foam quality and structure is evaluated, then hair is rinsed-off. During rinse off, hair is combed first by the large tooth of comb, then by the fine tooth part. After hair tress is completely rinsed off, excess water is removed and it is left for 5 minutes, then hair is combed first by the large tooth of comb, then by the fine tooth part. This is the wet combing evaluation. Hair is dried naturally, then combed the same way. This is the dry combing evaluation. The hair is evaluated by hands for its softness and conditioning and also shine.

Formula 1

Foam: 4, creamy and rich foam is obtained

Wet combing: 3

Dry combing: 4

Conditioning: 4

Formula 2

Foam: 5, better than 1, less bubbles and richer foam. Feels more conditioned during rinse-off.

Wet combing: 4; obviously better than 1.

Dry combing: 4

Conditioning: 4

Formula 3

Foam:4, similar to formula 2, but with less texture

Wet combing: 4; same as formula 2

Dry combing: 4

Conditioning: 4

Formula 4

Foam: 5; rich and dense foam

Wet combing: 3; similar to 1

Dry combing: 4

Conditioning: 4

Formula 5

Foam: not as rich as the other formulations

Wet combing: 5; very good combing

Dry combing: 4

Conditioning: 4

Formula 6

Foam: 4 rich and dense foam

Wet combing: 5; formula 5 is still better than 6

Dry combing: 4

Conditioning: 4

The shampoos of experiment 6 had differences only in wet combing, on the other hand, they did not have major differences in dry combing. Shine effect of all shampoos are the same, no visible differences are assessed.

Figure 4.1 : Hair tresses after they are shampooed and dried.

Since almost all formulations had shown ease of combing during and after washing, all formulations can further be developed for commercial purposes. Figure 4.1 is showing the dried condition of the hair tresses at the end of Experiment 6.

5. CONCLUSION

This study is a wide look at the basic properties of shampoos which contain different types of silicones. The silicones used in first trials were basically graft polymers. Experiment 1 showed that graft silicone of 60 EO/40 silicone and polyether terminated polydiloxane provided the best effects on hair. This experiment also shows that most of the remaining graft silicones have negative effect on the thickening of the shampoo system.

Experiment 2 clearly shows that increasing the amine groups of the cationic silicones resulted in better conditioning properties.

Experiment 3 and 4 are done by addition of a thickening agent to the formulations used in experiment 1 and 2. It was proved that much less salt is used when a compatible thickener is used in the formulations. Effect of silicones in these formulations did not change significantly which is in line with expectation.

Experiment 5 is done by silicones oils directly, in order to see their behavior in shampoo system. Denge silicone 1 and Denge silicone 3 showed instability in shampoo formulations. Silsoft A+ shampoo is found to behave similar to Denge silicone 5.

Finally, looking at the 5 sets of experiments, emulsions of the same silicones in Experiment 5 were prepared and tried in the same formulation base which corresponds to experiment 6. Formula no 5 which corresponds to Denge emulsion 5 is found to have the best effects on hair via this final experiment. This silicone emulsion can be improved or used as is for commercial purposes in various types of hair care products. It is also approved that too much quaternization of a silicone leads to a polymer which has too heavy effect on hair which is also known as weighing-down. So it is best to use a half-quaternized silicone polymer for optimum results.

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Dimethicone, C24-28 Alkyl Methicone, C30-45 Alkyl Methicone, C30-45 Alkyl Dimethicone, Cetearyl Methicone, Cetyl Dimethicone, Dimethoxysilyl Ethylenediaminopropyl Dimethicone, Hexyl Methicone, Hydroxypropyldimethicone, Stearamidopropyl Dimethicone, Stearyl Dimethicone, Stearyl Methicone, and Vinyldimethicone. International Journal of Toxicology.

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CURRICULUM VITAE

Name and Surname : Pınar Taşkın
Place and Date of Birth : İstanbul / 1982
E-mail : pinartaskin25@gmail.com

WORK EXPERIENCE

Business Development Assistant Manager, Sojitz Europe plc Istanbul Branch

02.2016 – Present

Chemicals Division of Europe, Russia & NIS; Specialty Chemicals Section

Responsible for maintaining and developing the contract-based sales and establishing new business/sales within and across Turkey, surrounding countries and Far East.

Visiting current and potential customers in Turkey, following up with their requirements and conducting sales activities, following commercial steps and taking part in post-sales services, in line with the annual sales targets.

Establishing stock operation of selected chemicals.

Assessing JV opportunities in current/new businesses and developing initial business cases.

Collaborating mainly with major accounts while also focusing on medium size companies to develop business in line with market requirements.

Main ingredients and areas of focus are coating chemicals, soda ash, aluminium, paint, alkyd and unsaturated polyester resins, plasticizers, rubber.

EDUCATION

- B. Sc. 2005, Istanbul Technical University, Faculty of Science & Letters, Chemistry