ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

INVESTIGATION ON OIL REMOVAL PERFORMANCES OF ALTERNATIVE SURFACTANT STRUCTURES

M.Sc. THESIS

Fulya FURAT

Department of Textile Engineering

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

FARKLI YAPILARDAKİ YÜZEY AKTİF MADDELERİN YAĞ SÖKME PERFORMANSLARININ İNCELENMESİ

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Fulya FURAT, a M.Sc. student of İTU Graduate School student ID 503191807, successfully defended the thesis entitled "INVESTIGATION ON OIL REMOVAL PERFORMANCES OF ALTERNATIVE SURFACTANT STRUCTURES", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my family and friends,

FOREWORD

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TABLE OF CONTENTS

Page

ABBREVIATIONS

EO	: Ethylene oxide
PO	: Propylene oxide
C	: Carbon
HLB	: Hydrophilic-Lipophilic Balance
HLD	: Hydrophilic-Lipophilic Deviation
CMC	: Critical Micelle Concentration
SLES	: Sodium laureth sulfate
SDS	: Sodium dodecyl sulfate
TPH	: Total Petroleum Hydrocarbons
GC-FID	: Gas Chromatography-Flame Ionization Detector

SYMBOLS

P_C	: The molecular packing parameter
v_o	: Volume of surfactant tail
l_o	: Length of surfactant tail
a	: Surface area of hydrophilic head group on the surface of the aggregate
γ_{SB}	: The substrate-cleaning bath interfacial tension
γ_{SO}	: The substrate-oil bath interfacial tension
γ_{OB}	: The oil-cleaning bath interfacial tension
θ	: The contact angle
W_{OS}	: The adhesion of the oil on the solid
Y	: The tristimulus Y value
S_D	: The amount of solvent extractable material
W	: Oven-dried mass of specimen
S	: The salinity in wt% of NaCl
EACN	: Effective Alkane Carbon Number, represents the hydrophobicity of the oil phase.
T	: The temperature
Cc	: A characteristic value for the hydrophobic/philic nature of the surfactant
c_T	: The temperature coefficient

LIST OF TABLES

Page

LIST OF FIGURES

Page

INVESTIGATION ON OIL REMOVAL PERFORMANCES OF ALTERNATIVE SURFACTANT STRUCTURES

SUMMARY

Undesirable stain formation on the textile surface can occur in both daily life and the production processes of the textile materials. In various machines used in textile production, including weaving and sewing machines, the use of machine oil is essential to reduce friction and prevent wear on machine elements. At any stage of production, machine oil can spill or come into contact with the textile material. An oil stain that has been smeared and not noticed during the production phase is fixed with an iron with high heat and it may become more difficult to remove the stain.

Washing is a common method used to remove these stains from textile products. The purpose of the washing process is to remove the stain on the fabric, to prevent it from adhering to the textile again, and to remove dirt and additives from the textile with rinsing processes. There are three important components in the cleaning process: (1) the surface to be cleaned, (2) the characteristic of the soil/stain, (3) the bath containing the cleaning agent. Different surface-soil relationships can complicate the cleaning process, emphasizing the importance of the cleaning agent.

Laundry detergents are commonly used to clean the textile material and create the desired chemical effect. Unlike other detergent ingredients, surfactants act on most types of soil, significantly influencing the performance of laundry detergents. Surfactants are basically divided into four main groups: anionic, cationic, nonionic, and amphoteric. Nonionic surfactants show good cleaning, wetting, and emulsifying properties. The prominent group of nonionic surfactants is ethoxylated surfactants. A number of characteristic features can be mentioned for nonionic surfactants. These properties explain the cleaning mechanism of the surfactant and affect its performance. The oil remover chemicals used in the study are nonionic surfactants, specifically alcohol ethoxylates and alcohol ethoxylate-propoxylates. The chemicals used have hydrophobic chains of different structures, linear or branched. Among the chemicals, there are chemicals that have the same hydrophilic part (ethylene oxide) but a different structure and length of carbon chain. On the contrary, there are chemicals that have the same hydrophobic part but a different hydrophilic part (different ethylene oxide number).

This study focused on cotton fibers, which are widely used in the textile industry. A 100% cotton twill fabric was used and simulated to be stained with oil from a sewing machine. A mineral-based oil from Sosan Industrial Machine Oils was used. Three different drying methods were used to simulate what the fabric may be exposed to in different production steps - steam ironing, hand ironing and hang drying.

The alkali bath was adjusted and the surfactant solution was adjusted to 2 g/l concentration. Each tube contains only one of the surfactants used. Thus, the washing performances of different surfactants were determined. Washing was carried out at

40ºC and 60ºC. It cannot be said clearly that fixation makes the oil removal process difficult in washing at 40ºC. However, as a result of washing at 60ºC, it is easier to remove oil from hanging dried fabrics, followed by normal ironing and steam ironing.

After the oiled fabrics are washed and dried, the oil removal performance is evaluated with the spectrophotometer and soxhlet extraction method. The results of the oil removal rates for the blue fabric, obtained through spectrophotometer and extraction, are compared. However, these results are not consistent with each other. The reason behind this discrepancy is that the blue fabric changes color during the washing process. After the washing, a blue color is detected in the water used for washing. For beige fabric, the oil removal performance results obtained by spectrophotometer and extraction are compatible with each other. No change was observed in the color of the beige fabric itself, which led to the correct result. Finally, a formulation recipe was created, taking into account effective chemicals and different structures, and this recipe has proven to be more successful than individual performances.

FARKLI YAPILARDAKİ YÜZEY AKTİF MADDELERİN YAĞ SÖKME PERFORMANSLARININ İNCELENMESİ

ÖZET

Tekstil yüzeyinde istenmeyen leke oluşumu hem günlük yaşamda hem de tekstil malzemelerinin üretim süreçlerinde meydana gelebilmektedir. Dokuma ve dikiş makineleri de dahil olmak üzere tekstil üretiminde kullanılan çeşitli makinelerde, sürtünmeyi azaltmak ve makine elemanlarındaki aşınmayı önlemek için makine yağının kullanılması şarttır. Üretimin herhangi bir aşamasında makine yağı dökülebilir veya tekstil malzemesiyle temas edebilir. Fark edilmeyen bir yağ lekesi, yüksek sıcaklıktaki ütüyle sabitlenebilir böylece lekenin çıkması daha da zorlaşabilir.

Yıkama, tekstil ürünlerinden bu lekeleri çıkarmak için yaygın olarak kullanılan bir yöntemdir. Yıkama işleminin amacı kumaş üzerindeki lekeyi çıkarmak, tekrar tekstile yapışmasını önlemek, durulama işlemleri ile kir ve katkı maddelerinin tekstilden uzaklaştırılmasıdır. Temizleme işleminde üç önemli bileşen vardır: (1) temizlenecek yüzey, (2) kirin/lekenin özelliği, (3) temizlik maddesini içeren banyo. Farklı yüzey-leke ilişkileri, temizlik maddesinin önemini vurgulayarak temizleme işlemini karmaşıklaştırabilir.

Çamaşır deterjanları, tekstil malzemesini temizlemek ve istenilen kimyasal etkiyi yaratmak amacıyla yaygın olarak kullanılmaktadır. Diğer deterjan bileşenlerinden farklı olarak yüzey aktif maddeler çoğu kir türüne etki ederek çamaşır deterjanlarının performansını önemli ölçüde etkiler. Yüzey aktif maddeler anyonik, katyonik, noniyonik ve amfoterik olmak üzere temel olarak dört ana gruba ayrılır. En yaygın olarak kullanılan sınıf anyonik yüzey aktif maddeler olmasına rağmen dezavantajları bulunmaktadır. Suyun sertliğine karşı toleransları düşüktür, bazı uygulamalarda istenmeyen yüksek köpük üretme kabiliyetleri bulunmaktadır, katyonik yüzey aktif maddeler ile uyumlu değillerdir, yüksek konsantrasyonlarda kullanımı cilt ve göz tahrişine neden olurken belirli tipleri çevre için oldukça zararlıdır. İyonik olmayan yüzey aktif maddeler ikinci en yaygın olarak kullanılan gruptur ve iyi temizleme, ıslatma ve emülsifiye etme özellikleri gösterirler. Diğer tüm yüzey aktif madde grupları ile birlikte kullanıma uygundur, daha düşük köpük üretirler ve suyun sertliğine toleransları yüksektir. İyonik olmayan yüzey aktif maddelerin öne çıkan grubu etoksillenmiş yüzey aktif maddelerdir. İyonik olmayan yüzey aktif maddeler için bir takım karakteristik özelliklerden söz edilebilir. Bu özellikler yüzey aktif maddenin temizleme mekanizmasını açıklamakta ve performansını etkilemektedir. Bulutlanma noktası noniyonik yüzey aktif maddenin yapısına göre değişen, genel olarak %1'lik sulu çözeltisinin bulanık hale geçtiği sıcaklıktır. HLB değeri Griffin tarafından tanımlanmış aynı moleküldeki hidrofilik ve hidrofobik grupların dengesinin sayısal ifadesidir. Daha sonra HLD teorisi sistemdeki diğer etmenleri de katmak üzere geliştirilmiştir. Noniyonik yüzey aktif maddelerin kritik bir konstrasyon değerinin üstünde misel formu oluşturması yağ sökme mekanizması için önemlidir. Misel yağ molükülünü hapsedip kumaştan ayrılmasına ve yeniden yapışmamasına neden

olacaklardır. Çalışmada kullanılan yağ sökücü kimyasallar iyonik olmayan yüzey aktif maddeler olmak üzere, özellikle alkol etoksilatlar ve alkol etoksilat-propoksilatlardır. Kullanılan kimyasallar doğrusal veya dallanmış farklı yapılarda hidrofobik zincirlere sahiptir. Çalışma, aynı hidrofilik kısma (etilen oksit) sahip ancak farklı yapı ve karbon zinciri uzunluğuna sahip kimyasallar, ve aynı hidrofobik kısma sahip fakat farklı bir hidrofilik kısma (farklı etilen oksit numarasına) sahip kimyasalları içermektedir.

Bu çalışmada tekstil endüstrisinde yaygın olarak kullanılan pamuk lifleri üzerinde durulmuştur. %100 pamuklu dimi kumaş kullanıldı ve bir dikiş makinesinden gelen yağla lekelenecek şekilde simüle edildi. Sosan Endüstriyel Makine Yağları'nın mineral bazlı yağı kullanıldı. FTIR ve GC-FID ile yapılan analizler sonucu yağın C10 ve C18 aralığında alkanlardan oluştuğu, parafinik yapıda mineral yağ olduğu tespit edilmiştir. Kumaşın farklı üretim aşamalarında maruz kalabileceği durumları simüle etmek için, yağlanmış kumaş buharlı ütüleme, normal ütüleme ve asarak kurutma olmak üzere üç farklı metoda maruz bırakıldı.

Yüzey aktif madde çözeltisi 2 g/l konsantrasyon ile alkali çözelti hazırlandı. Her tüp, kullanılan yüzey aktif maddelerden yalnızca birini içermektedir. Böylece farklı yüzey aktif maddelerin yıkama performansları belirlendi. Ön çalışma olarak yıkama 40^{o}C'de gerçekleştirildi. 40^{o}C'de yıkamalarda fiksasyonun yağ giderme işlemini zorlaştırdığı net olarak söylenemez. Çalışmaya ve 60^{o}C'de yıkama yapılarak devam edilmiştir ve tüm değerlendirmeler bu yıkamanın sonucunda yapılmıştır. Spektrofotometre ile elde edilen sonuçlara göre buharlı ütüyle ütülenen kumaşta yağın %62,77'si, normal ütüyle ütülenen kumaşta %69,30, asılarak kurutulan kumaşta ise yağın %73,53'si giderildiği tespit edildi. Bu durum fiksasyon seviyesi arttıkça ısı ve basıncın etkisiyle yağın uzaklaştırılmasının zorlaştığını göstermektedir. Bu etki yağ sadece oksitlendiğinde değil, ütüleme yoluyla yağın pamuğun yapısına daha fazla nüfuz etmesi nedeniyle gözlenir. Ekstraksiyon ile belirlenen yağ söküm performanslarına göre iki kumaştaki yağ sökümler arasında belirgin bir farklılık yoktur.

Yağlı kumaşlar yıkanıp kurutulduktan sonra spektrofotometre ve soxhlet ekstraksiyon yöntemi ile yağ sökme performansları arasında bir karşılaştırma yapılmıştır. Mavi kumaş için spektrofotometre ve ekstraksiyon yoluyla elde edilen yağ sökme oranlarının sonuçları karşılaştırılmıştır. Ancak bu sonuçlar birbiriyle tutarlı değildir. Bu farklılığın nedeni mavi kumaşın yıkama işleminde bir kaybının olmasıdır. Yıkama sonrasında yıkamada kullanılan suda mavi bir renk tespit edilir. Bu mavi kumaş için spektrofotometre sonuçlarını geçersiz kılar. Bej kumaş için spektrofotometre ve ekstraksiyon ile elde edilen yağ giderme performansı sonuçları birbiriyle uyumludur. Bej kumaşın renginde herhangi bir değişiklik gözlenmedi ve bu da doğru sonuca yol açmıştır. Bu spektrofotometre yönteminin bej kumaş için uygunluğunu kanıtlamıştır. Son olarak etkili kimyasallar ve farklı yapılar dikkate alınarak bir formülasyon reçetesi oluşturuldu ve bu tarifin bireysel performanslardan daha başarılı olduğu kanıtlandı. Her iki kumaş için de (mavi kumaş için %92.37 ve bej kumaş için %96.15) en başarılı yağ çıkarma performansı edilen formülasyon Lorodac 3/24, Lutensol TO5 ve Marlipal 3190'ın kombinasyonudur. Lorodac 3/24, lineer yapıda 12 ve 14 karbon sayılı 3 etilen oksit içeren alkol etoksilattır. Lutensol TO5, Dallanmış yapıda 13 karbonlu 5 etilen oksit içeren alkol etoksilattır. Marlipal 3190 ise dallanmış ve lineer yapıda 11 karbonlu ve dallanmış yapıda 13 karbonlu 9 etilen oksit içeren alkol etoksilattır. İkincil en iyi performans Marlox 11027, Lutensol TO5 ve Novel 1218-7'ye aittir. Marlox 11027 diğerlerinden farklı olarak Etilen oksit ve propilen oksit gruplarına sahiptir ve tekli performanslarda bulutlanma noktasının üzerindeki yıkama sıcaklığında iyi yağ sökme performansı gösterdiği tespit edilmiştir.

1. INTRODUCTION

When an undesirable substance comes into contact with a fabric, its molecules infiltrate between the fibers and pores of the material, forming a stain. The stain reflects the light and becomes visible to the naked eye. Stains are considered a type of defect in clothing because they leave undesirable marks on the garment.

Stain can occur due to different reasons and sources. They can be observed in the finished products in daily life as well as during the production processes in the industry. In the textile industry, one common source of staining is the presence of machine oils used in various production processes.

For instance, in the production of woven fabric using a weaving machine, machine oil is frequently used to reduce friction and prevent wear. This oil may spill or come into contact with the fabric during production. Similarly, the risk of oil contamination exists during the sewing process on the sewing machine. The product may have already been ironed when any oil smears on the sewing machine or during weaving are unnoticed. Thus, stains can be fixed especially with pressure and heat. Washing is applied to remove these stains on textile products. The washing is a process in which physical and chemical effects work together. In this process, additives are used to remove unwanted substances called soil on the textile material, and these additives create a chemical effect. The washing process involves a series of steps, including removing soil from the fabric, preventing soil from adhering to the textile again, and rinsing to remove the soil and additives from the fabric.

The washing process is based on the composition and properties of the soil, soiling conditions, the fabric's structure and chemical composition, time, temperature, chemical additives, washing conditions, and mechanical action [1].

In this study, we specifically focus on examining the effectiveness of nonionic surfactants, specifically alcohol ethoxylates and alcohol ethoxylate-propoxylates, as additives for chemical action in removing oil stains from cotton woven fabrics contaminated with sewing machine oil.

The purpose of this study is to systematically examine the strength of specific nonionic surfactants with various structures in removing mineral oil from cotton woven fabrics. The selected nonionic surfactants, alcohol ethoxylates, and alcohol ethoxylate-propoxylates, will be applied to fabrics simulating sewing machine oil contamination. The oiled fabrics will undergo three distinct treatment methods: hanging drying, normal ironing, and steam ironing. These methods were chosen to determine how different oil stain fixing methods would affect the oil removal performance. This research is important in terms of determining the oil removal performance with spectrophotometry, which is a more environmentally friendly and easier method, and comparing it with the extraction method. The findings are expected to contribute to the fields of household cleaning and industrial cleaning. The results of the study can provide information about the determination of the oil removal performance of the spectrophotometer from fabrics of different colors and the oil removal performances of different alcohol ethoxylate and alcohol ethoxylate-propoxylates.

2. ELEMENTS OF OIL REMOVAL PROCESS

In each cleaning process, there are three essential elements:

1. The substrate: This refers to the surface that requires cleaning.
2. The soil: This refers to the substance that needs to be eliminated from the substrate during the cleaning process.
3. The cleaning solution: This is the medium in which oil remover chemicals are added.

The diversity of substrate and soil elements and their combinations with each other create difficulties for effective cleaning operations. Considering the substrate and soil, the soil is removed from the substrate with an appropriate cleaning solution with chemical additives. In this study, the oil removal process will be carried out by wet process and the liquid to which the chemicals will be added is water. Nonionic surfactants were employed as oil remover chemicals in the cleaning solution.

2.1 The Substrate–Textile Surface

In general cleaning operations, the surface to be cleaned can range from an impermeable, non-porous, hard surface to a soft, porous, complex surface. This diversity reflects the wide array of substrates encountered in cleaning tasks. Textile surfaces are also frequently encountered and require cleaning. In the scope of this study, the textile surface selected for evaluation is cotton fabric.

2.1.1 Cotton

Cotton fiber is a natural polymer obtained from cotton plants belonging to the Gossypium genus. After maturing, the boll of the cotton plant bursts, revealing soft and fluffy cotton fibers. Cotton fiber is a fiber that is typically white or yellowish-white, and it is known for its distinctive properties.

Cotton fibers are widely used in the textile industry. China and India are the leading cotton-producing countries. Cotton is also produced in the USA and Brazil.

Approximately 80% of the produced cotton is utilized in the textile industry for clothing purposes. Another 15% is allocated for home furnishings, while the remaining 5% finds applications in non-woven products like filters and padding [2].

The chemical and physical attributes of cotton fibers, including features such as fiber length, convolution, moisture regain, spiral angle, linear density, and cross-sectional shape, are determined by the specific species type. Cotton fibers have good tenacity in the range of 26.5–44.1 cN/tex. Cotton fiber exhibits very good tensile strength in the range of 2800–8400 Kg/cm2. The specific gravity of cotton is 1.54% and the moisture regain is 8%. Having a large number of hydroxyl groups makes cotton fiber water absorbent. Cotton fiber is inelastic and rigid. Cotton fibers have higher thermal conductivity than synthetic fibers. Cotton is not resistant to concentrated acids. However, cotton is resistant to alkali and common solvents [3].

The structure of cotton fiber is characterized by distinct layers and components, as depicted in Figure 2.1. Additionally, cotton fiber contains microfibrils, which are bundles of cellulose chains. Cotton fibers consist of 88.0-96.5% α-cellulose. α-cellulose is a polysaccharide consisting of long chains of β(1.4)-linked D-glucose units. The specific chemical composition of cotton fibers can vary depending on the conditions in which they are grown, the different varieties, and whether they are mature or not. Non-cellulosic components are: proteins (1.0–1.9%), waxes (0.4–1.2%), pectins (0.4–1.2%), inorganics (0.7–1.6%) and other substances (0.5–8.0%). The waxes and pectins in the cotton fibers cause the hydrophobicity of the raw cotton fibers and hence the low water wettability [4].

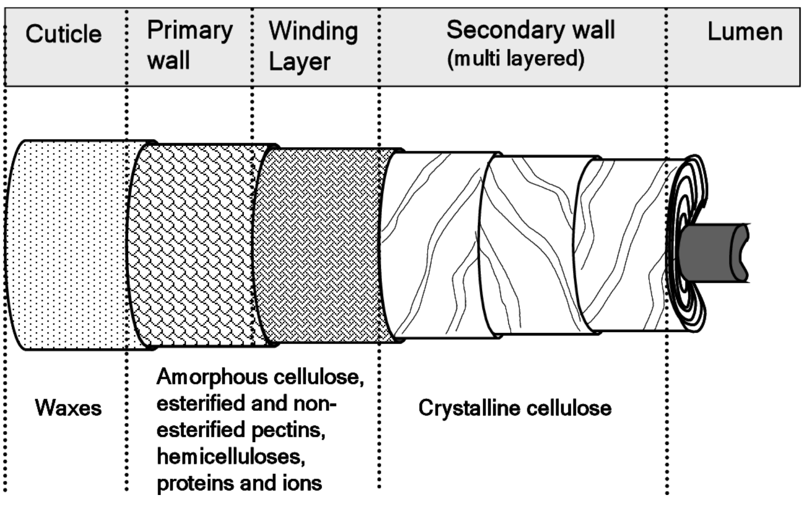


Figure 2.1 : A diagram of a mature cotton fiber showing its different layers [5].

Figure 2.2 shows the structure of cellulose. There are two main regions in cellulose fibers, crystalline and amorphous. The region with a high order of microfibrils is called crystalline, while the order of fewer microfibrils is called amorphous. Cellulose consists of repeat units of anhydroglucose with three hydrophilic -OH groups. In the structure of cellulose, most of the -OH groups form intrachain and interchain hydrogen bonds in a regular manner. This structure results in the insolubility of cellulose in most solvents and moderate affinity with water [6].

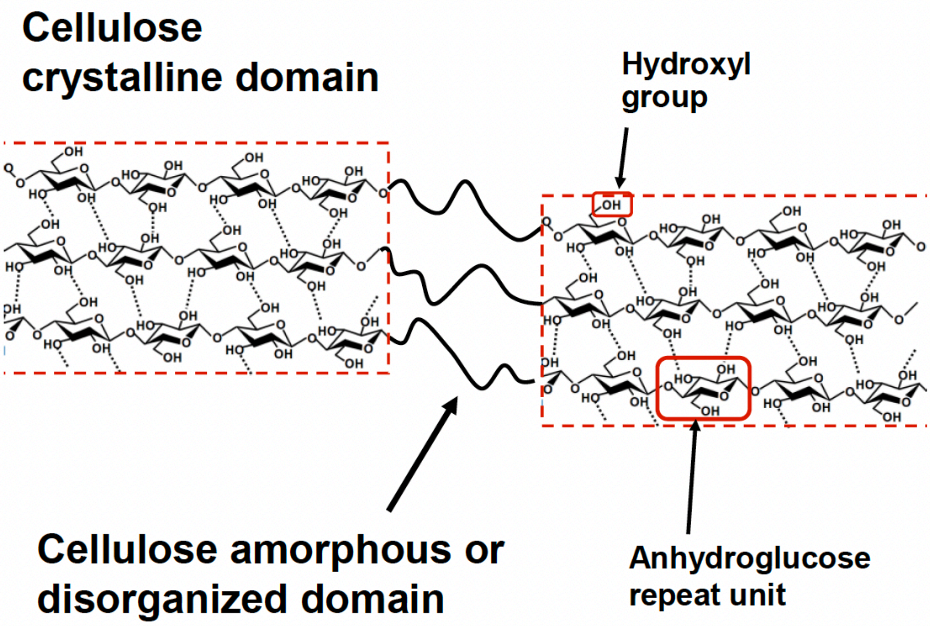


Figure 2.2 : Schematic diagram of the structure of cellulose [6].

Small amounts of wax are usually removed during processing. The wax content in cotton is low, but their presence near the surface of the fibers affects processes such as laundry. If the cotton fabric contains waxy materials, oily dirt adheres to the surface more easily due to its hydrophobic feature [6].

2.1.2 Comparison of cotton fabric with other fabrics in terms of cleaning

The structure of the cotton fiber affects the cleaning process. When cleaning areas where soil has penetrated, cleaning components must reach the interface between the soil and the substrate. Cotton contains different ways with its natural, different structure. There have been numerous studies in the literature about removing oil from fabrics that are made of polyester, polyester/cotton, and cotton, as these fabrics are widely utilized. A common belief is that a fiber with higher hydrophilicity would enhance the average rating for removing oily soils. The percentage of oil removal can vary depending on factors such as the type of surface, the type of oil, and washing conditions. The interactions between the surface and existing soil are crucial.

According to the findings of Morris and Prato, non-polar oily soils such as triolein and tristearin have a tendency to stick to polyester fabric. Following the cleaning process, it was observed that 51.8% of the non-polar fraction still remains on the polyester fabric, whereas only 26.2% remains on cotton fabric and 25.5% on blended fabric [7].

In a study conducted by Chi and Obendorf on the removal of used motor oil from textile materials with detergent, oil concentrations are indicated for the regions of cotton and polyester fibers defined in Figure 2.3.

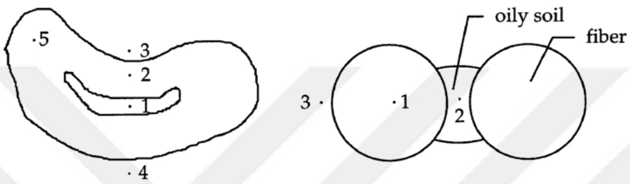


Figure 2.3 : Locations (A) for cotton fiber, these locations are 1. lumen, 2. concave, 3. crevice, 4. exterior, and 5. convex. (B) for polyester fiber, the locations are 1. interior, 2. interfiber space, and 3. exterior [8].

After being soiled, the oil concentration within cotton fibers varies across regions, with the lumen (central cavity) and concave region of the secondary cell wall in 100% cotton having the maximum concentration. Notably, elevated levels of used motor oil are present in the secondary cell walls compared to other human sebum and model oily soils, attributed to dispersant additives in motor oil facilitating penetration into the microfibrillar structure. However, despite the high concentration in the lumen, it represents only a small portion of the cotton fiber volume, approximately 2-4%. The post-wash analysis revealed that the concave preserved the maximum level of oil concentration. On the other hand, the crevice and outer portion of the fiber exhibited the lowest oil concentration. In P/C blend fabric, the cotton crevice retained higher oil concentrations after soiling than in 100% cotton fabric, Because it is in a blend, fewer cotton fibers absorbed the oil than 100% cotton. Since cotton fibers are saturated with oil, oil accumulates in the crevices and on polyester surfaces. Washing the P/C blend fabric led to a notable reduction in oil concentration within the cotton fiber crevices, indicating effective cleaning. However, only a small portion (1.51%) of the oil was removed from the P/C fabric. This suggests that oil from the crevices of the cotton may have transferred to the cotton walls and then spread onto the polyester fibers during the washing process. Polyester is the main cause of inadequate removal of oil from the P/C blend. The presence of an oily layer on the polyester surface causes strong adhesion of particles to the fibers. The difficulty in removing oil is attributed to the affinity between used motor oil and non-polar polyester [8].

2.2 The Soil - Oily Soil

Commonly encountered soils on clothes can be broadly classified into two categories: liquid (oily) soils and solid (particulate and nonparticulate) soils.

Particulate soils, deposited mainly from air suspension, consist of solid particles like carbon black, silica, clay, iron, etc. These particles typically have a substantial specific surface area, facilitating the co-adsorption of oil and greases, resulting in mixed soils. The challenge in removing particulate soils lies in their rigidification and water insolubility [9]. Solid non-particulate soils, or solid fat soils, represent a type of soil with properties between a liquid and a solid, as seen in temperature-dependent substances such as margarine and butter. These soils pose a significant challenge for detergent formulations, where semi-solid or oily soils are challenging to remove from fabrics [10]. Stains caused by oils are prevalent, with examples such as cooking oils, mineral oils, body oils and sebum, industrial oils, and petroleum-based oils.

Both types of soil adhere to surfaces through effective dispersion and van der Waals forces. Additionally, for highly polar soils and substrates, adhesion through acid-base interactions or hydrogen bonds plays a crucial role. Electrostatic interactions have minimal impact on liquid soil systems in general, but they are significant in certain mineral and biological soils. The adhesion of soil to surfaces is facilitated by dispersion and van der Waals interactions. For non-polar oils like carbons and hydrocarbon oils, removing them from hydrophobic surfaces such as polyester may pose greater difficulty. Conversely, hydrophilic soils like clays and fatty acids may present challenges in removal from hydrophilic surfaces like cotton [11].

2.2.1 Textile oils

Textile oils serve two primary purposes: lubricating textile machinery or acting as components of process oils used in various stages of textile production, such as processing natural fibers, manufacturing synthetic fibers, or finishing intermediate and final products [12]. Machine oil is extensively used in the textile industry, particularly in machines such as spinning machines, weaving looms, knitting machines, sewing machines, and textile finishing machines, all of which require the use of oil.

The utilization of oils guarantees the smooth operation of machines and plays a noteworthy role in the textile industry. Without the application of oil during mechanical operation, the heat generated from dry friction and cause damage to the machine. Machine oils produce an oil film or membrane on the surface of parts during operation, which decreases the resistance of the parts. By lubricating the machines, the friction in the machine decreases, contact fatigue decreases by reducing the wear on the interacting surfaces, and thus durability and efficiency increase. Generally, machine oil contains a basic oil and additives. The basic oil determines its basic properties, while additives increase performance and can provide new functions [13].

The majority of machine oils are in liquid form and are divided into two groups: mineral oils obtained from petroleum and synthetic oils. Mineral oils with various physical and chemical properties are frequently used. To obtain oils with the required properties, the selection of the right crude oil source must be combined with the right production processes and the use of the correct additives at ideal rates and dosages [14]. Mineral oils are classified as paraffinic (C_nH_{2n+2}), naphthenic (C_nH_{2n}) and aromatic (C_nH_{2n-6}), depending on their main composition. The Figure 2.4 shows the different hydrocarbon structures that can be found as the main structure in mineral oil.

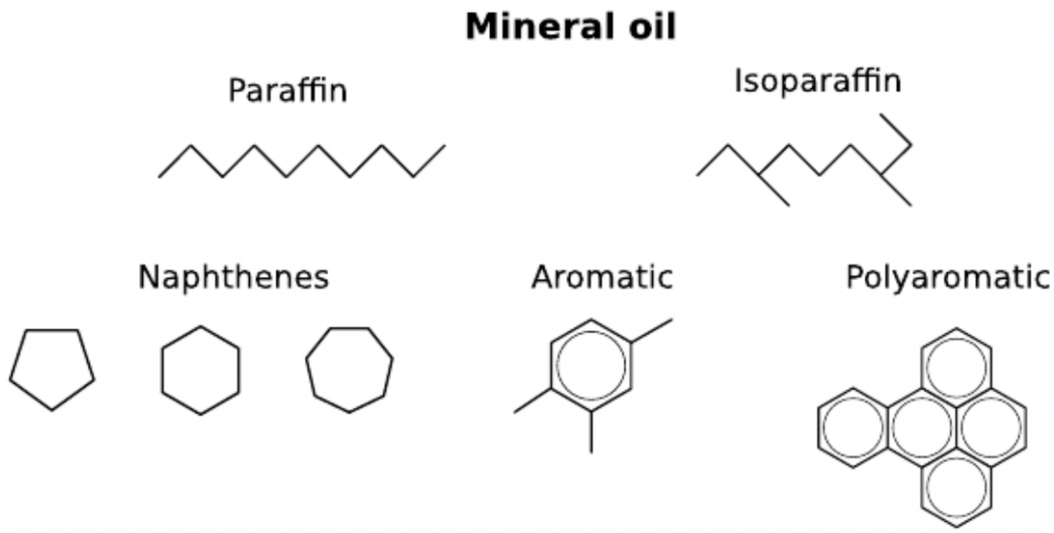


Figure 2.4 : Different hydrocarbon structures in mineral oil content.

A paraffinic structure can be classified as a straight or branched chain of carbon atoms which is referred to as an isoparaffin. Naphthenes have ring structures, with six-membered rings being the most common. Aromatics are six-membered rings with some carbon atoms connected by double bonds. Aromatics are unsaturated and more reactive compared to other hydrocarbons. Aromatics can be categorized as monoaromatic and polyaromatic. Naphthenes and paraffins are used more frequently than aromatic mineral oils. Paraffins and naphthenes are saturated hydrocarbons and are classified as nonpolar and hydrophobic. Additionally, they have relatively low boiling points. The main difference between paraffinic oil and naphthenes is the lower density and the higher viscosity index of the paraffinic structure [15].

2.2.2 Oily soil formation on the fabric

Machine oil used in the textile industry is a source of staining for fabrics. In this study, the oil that contaminated the fabric during the sewing process on the sewing machine was studied. Oil in the sewing machine can pose a risk of contaminating the fabric in certain situations. These situations can be listed as follows: applying too much oil to the machine, using the wrong lubrication technique, and not cleaning or maintaining the sewing machine properly. Additionally, if particles such as lint or debris accumulate in the machine and are not cleaned, they can be transferred to the fabric along with the oil.

When an oily soil occurs, it may not be noticed immediately. Clothes with unnoticeable soil are then ironed normally. This means that the oily soil is exposed to the heat and pressure of the iron. Ironing an oily soiled fabric can accelerate the aging process of oily soiling and cause it to penetrate deeper into the fabric fibers.

Heat can also cause oil to oxidize and undergo chemical reactions. The oxidation behavior of saturated and unsaturated oily soil is different. Oxidation of unsaturated oily soils increases polarity, producing lower molecular weight products, and increases oil removal. On the other hand, saturated oils can be relatively stable against oxidation. Therefore, the aging of saturated oily soils causes the oils to penetrate deeper into fabric and fiber structures and becomes difficult to remove [16].

When the content of the oil is a mixture, it may be difficult to remove oil after aging. Chi and Obendorf investigated how the removal of squalene (non-polar) was affected by the presence of other oils before and after aging. Removing squalene before aging is easier when it is in a mixture (artificial sebum). Because the presence of polar oils increased the removal of non-polar oils. However, after aging, squalene in the mixture was more difficult to remove. This effect is more evident in cotton. When oily soil is in mixture, it undergoes oxidation to different degrees and mechanisms. Since all of radicals formed have a chance to react with each other, a radical larger than squalene can react with an oxidized squalene radical. In this case, it causes the formation of a larger compound. Such reactions can occur not only on the thread surfaces but also in the lumen or secondary walls, making removal by washing more difficult [17].

2.3 The Cleaning Solution - Surfactants

Detergents are the general name given to cleaning products that are in powder or liquid form and have cleaning and purifying properties. Laundry detergent is formulated as a mixture of raw materials. Detergent raw materials are divided into different classes, such as surfactants, builders, bleaching agents, enzymes, chelants, polymers, perfume, and other auxiliary ingredients that increase washing performance. Unlike other detergent ingredients, surfactants affect the performance of laundry detergents by acting on most soil types [18].

The term “Surfactant”, used as an abbreviation for Surface-Active Agent, is a chemical compound that significantly lowers the surface or interfacial tension between two components such as two liquids, a liquid and a gas, or a liquid and a solid. Surfactants are in the content of many products used today. The formulations where surfactants are used, mostly in the textile industry, are detergents, foaming agents, wetting agents, dispersants, and emulsifiers. Surfactants are essential ingredients in detergents used in kitchens and bathrooms, as well as removing soil from clothing, skin, and household items.

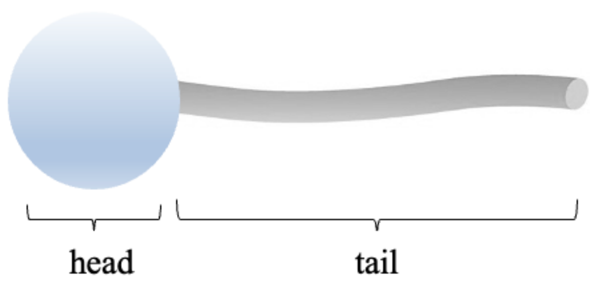


Figure 2.5 : Schematic structure of a surfactant.

Surfactants have an amphiphilic structure containing two different functional groups in the same molecule. One of the functional groups of surfactant molecules is the hydrophilic group with an affinity for water. The other functional group of surfactant molecules is the hydrophobic group, which has no affinity for water. Since surfactants are frequently used in water systems, the names of hydrophilic and hydrophobic groups are widely used. However, in lipid systems, the hydrophobic group is referred to as the lipophilic group. The tail-head model (Figure 2.5) is a commonly used schematic diagram in the graphical representation of simple surfactants. It represents the hydrophobic group as the tail and the hydrophilic group as the head. Surfactants can be divided into four classes based on the charge of the hydrophilic head (Figure 2.6).

a. Anionic surfactants: negatively charged head group,
b. Cationic surfactants: positively charged head group,
c. Zwitterionic surfactants: negatively and positively charged head group,
d. Nonionic surfactants: uncharged head group.

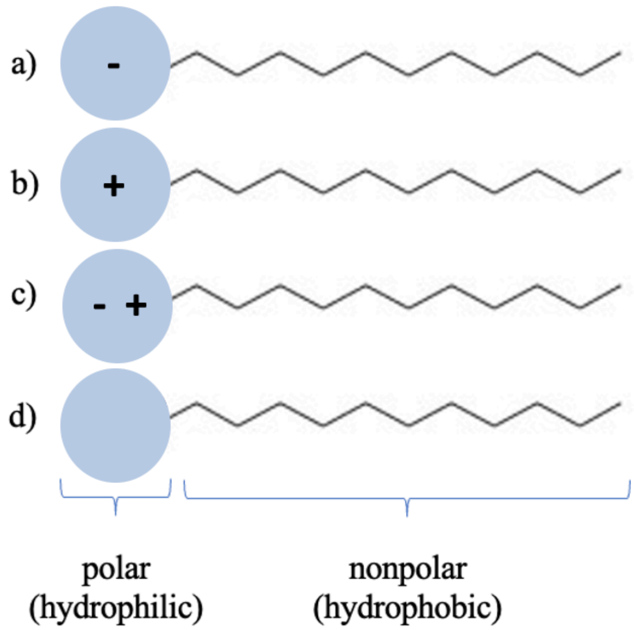


Figure 2.6 : Classes of surfactants.

2.3.1 Anionic surfactants

Anionic surfactants constitute the largest class of surfactants because of their ease of production and low cost, and they are commonly used in detergents. The molecular structure of anionic surfactants commonly used as detergent ingredients is shown in Figure 2.7.

Anionic surfactants include soap and synthetic variants like linear alkyl benzene sulfonate (LAS). LAS replaced soap due to improved performance. Anionic surfactants, like alkyl sulfates (AS), alkyl ethoxy ether sulfate (AES), and LAS, are essential for detergency. To address LAS precipitation in hard water, alternatives like higly soluble alcohol sulfates (HSAS) and modified LAS (MLAS) have been developed. Secondary alkyl sulfates (SAS) can be formulated as high surfactant particles for use in granular detergents and dry-mixed into granular detergent compositions. Environmentally friendly options include alkyl ester sulfonates (MES), which, when combined with certain surfactants, enhance detergency. Additional anionic surfactants include sodium alkyl glyceryl ether sulfonates, di-anionic surfactants, and anionic gemini surfactants [19].

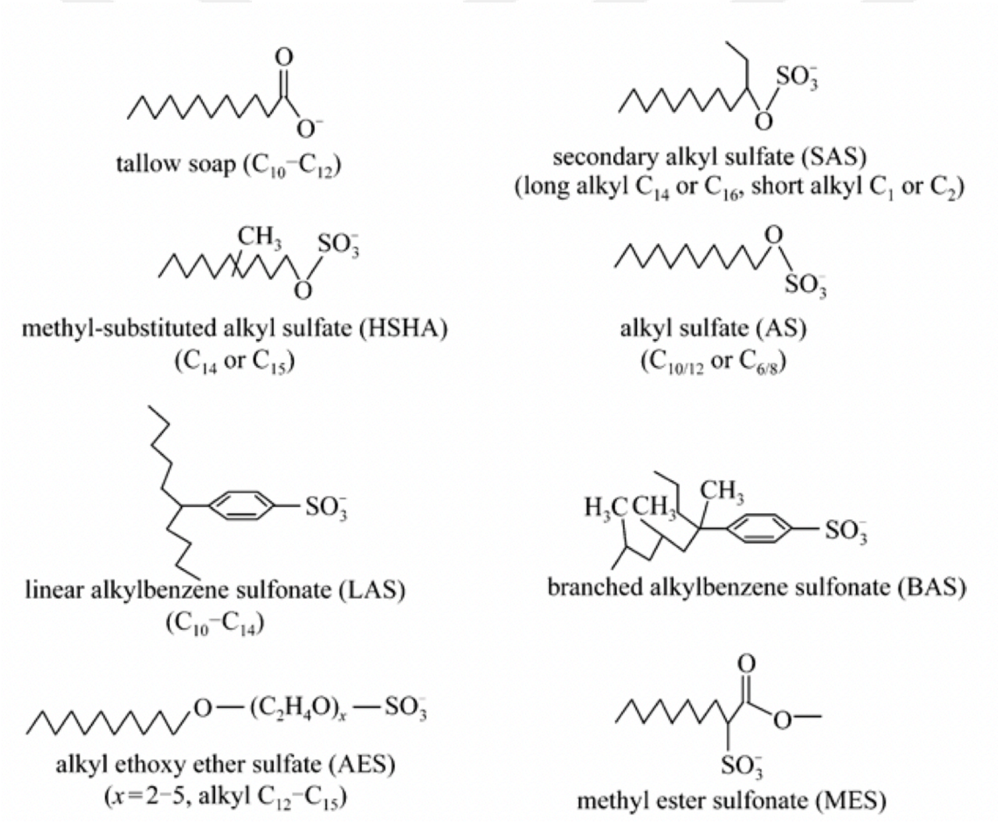


Figure 2.7 : Structures of anionic surfactants used in detergents [19].

There are numerous advantages to incorporating anionic surfactants into detergents. Due to their strong cleaning capabilities, anionic surfactants are able to effectively eliminate dirt, oil, and stains from various surfaces. Moreover, they possess good foaming properties. Anionic surfactants generate a plentiful and stable foam that enhances the perception of cleanliness. Furthermore, anionic surfactants generally interact well with a wide range of detergent ingredients including enzymes, builders, and other surfactants.

There are disadvantages associated with the use of anionic surfactants in detergents. Certain types of anionic surfactants can accumulate in the environment, posing potential harm to aquatic life. Furthermore, some anionic surfactants can cause skin and eye irritation, particularly when present at high concentrations.

According to research conducted by Gotoh et al., the surface tension of anionic surfactant solutions undergoes significant alterations in the presence of hardness salts. The introduction of hardness salts led to a decrease in foamability for each anionic surfactant solution, suggesting the formation of solid particles due to the interaction between anionic surfactants and divalent ions. In washing tests, the efficacy of soil removal decreased, and redeposition increased with rising water hardness. Analysis revealed the presence of a substance called $Ca(LAS)_2$, which adhered to cotton fibers and persisted after washing [20].

Another disadvantage is that they have poor compatibility with cationic surfactants, with shorter length surfactants being more compatible. In general, these surfactants are sensitive to hard water and decrease in the order of carboxylate, phosphate, sulfate, and sulfonate [21].

There are also formulations that specifically combine both anionic and nonionic surfactant components. This approach leverages the strengths of each surfactant type to achieve specific performance characteristics in various applications. For example, compounds containing an EO or PO non-ionic spacer between the hydrophobic tail and the polar head, such as $C_{12}EO_jSO_4Na$ and $C_{12}PO_jSO_4Na$, can be given. These compounds are referred to as "hybrid" because they demonstrate specific characteristics of both ionic surfactants and nonionic surfactants [22].

The advantages of this hybrid structure can be mentioned. Having a short chain of polyoxyethylene between the anionic group and the hydrophobic tail enhances its ability to withstand the effects of hard water. Furthermore, the presence of a short polyoxypropylene chain positioned between the anionic group and the hydrophobic tail enhances its solubility in organic solvents. However, it is worth noting that this modification could potentially reduce its biodegradation rate [21].

Sodium laureth sulfate (SLES) is an example of a hybrid structure. It is an ethoxylated anionic surfactant that is obtained through ethoxylation modification from the more frequently used sodium dodecyl sulfate (SDS), which is a conventional anionic surfactant. In addition, another hybrid surfactant, n-C12P9S (extended surfactant), can be obtained by polypropoxlation and sulfanation of long-chain fatty alcohol. Figure 2.8 gives the molecular representation of these three conventional/ethoxylated/extended n-alkyl sulfate surfactants.

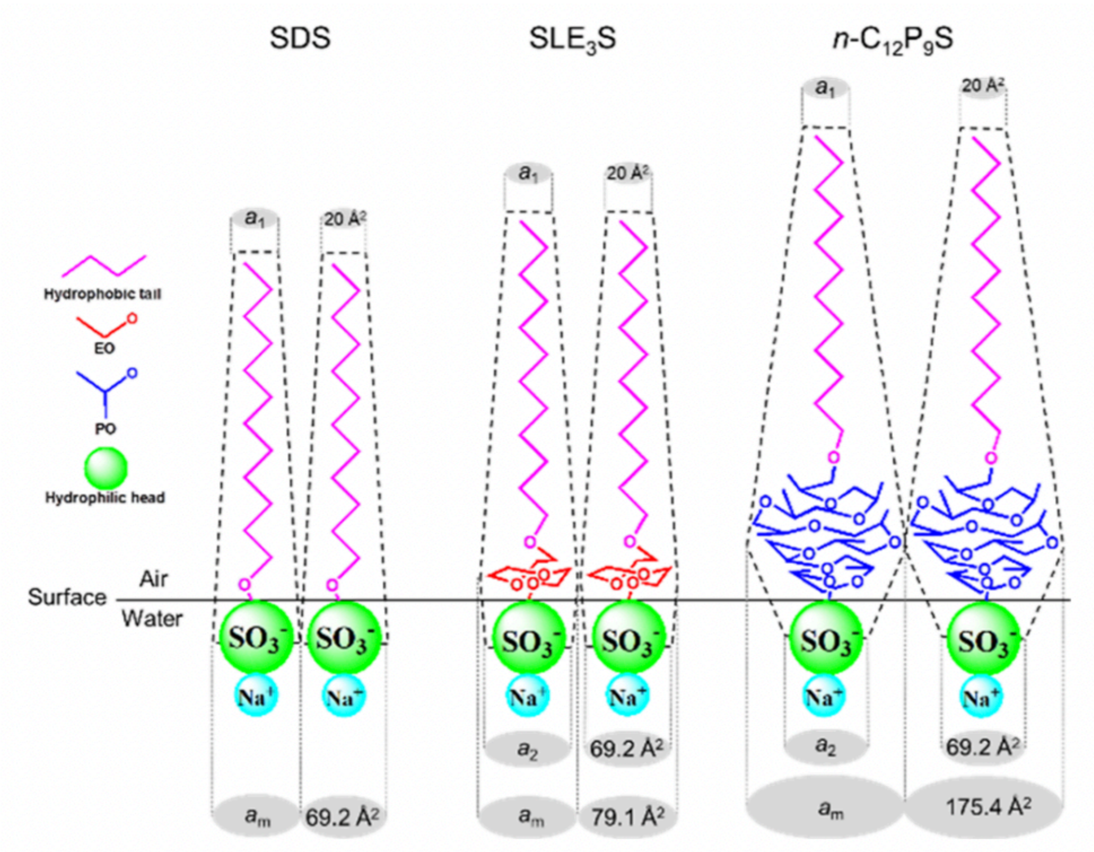


Figure 2.8 : Molecular Geometries of SDS, SLE_3S, and n-$C_{12}P_9S$ [16].

Based on the interfacial characteristics of extended surfactants, it is observed that the PPO (polypropoxlate) spacer contributes both hydrophilic and lipophilic properties to a surfactant molecule. This unique rugby-shaped molecular geometry, resulting from the extensive wrapping of a long PPO spacer, and the dynamic amphipathicity of the PPO spacer, contribute to the superior interfacial and solution properties of extended surfactants in cleaning processes. In comparison to two reference surfactants, the PPO spacer not only enhances lipophilicity but also reduces polarity, leading to a lower critical micelle temperature (CMT) [23].

2.3.2 Cationic surfactants

Although not frequently used in detergent compositions, the majority of cationic surfactants used are based on the positively charged nitrogen atom. Some examples of commonly used quat structures are shown in Figure 2.9. Cationic surfactants may be present in certain formulations for specific purposes, such as antistatic agents and fabric softeners.

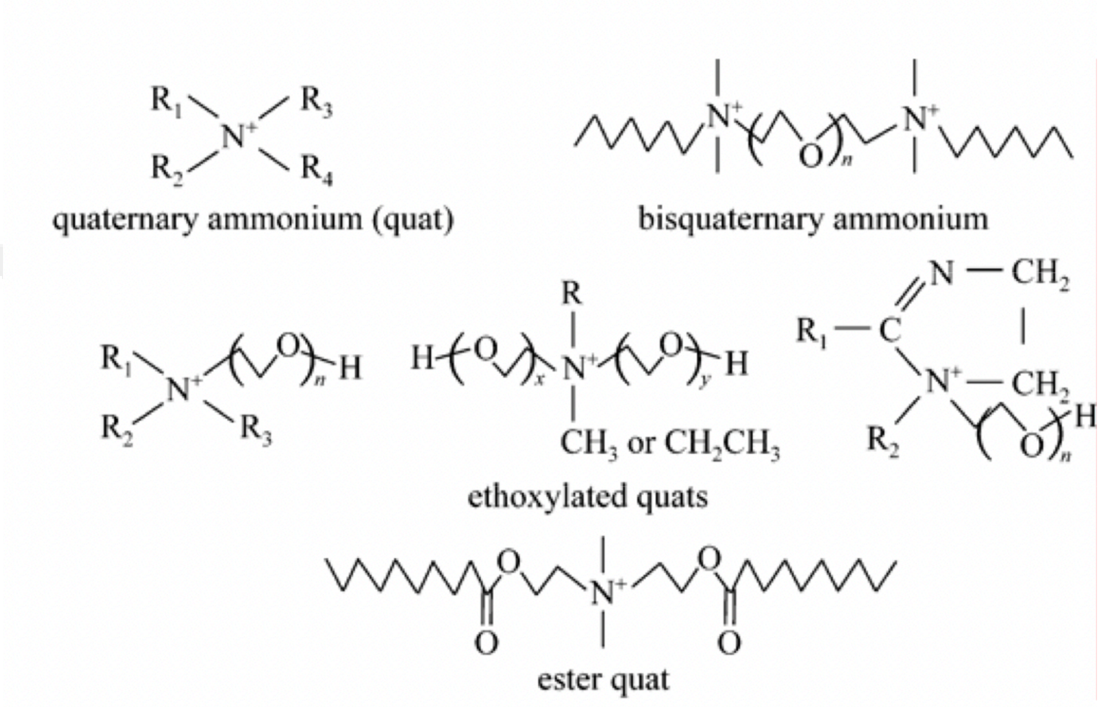


Figure 2.9 : Structures of cationic surfactants used in detergents [19].

Studies have found that some cationic surfactants exhibit properties that increase cleaning efficiency. Quat salt, combined with certain components, reduces the fading of dyes on colored fabrics and improves stain removal. It has been discovered that polyanionic ammonium surfactants exhibit different properties than cationic surfactants and anionic surfactants and perform significantly better at removing soil. Additionally, the use of polyanionic ammonium surfactant in detergent greatly increases the deposition of fluorescent whitening agents on the fabric [19].

2.3.3 Zwitterionic surfactants

Zwitterionic surfactants have both positively and negatively charged groups within their molecules. Amphoteric surfactants belonging to this group can carry both positive and negative charges, but they behave depending on the pH of the solution they are in.

Zwitterionic usually have a large hydrophilic portion because they can carry both positive and negative charges. In general, they are preferred as secondary surfactants in formulations containing anionic or non-ionic surfactants. Because they can change the micellar structure, solubility of emulsions, micelle size, foam stability, detergency and viscosity [24]. Types such as betaines and sulfobetaines are widely used in detergents. Some examples of commonly used zwitterionic structures are shown in Figure 2.10.

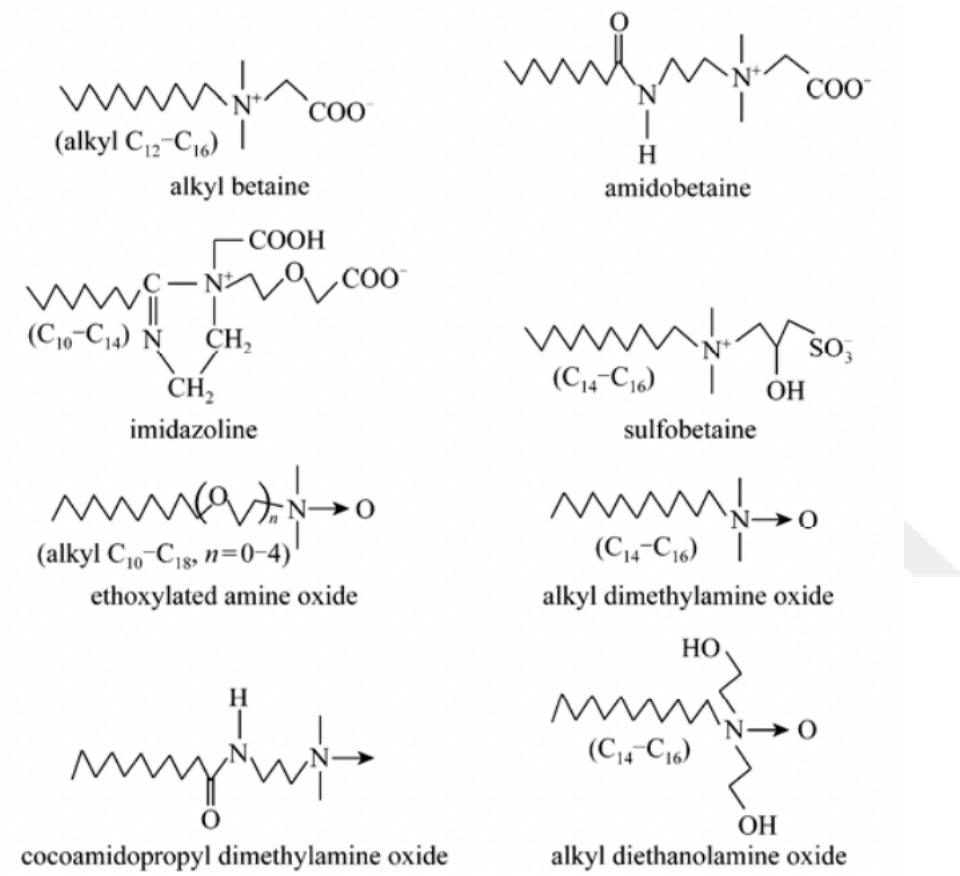


Figure 2.10 : Structures of zwitterionic surfactants used in detergents [19].

2.3.4 Nonionic surfactants

Non-ionic surfactants are the second largest class, following anionics, and represent approximately 30-35% of the market [25].

The properties of nonionic surfactants can be listed as follows [26].

- Nonionic surfactants show good detergency, wetting, and emulsifying properties.

- Nonionic surfactants are available in powder or liquid forms in various household and industrial products.
- Since there is no ionic charge, nonionic surfactants are compatible with all other surfactants.
- They are less sensitive to electrolytes, especially divalent cations, compared to ionic surfactants so they can be used with high salinity or hard water. Its physicochemical properties are not significantly affected by electrolytes.
- Some categories have very low toxicity and are mostly used in pharmaceuticals, cosmetics and food products.

Figure 2.11 displays structures of the more commonly found nonionic surfactants. Nonionic surfactants have either a polyether or a polyhydroxyl unit as their polar group. Among these, the polyether-based surfactants are most prevalent and are comprised of oxyethylene units made by ethylene oxide (EO) polymerization. The most commonly used starting materials are fatty alcohols, alkylphenols, fatty acids, and fatty amines. On the other hand, polyhydroxyl-based (polyol-based) surfactants include sucrose esters, sorbitan esters, and alkyl glucosides. Polyglycerol esters included in this group are actually a combination of polyol and polyether surfactant. Polyol surfactants may also be ethoxylated. A typical example in this group is sorbitan fatty acid esters. They are commonly referred to as Span. On the other hand, their ethoxylated products are known as Tween [21].

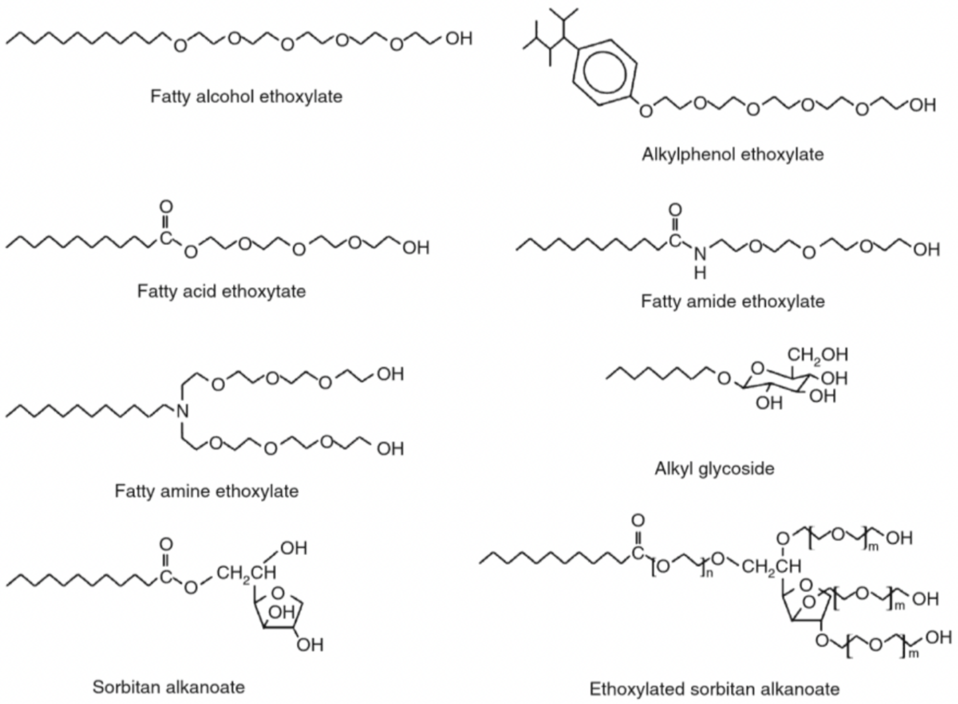


Figure 2.11 : Common nonionic surfactants [21].

One of the main nonionic surfactants is ethoxylated surfactants based on ethylene oxide (EO). Ethoxylation reactions are carried out to prepare the ethoxylated surfactant. The initiator is a fatty alcohol, an alkyl phenol, or a fatty acid, that is, a hydrophobic molecule containing a polar group with an active hydrogen. The initiator reacts with ethylene oxide (EO) to place a hydrophilic head on the molecules.

Ethoxylated surfactants can be classified as follows [27]:

- alcohol ethoxylates,
- fatty acid ethoxylates,
- alkyl phenol ethoxylates,
- fatty amine ethoxylates,
- monoalkaolamide ethoxylates,
- sorbitan ester ethoxylates,
- ethylene oxide–propylene oxide copolymers (sometimes referred to as polymeric surfactants).

Alcohol ethoxylates (AEO) are an important class of nonionic surfactants. This class of surfactants can be called by different names. Alkyl polyoxyethylene glycol, ethoxylated fatty alcohols and monoalkyl poly(ethylene oxide) glycol ethers are among these names. Various abbreviations can also be used, for example dodecyl hexaoxyethylene glycol monoether (having the chemical formula C12H25(OCH2CH2O)6OH), abbreviated as C12E6 [27].

AEO is obtained by the ethoxylation reaction of fatty alcohols with ethylene oxide (see Figure 2.12). Different types of catalysts used cause AEO to have different molecular weight distribution. Acidic catalysts (such as BF3 and SbCl4) are used for products with a narrower molecular weight distribution, but the byproducts of the reaction are more. Commonly used alkaline (such as NaOH and KOH) catalysts catalyze products with a higher concentration of unreacted primary alcohols and a wider molecular weight distribution. In some cases, heterogeneous catalysts can be used. In most cases, the molecular weight distribution of AEO products affects the applications of the products. Therefore, a narrower molecular weight is preferred [28].

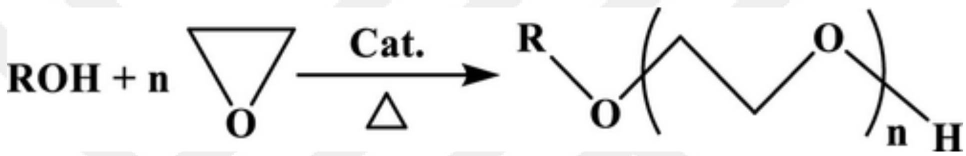


Figure 2.12 : Reaction of ethoxylation [28].

Alcohol ethoxylates are available in different linear and branched versions because alcohol ethoxylates can be the synthesis of different alcohols containing primary, secondary or tertiary OH groups. As an example of these structures, alcohol ethoxylates with a hydrophobic chain consisting of 10 carbon atoms are shown in Figure 2.13. The hydrophobic chain can either be in a linear or branched form. Additional alcohols used in the process are 1-decanol, 3,7-dimethyl-1-octanol, 2-decanol, 4-decanol, respectively.

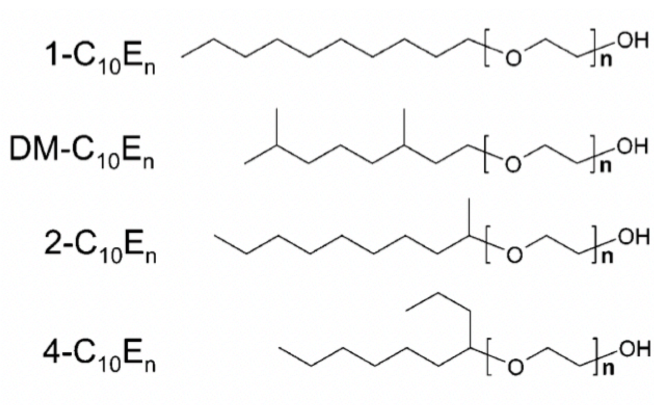


Figure 2.13 : Chemical structure of alcohol ethoxylates with differently branched hydrocarbon tails [29].

Alcohol ethoxylates have many advantages. They are more readily biodegradable than the alkyl phenol ethoxylates (APEs) in the ethoxylated surfactant group. The structure of alcohol ethoxlates can be optimized for desired performance by varying the distribution of hydrophilic, hydrophobic and ethoxymers. They have compatibility with enzymes in detergent formulations. Compared to anionic surfactants, it is more tolerant to hard water and ionic compounds. They emulsify better than the corresponding APE (alkyl phenol ethoxylates). They have better stability in hot alkali solutions than the ethoxylated fatty acids in the ethoxylated surfactant group. They have better wetting power and water solubility than fatty acid ethoxylates. When detergent efficiency is compared with LAS (Alkylbenzene sulfonates); They are more water soluble than LAS and more effective on synthetic fabrics and cold wash conditions than LAS [26].

Alcohol ethoxylate/propoxylate copolymers with the chemical formula CiEOmPOn or CiPOmEOn are a class of nonionic surfactants that have been used recently. EO stands for ethylene oxide and PO stands for propylene oxide. Propylene oxide, the lipophilic unit, is another fundamental component used in the manufacturing of propoxylated surfactants. An example C-PO-EO molecular structure is shown in Figure 2.14.

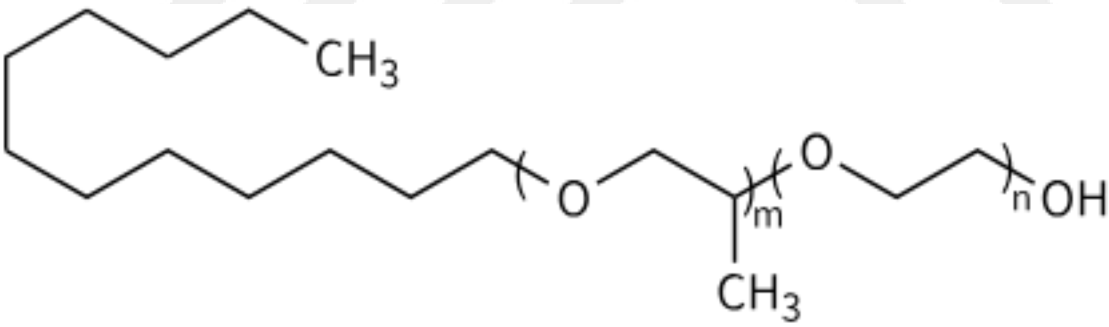


Figure 2.14 : Lauryl alcohol, ethoxylated, propoxylated.

The position of polyoxyethylene (PO) groups in the surfactant molecule affects the physical-chemical properties of the surfactant differently. In a study conducted to reveal the changing characteristics, Alcohol ethoxylate (C_{11}EO), which is a mixture of linear and mono-branched fatty alcohols with an alkyl chain length of eleven carbon atoms, and ethoxylate-propoxylates (C_{11}EOPO) and propoxylate-ethoxylates (C_{11}POEO) were compared. There was an increase in surface tension regardless of the position of the PO group before or after the EO groups. There was a slight increase in C_{11}POEO status and a significant increase in C_{11}EOPO status compared to C_{11}EO.

When placed as the last unit, PO groups provide very low foaming and non-gelling behavior with weak surface activity. When PO groups are placed as intermediate units, they retain their wetting behavior and have less foam than $C_{11}EO$ but more than $C_{11}EOPO$. Lastly, when the PO groups are placed between the hydrophobic alkyl chain and the hydrophilic polyethylene glycol chain, cmc values decrease, while when PO groups are located at the end, cmc values increase [30].

Another example of this group is the chemical compounds of BASF in Figure 2.15. The alkyl ethoxylate (Lutensol XP-series) surfactants compositionally resemble CiEOj surfactants, while the alkyl alkoxylate (Lutensol XL) surfactants resemble CiPOnEOj surfactants. These two chemical compounds are widely used as ingredients in detergents.

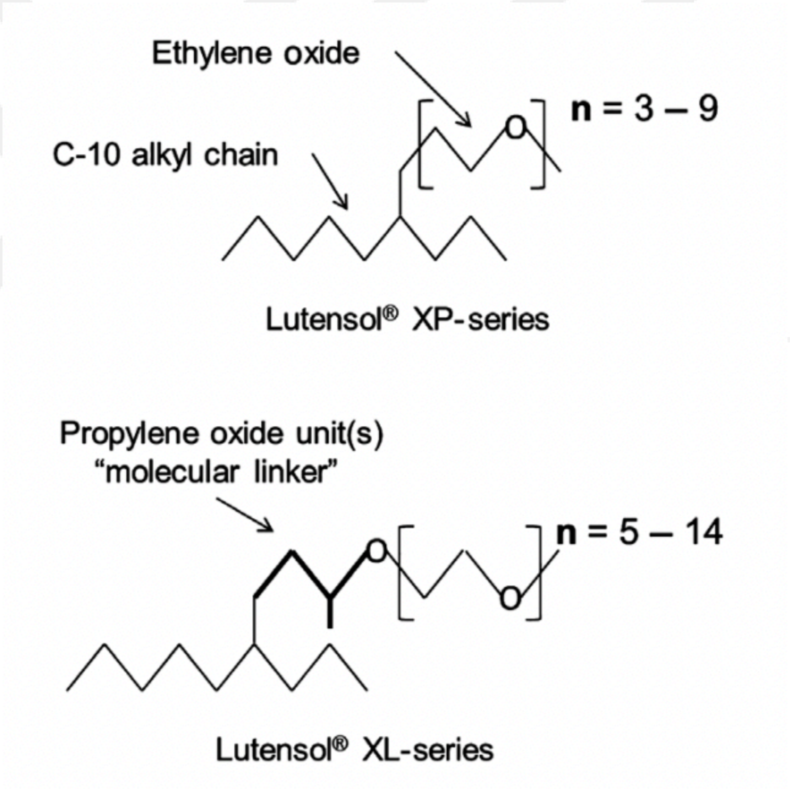


Figure 2.15 : Chemical structure of Lutensol XP and XL-series [31].

2.3.4.1 Cleaning efficiency and characteristic features of nonionic surfactants

Anionic surfactants in micellar solutions are unable to retain and eliminate all of the oily residue that may be present during a washing cycle. However, non-ionic surfactants can accomplish this due to their enhanced solubility properties. The superior solubilizing ability is closely related to the effectiveness of a quality detergent [32].

The cleaning effectiveness of a nonionic surfactant is influenced by its chemical structure. Although certain regularities can be observed within a specific group, it is not possible to generalize about the relationship between structure and cleaning performance for all groups. In the case of alcohol ethoxylates, detergency varies depending on the ethylene oxide chain and hydrophobic group. In general, the best cleaning is achieved with a chain containing 12-16 carbon atoms and a HLB value of approximately 12. When the hydrophilic part remains the same, the cleaning ability increases as the carbon chain length increases, reaches a peak, and then decreases [32].

In examining the oil removal mechanism of nonionic surfactants, it is crucial to highlight several characteristic features that contribute to their cleaning performance. These features encompass the cloud point, emulsion, hydrophilic-lipophilic balance (HLB), micelle formation, hydrophilic-lipophilic difference (HLD), the critical micelle concentration (cmc). Together, these attributes define the efficacy of nonionic surfactants in the cleaning process.

Cloud point

The cloud point is the temperature above which the sample becomes cloudy for a nonionic surfactant in water. This imposes technical restrictions on their use.

For alcohol ethoxylates, the cloud point depends on its molecular structure and is controlled by the HLB. The cloud point by number of alkyl and EO chains is listed in Table 2.1 for the compound $C_n(EO)_pH$. A decrease in EO chain length (for a constant p-value, p=5,6,7,8) and an increase in alkyl chain length (for a constant p-value, n=10,12,14,16) decrease HLB , thus lowering the cloud point [33].

Table 2.1 : Changes on the cloud point of AEO relative to alkyl and EO chains [33].

	n	p	Cloud Point (°C)
$C_n(EO)_8H$	10	8	84.5
	12	8	77.9
	14	8	70.5
	16	8	65.0
$C_{12}(EO)_pH$	12	5	28.9
	12	6	51.0
	12	7	64.7
	12	8	77.9

Generally, the cloud point of the surfactant at a concentration of 1% (w/w) is determined. However, concentration change affects the cloud point. In the study conducted by Li et al., the cloud point change of selected alcohol ethoxylates is as shown in Figure 2.16. Tergitol 15-S-7, Tergitol 15-S-9 (linear secondary alcohol ethoxylated alcohols with 11-15 carbons, 7 EO and 9 EO number, respectively.) and Neodol 25-9 (linear primary alcohol ethoxylated alcohols with 12-15 carbons, 9 EO number) was used.

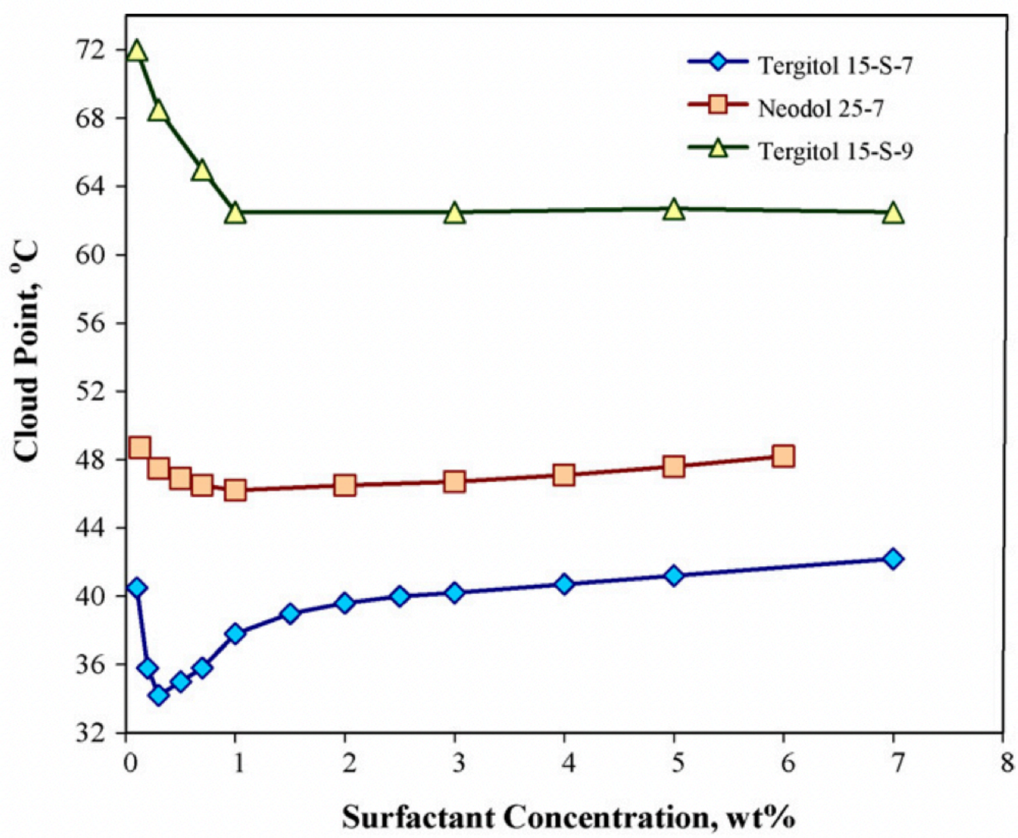


Figure 2.16 : The relationship between the concentration and cloud point of certain alcohol ethoxylates [34].

At the same time, this study revealed that the presence of inorganic salts, ionic surfactants, alcohols, and water-soluble polymers changes the cloud point of these chemicals. These factors have the ability to decrease or enhance the cloud point. The cloud points of binary mixtures of nonionic surfactants are between the two cloud points [34].

Emulsions

Emulsions are temporarily stable homogeneous-appearing systems of immiscible liquids such as oil and water. Common emulsions are water-in-oil (w/o) or oil-in-water (o/w) emulsions (see Figure 2.17). Water in oil (W/O) consists of a dispersed aqueous phase within an oil phase. Oil-in-water (O/W) is composed of an oil phase dispersed in a continuous aqueous phase. Stabilization of emulsions is usually accomplished with surfactant molecules.

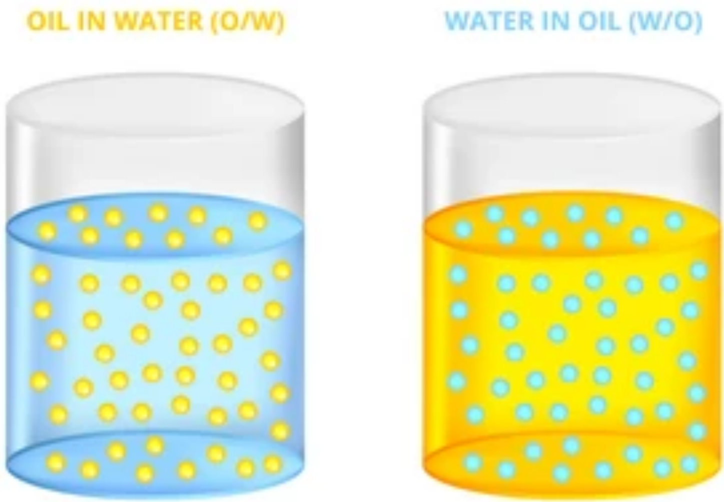


Figure 2.17 : Emulsion Types: oil in water (o/w) and water in oil (w/o).

A more comprehensive classification of emulsions was made by Winsor (1954). Three types of Winsor emulsions are shown in Figure 2.18. Categories are defined as follows:

- Type I microemulsion: some of the oil in the water phase containing surfactant (O/W micro emulsion) is combined with excess oil phase.
- Type II microemulsion: water-in-oil (w/o) microemulsions are formed and combined with excess water phase.
- Type III microemulsion: both oil and water are soluble by surfactant and it is a three-phase system with excess oil phase and water phase.

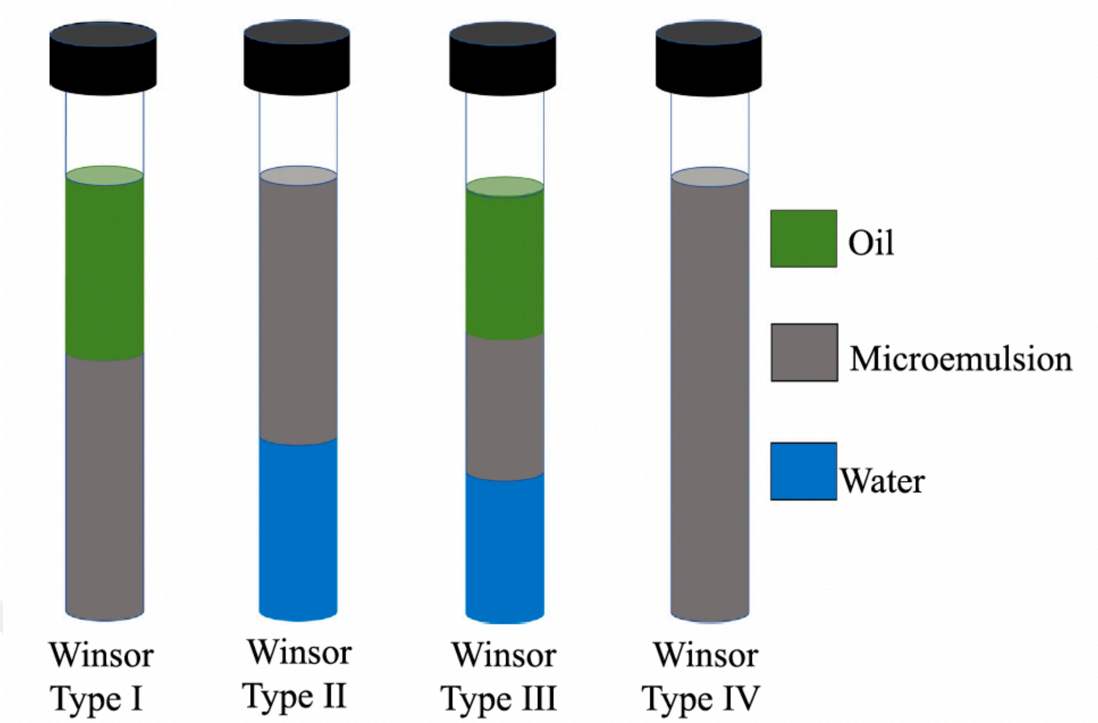


Figure 2.18 : Winsor's classification of microemulsions. Source: Modified from Winsor (1948) [35].

Water-soluble nonionic surfactants create oil-in-water (o/w) micelles, which correspond to Type I. Conversely, oil-soluble surfactants form water-in-oil (w/o) micelles, corresponding to Type II. The phase inversion temperature (PIT) serves as a critical temperature value that facilitates the transition between Winsor I and Winsor II emulsions. Typically, emulsions composed of equal proportions of oil and water-based phase, along with around 5% nonionic surfactant, are shaked and observed for changes upon raising the temperature. This temperature range can be identified by a sudden decrease in conductivity. Within the PIT range, it is possible to achieve Type III or Type IV emulsions. The transition from Type I to Type II emulsions can be accomplished by increasing the concentration of electrolytes, adjusting the hydrophobicity of the surfactant and oil, and raising the temperature [36,37].

Hydrophilic-lipophilic balance (HLB)

Hydrophilic-lipophilic balance (HLB) is a numerical value that expresses the strength and size balance of lipophilic and hydrophilic groups in the same molecule. The concept of HLB was first published in the Atlas Powder Company's brochure in 1948. As stated in the brochure, HLB values refer to the hydrophilicity or lipophilicity of the material. A low HLB value means the material is lipophilic. A high HLB value means the material is hydrophilic. Those in the 10-11 HLB range are moderate. As an example from commercial products, the Span type product is therefore lipophilic and most of the Tween type is hydrophilic. The following Figure 2.19 shows the Span 80 (Sorbitan Monooleat) and Tween 80 (Polioksietilen Sorbitan Monooleat) molecules.

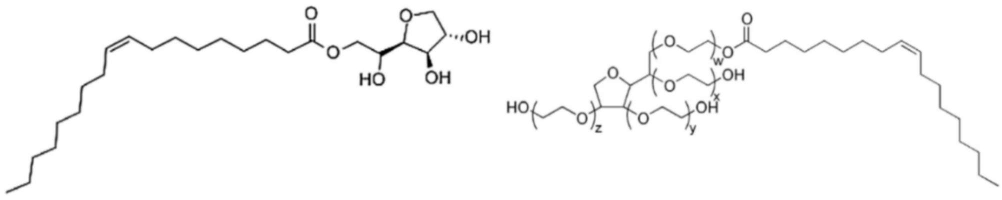


Figure 2.19 : Molecular structure of surfactants (a) Span 80 and (b) Tween 80 Sum of x+y+z+w=20 [38].

In 1950, William C. Griffin's article on the HLB concept was published in the first issue of the Journal of the Society of Cosmetic Chemists. This article gives some experimental methods for determining the HLB values of emulsifiers and the required HLB for oils [39]. Also, applications of surfactants with different HLB range are listed in Table 2.2 [40]. The table guides the selection of surfactant for the desired emulsion or application.

Table 2.2 : Applications of HLB range.

Application	**HLB range**
W/O emulsions	4–6
Wetting agents	7–9
O/W emulsions	8–18
Detergent	13–15
Solubilizer	15–18

If two emulsifyiers (with known HLB) are mixed with an oil for emulsification, the HLB (in the optimum ratio) is the required HLB for the oil. This is expressed by the equation [40].

$$\frac{W_A\, HLB_A + W_B\, HLB_B}{W_A + W_B} \text{ (optimum ratio)} = \text{HLB oil} \quad (2.1)$$

wherein:

WA = the amount (weight) of the A emulsifier,

WB = the amount (weight) of the B emulsifier,

HLBA, HLBB = the assigned HLB values for emulsifiers A and B,

HLB oil = the "required HLB" of the oil for the type of emulsion.

The determination of HLB values for non-ionic surfactants by the experimental procedure is very time-consuming. In addition, formulas for calculating HLB values can be based on compositional or analytical data [41]. Approximate values for most polyhydric alcohol fatty acid esters can be calculated by the equation 2.2:

$$\mathrm{HLB} = 20\left(1 - \frac{S}{A}\right) \tag{2.2}$$

A= acid number of the acid

S= saponification number of the ester

Many fatty acid esters, such as beeswax esters, lanolin esters, tall oil and rosin esters, do not have good saponification number data. Therefore, the HLB values of these fatty acid esters can be calculated with equation 2.3.

$$\mathrm{HLB} = \left(\frac{E+P}{S}\right) \tag{2.3}$$

P= weight percentage of polyhydric alcohol content (glycerol, sorbitol, etc.)

E = weight percentage of oxyethylene content

S= saponification number of the ester

Equation 2.4 can be used for fatty alcohol ethylene oxide condensation products and products where only ethylene oxide is used in the hydrophilic part.

$$\mathrm{HLB} = \left(\frac{E}{5}\right) \tag{2.4}$$

These formulas give valid results for most nonionic surfactants. However, propylene oxide, butylene oxide, nitrogen, sulfur, etc. containing non-ionic surfactants may exhibit unrelated behavior. In addition, experimental methods should be used to determine the HLB values of ionic surfactants, not the equations mentioned above.

Because although the molecular weight of the hydrophilic part is low, its ionization makes the product more hydrophilic.

Hydrophilic lipophilic difference (HLD)

The HLD theory was developed to facilitate surfactant selection. It allows comprehensive estimates of the emulsion type (o/w, w/o, micro-emulsion) and the suitability and effectiveness of a surfactant used for this purpose. Phenomena such as phase reversal temperature can also be understood through HLD. Contrary to the HLB (Hydrophilic Lipophilic Balance) theory, the HLD approach is generally applicable to both anionic and nonionic surfactants.

In the case of HLD=0, the oil-water interfacial tension is quite low, and the surfactant-water-oil-containing emulsion represents the Winsor type III state. However, when HLD is negative, the formulation is Winsor Type I emulsion. When HLD is positive, the formulation is Winsor Type II emulsion.

The HLD concept is used in the optimization and design of water-oil- surfactant formulations for specific salinity conditions and temperature. Depending on the nature of the surfactant headgroup, two HLD equations exist. The HLD equation to be used for ionic and nonionic surfactants, respectively, is expressed as follows (Eq. 2.5 and 2.6):

$$HLD = \ln(S) - kEACN + Cc - c_T(T - T_0) \quad (2.5)$$

$$HLD = bS - kEACN + Cc + c_T(T - T_0) \quad (2.6)$$

S – the salinity in wt% of NaCl

EACN - Effective Alkane Carbon Number, represents the hydrophobicity of the oil phase.

T - the Temperature, in °C, T_0 has a value of 25°C.

Cc - a Characteristic value for the hydrophobic/philic nature of the surfactant.

b and k are empirical constants that depend on the type of the system.

c_T is the temperature coefficient.

The variable b relies on the type of electrolyte used, like for instance, b = 0.13 for NaCl. The parameter S represents the concentration of salt present in the system.

Traditional surfactants typically exhibit k values ranging from 0.15 to 0.17. Nevertheless, certain extended anionic or cationic surfactants may have experimentally obtained constants from 0.05 to 0.7. Ethoxylated nonionic surfactants become more lipophilic with rising temperature, resulting in a positive cT (approximately ~ +0.06). The characteristic curvature of nonionic surfactants is denoted by Cc, where a negative value indicates greater hydrophilicity and a positive value indicates increased hydrophobicity. Remarkably, the HLD equation remains unaffected by surfactant concentration, enabling the calculation of HLD for pure surfactant systems based solely on oil and aqueous phase nature and temperature. However, for commercial surfactants with polydisperse EO groups, surfactant concentration impacts Cc, necessitating consideration [42].

Micelle formation

The relationship between the geometry of a surfactant molecule and its aggregate structure in aqueous solutions is defined by the molecular packing parameter (P_C). Representative molecular geometry of surfactants is given in Figure 2.20.

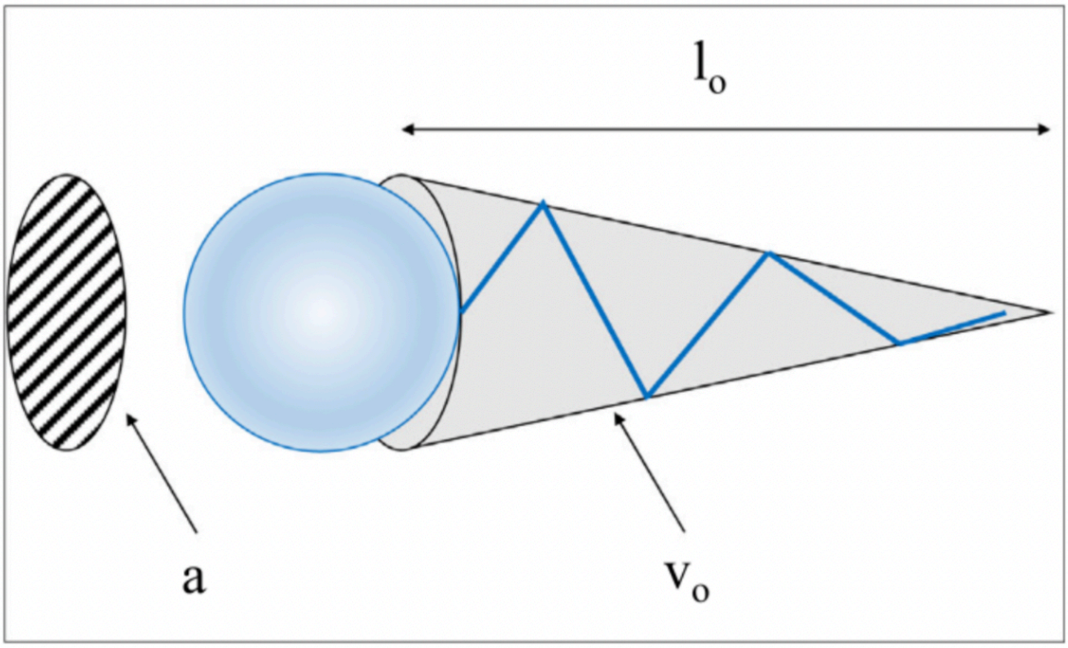


Figure 2.20 : Schematic representation of the terms used for the packing parameter [43].

With these geometric parameters, Pc is calculated by the following equation (Eq 2.7):

$$Pc = \frac{v_o}{l_o\, a} \tag{2.7}$$

vo: volume of surfactant tail

lo: length of surfactant tail

a: surface area of hydrophilic head group on the surface of the aggregate

Examples of aggregate structures are spherical micelles, rod-like micelles, bilayer vesicles etc. are included. In Figure 2.21, different micelle geometries of surfactant molecules are shown according to the value of the packing parameter. These geometries affect the bulk properties of the solution, such as its viscoelastic properties and solubility capacity [43].

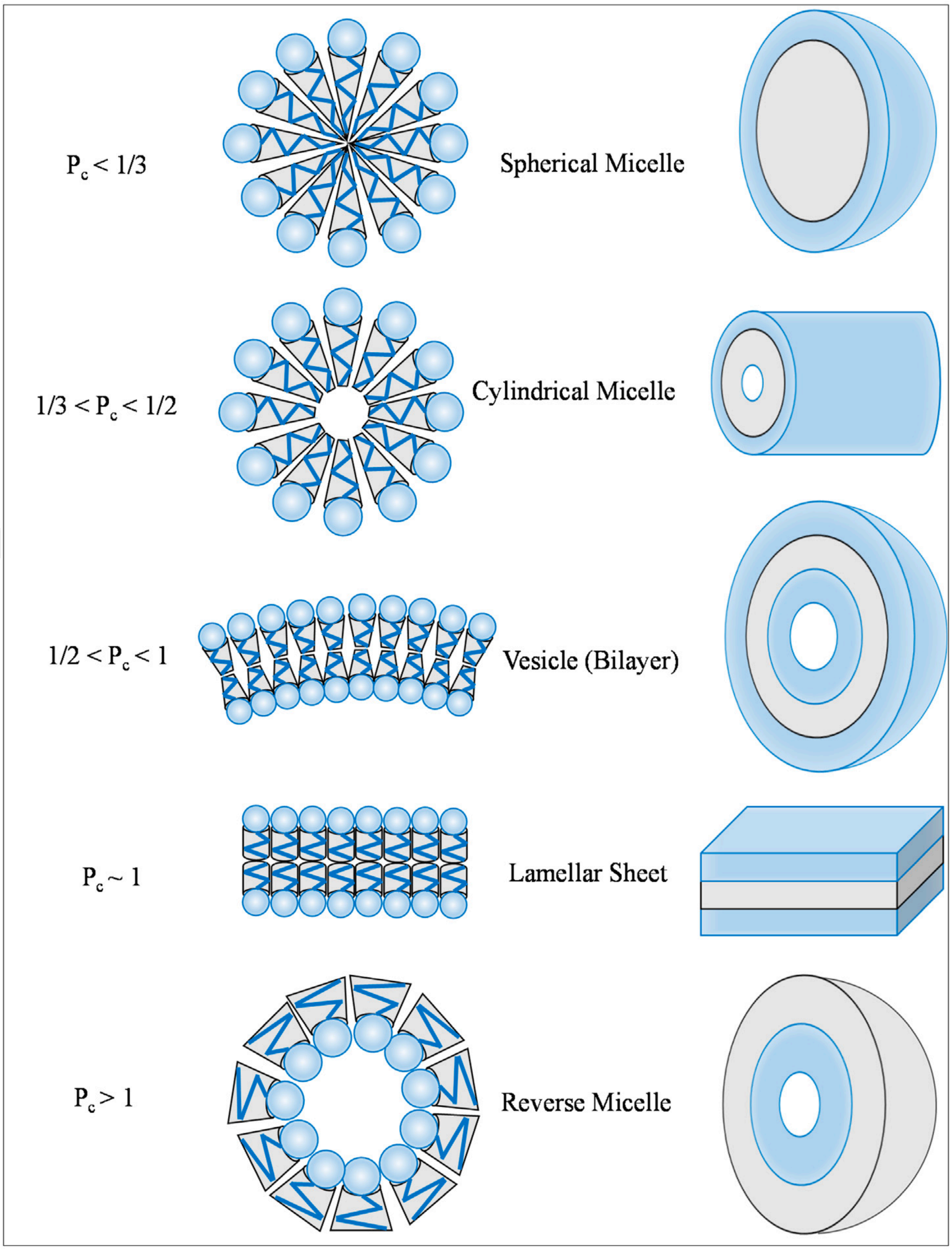


Figure 2.21 : Effect of critical packing parameter (P_c) on the aggregate structure of surfactants [43].

The critical micelle concentration

The critical micelle concentration (CMC) is a critical transition concentration value of the surfactant. Above this concentration, self-assembly aggregation, which is called micelle, begins to form. CMC is important for surface activity and self-assembly aggregation characterizations of surfactant. Above the CMC, the surface tension does not decrease any more. When the surfactant concentration increases, adsorption takes place on the surface until the surface tension reaches its minimum value, and finally the surface is completely covered with surfactant. In general, it serves to determine the concentration for use, as no further surface tension changes are observed above the CMC.

In the Figure 2.22, there is a graph showing the relationship between concentration increase and surface tension.

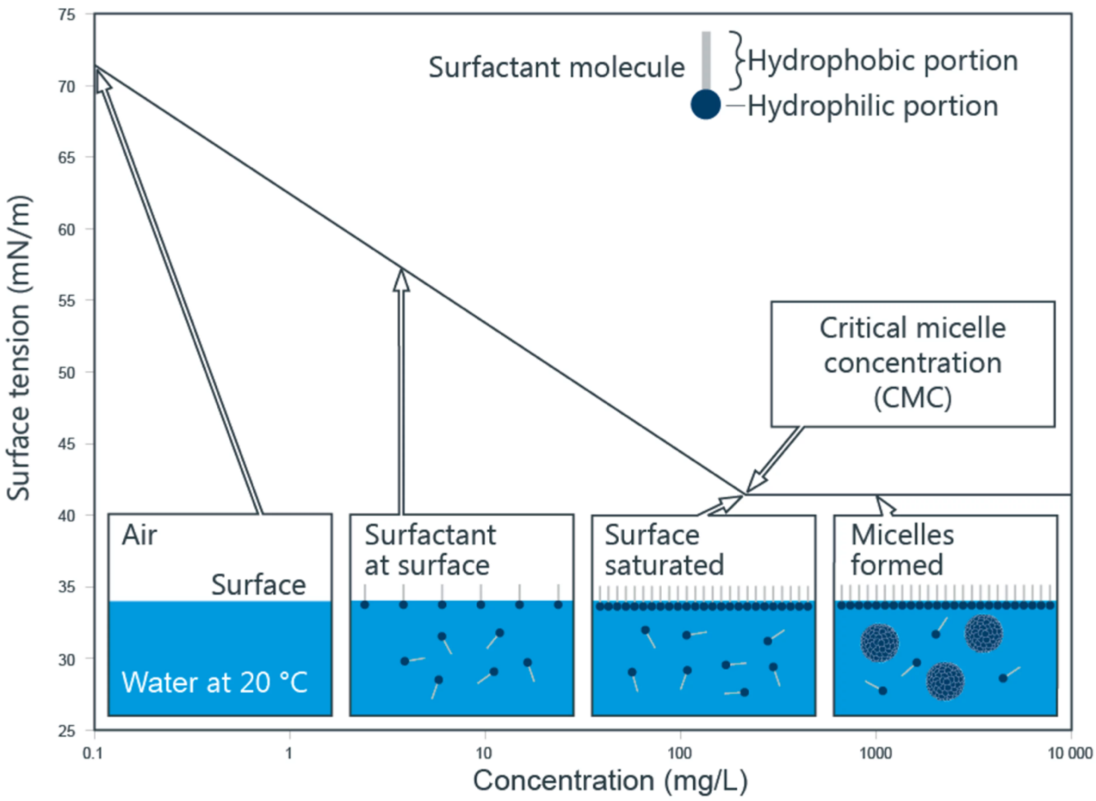


Figure 2.22 : Surface tension of a solution composed of surfactant with increasing concentration and formation of micelles [44].

Surfactant with a low CMC value shows micelle formation at a lower concentration, meaning it self-assembles. This also means that the surfactant self-assembles at the interfaces at low concentration. Therefore, if its CMC is low, less surfactant is needed for a particular task such as removing oily soils or dispersing pigments or emulsifying oil.

CMC values can be calculated by different techniques (tensiometry, conductivity, spectroscopy, fluorescence). Above and below the CMC, the chemical-physical properties of the surfactant and especially the micelle status of the surfactants vary. For this reason, any technique that can detect a significant change can be used.

Below the CMC, individual surfactant molecules can still contribute to wetting and emulsification, but the formation of micelles enhances their cleaning efficiency. Detergent formulations are often designed to be used at or slightly above the CMC to ensure effective cleaning while minimizing the amount of surfactant needed.

Table 2.3 provides CMC values for various substances within surfactant classes [45]. There exists a correlation between the CMC values and the structure of nonionic and ionic surfactants. Generally, in any surfactant class, the CMC decreases as the length of the hydrophobic tail increases. The addition of a methylene group to the alkyl chain, without added salt, leads to a 2-fold reduction in CMC for ionic surfactants and a 3-fold reduction for nonionic surfactants. In nonionic surfactants, an increase in the length of the hydrophilic group (polyethylene oxide) results in an increased CMC value. Comparatively, nonionic surfactants with the same alkyl chain length exhibit lower CMC values than their ionic counterparts. The inclusion of a phenyl group in the alkyl group increases hydrophobicity to a lesser extent than increasing the chain length by the same number of carbon atoms. In ionic surfactants, the valency of the counterion influences the CMC; doubling the counterion value leads to a 4-fold reduction in CMC [46].

Table 2.3 : Critical micelle concentration values for some surfactants [45].

Surfactant	CMC (M)
Anionics	
Sodium octyl sulfate	1.3×10^{-1}
Sodium decyl sulfate	3.3×10^{2}
Sodium dodecyl sulfate	8.3×10^{-3}
Sodium tetradecyl sulfate	2.1×10^{-3}
Sodium octylbenzene sulfonate	1.5×10^{-2}
Sodium dodecylbenzene sulfonate	1.2×10^{-3}
Potassium perfluorooctanoate	2.9×10^{-2}
Cationics	
Decyltrimethylammonium bromide	6.5×10^{-2}
Dodecyltrimethylammonium bromide	1.6×10^{-2}
Hexadecyltrimethylammonium bromide	9.2×10^{-4}
Dodecylpyridinium chloride	1.5×10^{-2}
Nonionics	
Penta(ethylene glycol) monooctyl ether, C_8E_5	9.2×10^{-3}
Penta(ethylene glycol) monooctyl ether, $C_{10}E_5$	9.0×10^{-4}
Penta(ethylene glycol) monooctyl ether, $C_{12}E_5$	6.5×10^{-5}
Hexa(ethylene glycol)monododecyl ether, $C_{12}E_6$	6.8×10^{-5}
Hepta(ethylene glycol)monododecyl ether, $C_{12}E_7$	6.9×10^{-5}
Octa(ethylene glycol) monododecyl ether, $C_{12}E_8$	7.1×10^{-5}
Octyl glucoside	2.5×10^{-2}
Decyl glucoside	2.2×10^{-3}
Zwitterionics	
Dodecyldimethylammoniumpropyl sulfonate	3.0×10^{-3}
Dodecyldimethylamine oxide	2.1×10^{-3}

Commonly, numerous applications entail the combination of two or more surfactants. In such cases, surfactant mixtures typically give rise to mixed micelles. Mixed micelles all have the same composition and contain more than one type of surfactant. Where surfactants are not compatible in mixtures, they may consist of different micelles, each containing only one type of surfactant. The calculation of the CMC for a mixture containing two surfactants follows the formula [45]:

$$\frac{1}{\mathrm{CMC}} = \frac{x_1}{\mathrm{CMC}_1} + \frac{x_2}{\mathrm{CMC}_2} \tag{2.8}$$

x1 , x2 =molar fractions of surfactants 1 and 2, respectively.

CMC1, CMC2 = CMC of surfactant 1 and surfactant 2.

3. MECHANISM OF THE CLEANING

The cleaning process consists of several stages, and the effectiveness of each stage depends on various factors such as the nature of the soil, the type of surface being cleaned and the cleaning agents used.

3.1 Wettability and Contact Angle

Wetting can be described as a process that "involves reducing the surface tension of the cleaning solution, thus allowing it to better penetrate the substrate and the oily stain." In the first stage of washing, it is very important to ensure complete wetting of the textile fibers and soil by using the washing liquid. Wetting agents are used in relatively small amounts and can significantly reduce the amount of cleaning agent required to remove soils. Wetting is a critical step in the cleaning mechanism, especially for removing oil soils from fabric. It facilitates the contact, penetration, and subsequent removal of soils, contributing to the overall effectiveness of the cleaning process.

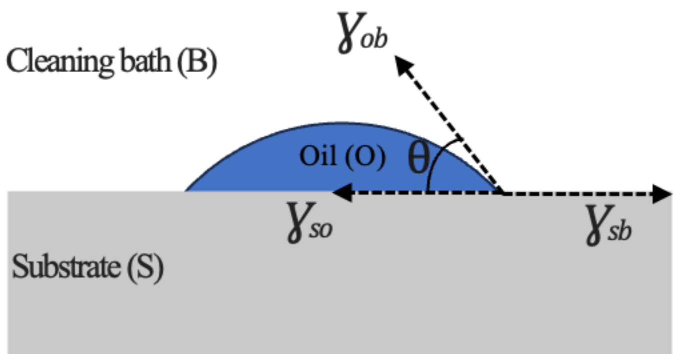


Figure 3.1 : Diagram of a liquid drop illustrating the quantities involved in the Young equation.

In general, oil is spread over a surface using the air. A contact angle θ is formed between the solid and a drop of liquid applied to its surface. This angle serves as an indicator of how well the liquid wets the solid surface. When a drop of oil is in contact with a surface, it spreads until an equilibrium that corresponds to the resultant of the surface energy of the solid and of the oil/air interface. In Figure 3.1 a drop of oil (O) and substrate as a solid surface (S) are considered. The oil spread at the air-substrate interface comes into balance with new interfaces and interactions in the cleaning bath.

The Young-Dupré equation, named after its contributors Thomas Young and Jules Dupré, is a fundamental equation in colloid and surface science. The equation describes the relationship between the contact angle (θ) formed by a liquid droplet on a solid surface and the interfacial tensions at the interfaces. The equation (3.1) is as follows:

$$\gamma_{SB} = \gamma_{SO} + \gamma_{OB} \cdot cos\theta \tag{3.1}$$

θ is the contact angle of characterizing the wettability of the oil drop on the surface solid.

γ_{SB} is the substrate-cleaning bath interfacial tension.

γ_{SO} is the substrate-oil interfacial tension.

γ_{OB} is the oil-cleaning bath interfacial tension.

When wetting occurs, two pre-existing surfaces disappear and two energy is released as substrate-bath and oil-bath. Substrate-oil interface energy is used to create the interface. The adhesion of the oil on the solid W_{OS} is given by the Dupré equation:

$$W_{OS} = \gamma_{SB} + \gamma_{OB} - \gamma_{SO} \tag{3.2}$$

As the adhesion work W_{OS} is small then it becomes easier to soil the surface solid. The surface tensions of the solid and the oil need to be as low as possible.

3.2 Oil Removal

Oil removal on fabric refers to the process of eliminating or reducing oil-based stains or residues from textile materials. This is done by using a cleaning bath that contains surfactant. Mechanisms play an important role in oil removal such as roll-up or snap-off (emulsification), solubilization.

3.2.1 Roll-up

A liquid soil can change shape as a result of its interaction with a cleaning agent. This is the basis of the rolling mechanism of the soil release. In the roll-up mechanism, the decrease of IFT between the oil-surfactant solution and the fabric-surfactant solution causes the contact angle of the bound oil droplet to increase, eventually reaching 180° and as a result, the oil droplet is completely separated from the substrate. Figure 3.2 presents a diagram depicting the roll-up mechanism. As illustrated, it transforms into a spherical shape as the surfactant monolayer gradually forms at the interface between the aqueous phase and the oily soil. As a result, such a process can cause soil to be released into the aqueous system [6,48].

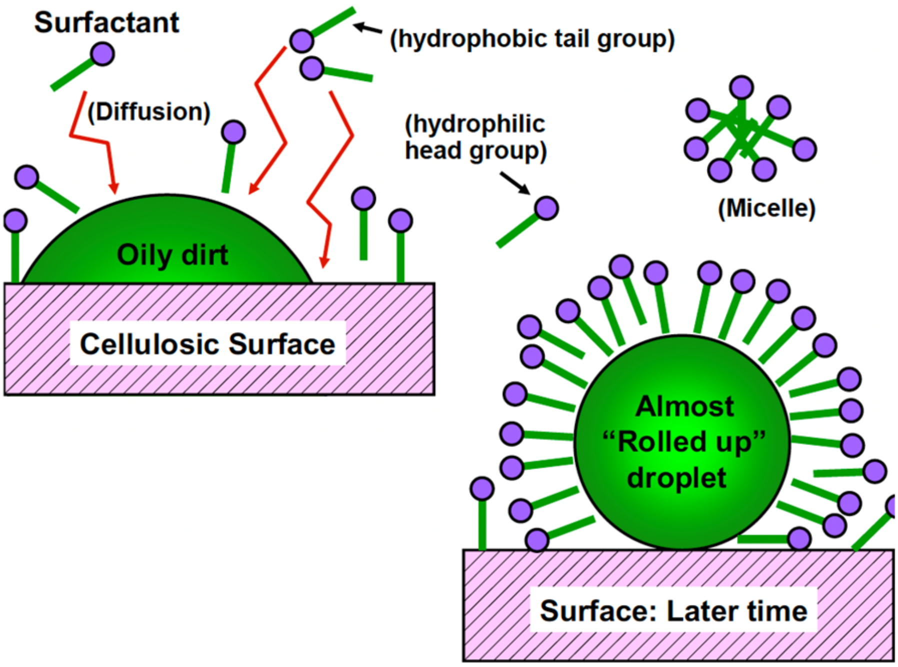


Figure 3.2 : Schematic illustration of the roll-up mechanism [6].

3.2.2 Snap off

In the snap-off mechanism, incomplete separation of the long droplet occurs. The separated oil is then emulsified. This mechanism is also known as "necking" or "emulsification". Figure 3.3 provides a schematic illustration of the snap-off mechanism.

The process of eliminating soil from materials with low surface energy, such as hydrophobic polyester, relies on achieving a contact angle below 90°. This facilitates hydraulic currents, allowing the removal of small portions of oily soil at the interface between the soil and water. This mechanism is observed when the fabric surface is entirely covered by oily soil, hindering surfactant solution access to the fiber surface. The emulsification process is particularly effective when there's low interfacial tension at the oil-water interface, enabling easy deformation of the oil film into small emulsion droplets. This mechanism has been studied in the context of removing mixtures of mineral oil and polar organic substances from polyester, resembling sebum soils from the skin. The rate of emulsification in such model systems is influenced by factors like the ratio of non-polar to polar constituents, with varying oleic acid content affecting the process. Additionally, electrolyte concentration and temperature have substantial effects on the rate of soil removal through this emulsification mechanism. In some cases, spontaneous emulsification of non-polar-polar soil mixtures has been observed without external agitation [49].

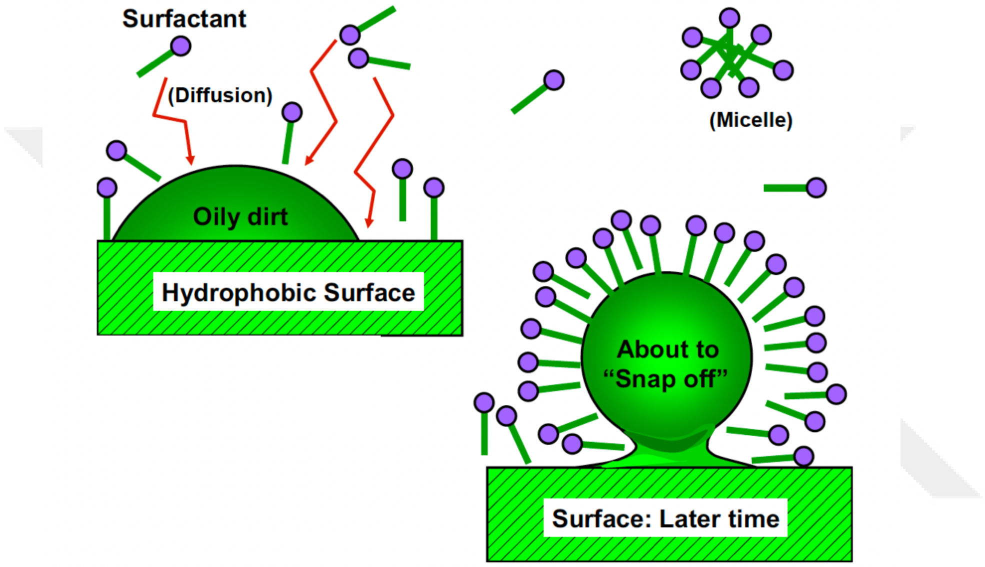


Figure 3.3 : Schematic illustration of the snap-off mechanism [6].

3.2.3 Solubilization

Solubilization occurs in parallel with emulsification but is an independent process. While emulsification requires a mechanical effect, solubilization can also occur spontaneously. The solubilization mechanism involves the formation of microemulsion with oil-water-surfactant. An example of the Winsor III system is obtained in this mechanism [50].

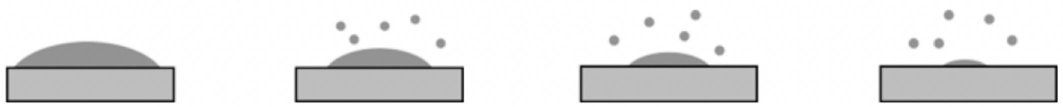


Figure 3.4 : Schematic illustration of the solubilization mechanism [50].

3.3 Stabilization of Removed Soil and Prevention of Redeposition

The stabilization of oil during the oil removal mechanism by surfactants involves the transformation of oil into a more stable form, typically in the context of emulsification or dispersion. Surfactants lower the interfacial tension between oil and water, allowing the oil to disperse more easily in the aqueous medium. When surfactant molecules surround oil droplets, the hydrophobic tails embed themselves into the oil, while the hydrophilic heads face outward, interacting with the water. This forms structures known as micelles, which encapsulate the oil droplets. The resulting oil-in-water emulsion is stabilized by the surfactant, preventing the oil droplets from coalescing and separating from the water. In addition to emulsification, surfactants can facilitate the dispersion of oil in water without forming a traditional emulsion. The surfactant molecules can coat the oil droplets, preventing them from agglomerating and aiding in their distribution throughout the water. The stability of the emulsion or dispersion is crucial for the effectiveness of the cleaning process. The surfactant's ability to keep the oil droplets separated prevents the reaggregation of oil, ensuring that the emulsion remains stable during the cleaning or separation process. The stabilization of oil by surfactants enhances the overall efficiency of oil removal. The resulting emulsion or dispersion can be more easily transported, processed, or separated from the water phase. The stability imparted by surfactants helps prevent the reformation of oil layers on surfaces and facilitates the eventual removal of oil from the system.

Redeposition is a common problem in the washing process. In the cleaning process, redeposition should be prevented after the oily soil is removed. When the removed oily soil cannot be kept in the washing bath, it returns to the fabric, resulting in white fabrics having a dirty appearance or colored fabrics having a duller appearance. Redeposition may occur if not enough cleaning agent is added to the washing bath, or if too much clothing is loaded into the washing machine.

A study was conducted that highlights detergency and redeposition trends for carbon black (model hydrophobic soil) removal from polyester (hydrophobic) and cotton fabrics (hydrophilic) using anionic, nonionic, and cationic surfactants. For polyester and cotton, it is obvious that detergency increased, and redeposition decreased for all surfactant types with increasing pH. Redeposition was low for both fabrics compared to the soil remaining after washing. Therefore, it has been shown that redeposition is not a significant factor in explaining the trends in detergent effectiveness [9].

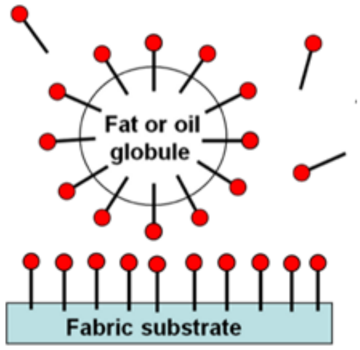


Figure 3.5 : Appearance of the substrate with surfactant after removal of oil from the substrate.

Compared to other surfactant systems used on fabrics, the surfactant called fatty alcohol ethoxylate with 9 moles of ethylene oxide performed the best in terms of detergent performance, resulting in the lowest oil redeposition. Moreover, the study found that oil redeposition decreases as the surfactant concentration increases for all examined surfactants and remains relatively constant when the concentration exceeds 0.2 wt% in both types of fabric [51].

4. EXPERIMENTAL STUDY

4.1 Materials

4.1.1 Fabric

The woven fabrics used are 2/1 Z Twill and have 100% cotton content. Dark blue and beige cotton fabric were studied.

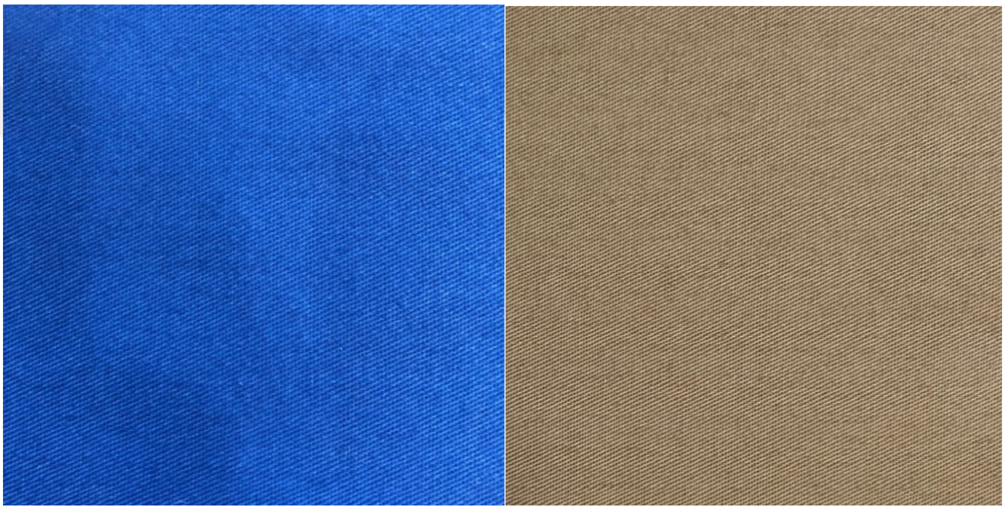


Figure 4.1 : The cotton fabrics used in this experiment are a)blue fabric, and b) beige fabric.

As stated in section 4.3.4.2, the fabrics were extracted and the foreign matter on them was determined. The blue fabric had approximately 0.20% foreign matter, whereas the beige fabric had nearly no foreign matter. Furthermore, the absorbency of both fabrics is less than 5 seconds.

4.1.2 Oil

Sosan Oil-Fine machine oil belonging to Sosan Industrial Machinery Oils company was used. Sosan oil is a mineral based oil. Chemical and Physical Properties of Sosan oil are as follows:

- Appearance: Clear bright liquid
- Flash Point (°C): min 180 °C
- Viscosity (40°C Cst): 14.4 - 33.0

- Viscosity (100°C Cst): 3.50 - 4.65
- Density (gr/cm^3): 0.833-0.885

4.1.2.1 Fourier transform infrared (FTIR) spectroscopy analysis of the Sosan oil

Figure 4.2 shows the spectrum of Sosan mineral oil over the entire wavelength range of 4000–650 cm^{-1}. Since the FTIR characteristic of Sosan oil corresponds to the mineral oil in paraffinic structure (long-chain alkanes), its main component is long-chain alkanes. The spectrums of simple alkanes display absorptions caused by stretching and bending of the C-H bonds. The stretching and bending bands of the C-C bonds are either too weak or have a frequency too low to be detected in infrared spectroscopy.

The peak identification of the sample is shown below.

- C–H stretch at 2921, 2852 cm^{-1}
- C–H bend or scissoring at 1462 cm^{-1}
- C–H rock, methyl at 1378 cm^{-1}
- C–H rock, methyl, seen only in long chain alkanes, at 722 cm^{-1}

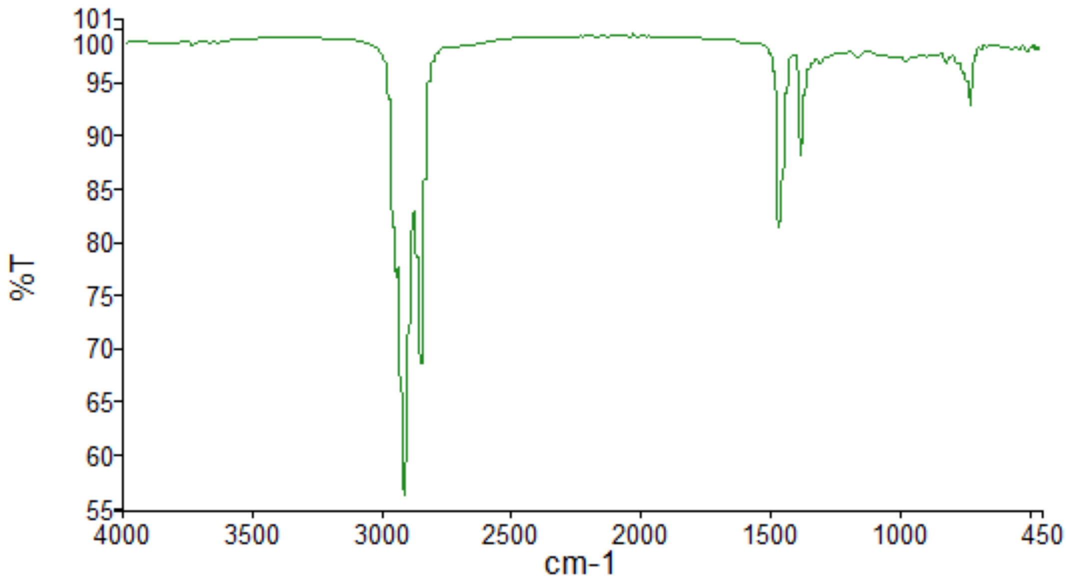


Figure 4.2 : FTIR characteristics of Sosan Oil.

4.1.2.2 Total petroleum hydrocarbons (TPH) analysis of the Sosan oil

Chromatograms generated from hydrocarbon fluids by gas chromatography with flame ionization detection (GC-FID) are interpreted to derive characteristic parameters.

Figure 4.3 shows the GC-FID chromatograms for a total petroleum hydrocarbon analysis of the Sosan Oil. The result demonstrates that Sosan oil is composed of hydrocarbons with carbon chains varying in length from 10 to 18 carbons.

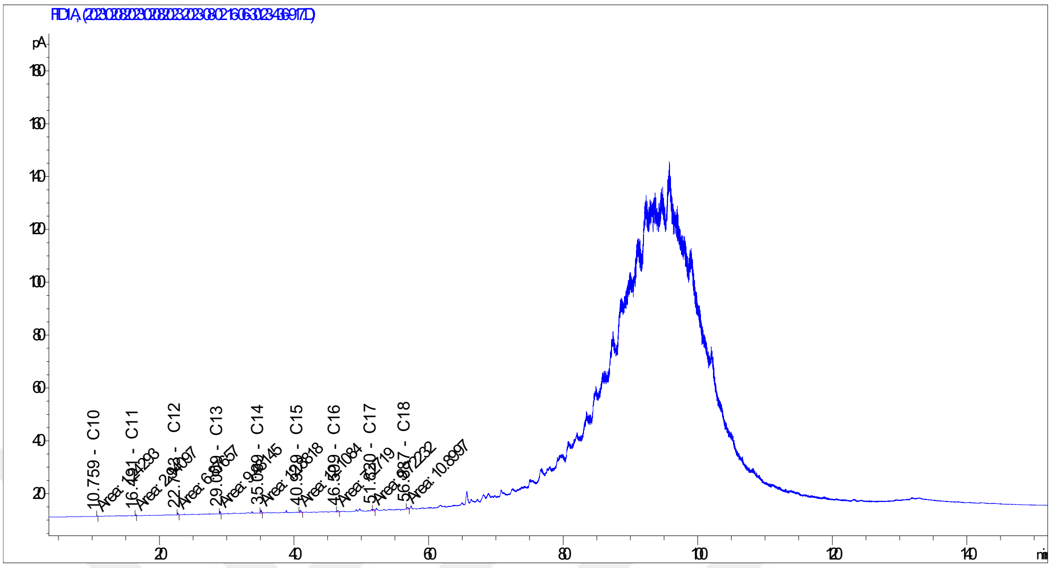


Figure 4.3 : The GC-FID chromatograms for a total petroleum hydrocarbon analysis of the Sosan oil.

4.1.3 Chemicals

In this study, nonionic surfactants were used as oil remover. Nonionic surfactants with spesification and properties used in this study can be listed as follows (Table 4.1). All chemicals used in this study are in liquid form and, have a concentration of 95% or greater.

Table 4.1 : Surfactants used in this experiment.

Chemical No	Chemical Name	Trade Name	Supplier	HLB	Cloud Point (°C)
1	C11–C13-alcohol polyethylene glycol ethers (9 EO) (Branched)	Marlipal 3190	Sasol	13.2	54-56
2	C11-alcohol polyalkylene glycol ethers (Alcohol-EO-PO-addition products)	Marlox 11027	Sasol	11.2	26-28
3	Alcohols, C12-14 ethoxylated propoxylated (5EO-4PO)	Dehypon LS54	BASF	unknown	30
4	C13-alcohol polyethylene glycol ethers (3 EO) (Branched)	Tridac Iso3	Sasol	8.1	50-52
5	C12–C14-alcohol polyethylene glycol ethers (7 EO)	Lorodac 7/24	Sasol	12.4	57-59

Table 4.1 (continued) : Surfactants used in this experiment.

Chemical No	Chemical Name	Trade Name	Supplier	HLB	Cloud Point (°C)
6	C11-alcohol polyalkylene glycol ethers (EO-PO addition)	Marlox 11009	Sasol	9.4	9-11
7	C13-alcohol polyethylene glycol ethers (5 EO) (Branched)	Lutensol TO5	BASF	10.5	66
8	C12–C15-alcohol polyethylene glycol ethers (3 EO) (Branched)	Lialet 125/3	Sasol	8.0	53-55
9	C12–C18-alcohol polyethylene glycol ethers (7 EO)	Novel 1218/7	Sasol	12	49-59
10	C12–C14-alcohol polyethylene glycol ethers (6 EO)	Lorodac 6/24	Sasol	11.5	41-42
11	C12–C14-alcohol polyethylene glycol ethers (3 EO)	Lorodac 3/24	Sasol	8.3	60-62
12	C12–C14-alcohol polyethylene glycol ethers (5 EO)	Tianol Ls5	Ataman	10.6	72-74

4.1.3.1 C11–C13-alcohol polyethylene glycol ethers (9 EO) (branched)

Marlipal 3190 with the chemical description C11–C13-alcohol polyethylene glycol ethers (9 EO) is from Sasol Limited. Marlipal 3190 is a fatty alcohol polyethyleneglycol ether containing branched and linear C11 alcohol - branched C13 alcohol and 9 moles of ethylene oxide. Its chemical formula is as follows:

$$R - CH_2 - O - (CH_2 - CH - O)_3 - H$$

$$R{=}C_{10}H_{21} \text{ or } C_{12}H_{25}$$

4.1.3.2 C11-alcohol polyalkylene glycol ethers (alcohol-EO-PO-addition products)

Marlox 11027 is a fatty alcohol poly-glycol ether, ethylene oxide and propylene oxide from Sasol Limited.

4.1.3.3 Alcohols, C12-14 ethoxylated propoxylated (5EO-4PO)

Dehypon LS54 is fatty alcohol C12 - C14 with approx. 5 moles EO and approx. 4 moles PO. It is also suitable for cleaning at high temperatures (above 60°C). The cloud point is 30°C and very little foam forms above this temperature. Its chemical formula is as follows:

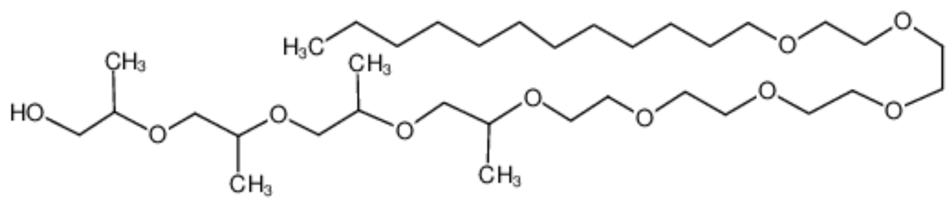


Figure 4.4 : Molecular structure of dehypon LS54

4.1.3.4 C13-alcohol polyethylene glycol ethers (3 EO) (Linear)

Tridac Iso-3 is a based fatty alcohol polyethyleneglycol ether from Sasol Limited. It consists of a combination of alcohol polyethyleneglycol with 13 carbon and 3 moles of ethylene oxide. Its chemical formula is as follows:

$$R - CH_2 - O - (CH_2 - CH - O)_3 - H$$

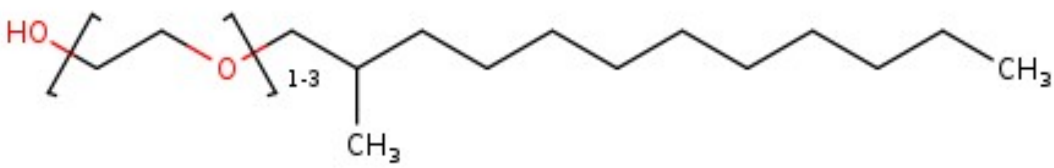


Figure 4.5 : Molecular structure of Tridac Iso-3.

4.1.3.5 C12–C14-alcohol polyethylene glycol ethers (7 EO)

Lorodac 7-24 is a fatty alcohol polyethyeleneglycol ether based on 12 and 14 numbers of carbon and 7 moles ethylene oxide. The chemical structure is the following:

$$R - CH_2 - O - (CH_2 - CH - O)_7 - H$$
$$R{=}C_{11}H_{23} \text{ or } C_{13}H_{27} \text{ (linear)}$$

4.1.3.6 C11-alcohol polyalkylene glycol ethers (EO-PO addition)

Marlox 11009 is a fatty alcohol poly-glycol ether, ethylene oxide and propylene oxide from Sasol Limited.

4.1.3.7 C13-alcohol polyethylene glycol ethers (5 EO) (Branched)

Lutensol TO 5 is based on a saturated iso-C13- alcohol with 5 moles ethylene oxide from BASF.

4.1.3.8 C12–C15-alcohol polyethylene glycol ethers (3 EO) (Branched)

Lialet 125-3 is a fatty alcohol polyethyleneglycol ether from Sasol Limited. It consists of a combination of alcohol polyethyleneglycol with 11, 12, 13 and 14 carbon (mixture of linear and mono-branched) and 3 moles of ethylene oxide. Its chemical formula is as follows:

$$R - CH_2 - O - (CH_2 - CH - O)_3 - H$$

R= $C_{11}H_{23}$ or $C_{12}H_{25}$ or $C_{13}H_{27}$ or $C_{14}H_{29}$ (mixture of linear and mono-branched).

4.1.3.9 C12 to C18 alcohol polyethylene glycol ethers with 7 ethylene oxide units

NOVEL 1218-7 Ethoxylate is with the following structural formula: CH3(CH2)xCH2(OCH2CH2)7OH where 'x' varies between 12 and 18 and 7 moles of ethylene oxide.

4.1.3.10 C12–C14-alcohol polyethylene glycol ethers (6 EO)

Lorodac 6-24 is a fatty alcohol polyethyleneglycol ether from Sasol Limited. It consists of a combination of alcohol polyethyleneglycol with 12 and 14 carbon (linear structure) and 3 moles of ethylene oxide. Its chemical formula is as follows:

$$R - CH_2 - O - (CH_2 - CH - O)_6 - H$$

R= $C_{11}H_{23}$ or $C_{13}H_{27}$ (linear)

4.1.3.11 C12–C14-alcohol polyethylene glycol ethers (3 EO)

Lorodac 3-24 is a fatty alcohol polyethyleneglycol ether from Sasol Limited. It consists of a combination of alcohol polyethyleneglycol with 12 and 14 carbon (linear structure) and 3 moles of ethylene oxide. Its chemical formula is as follows:

$$R - CH_2 - O - (CH_2 - CH - O)_3 - H$$

R= $C_{11}H_{23}$ or $C_{12}H_{25}$ or $C_{13}H_{27}$ (linear)

4.1.3.12 C12–C14-alcohol polyethylene glycol ethers (5 EO)

Tianol LS5 is based on a primary linear C12-C14 fatty alcohol with approx. 5 moles ethylene oxide.

4.2 Devices

The devices used during the preparation and washing of fabrics are Precisa XB 220A scale, Gyrowash, iron and steam iron. Perkin Elmer FTIR Spectrum Two and Agilent 6850 GC-FID devices are used to analyze mineral oil to be dropped on fabrics. Datacolor 3890 is the spectrophotometer device used in this study to evaluate the oil removal performance of chemicals.

Figure 4.6 : Gyrowash.

Figure 4.7 : Datacolor 3890 for spectrophotometer.

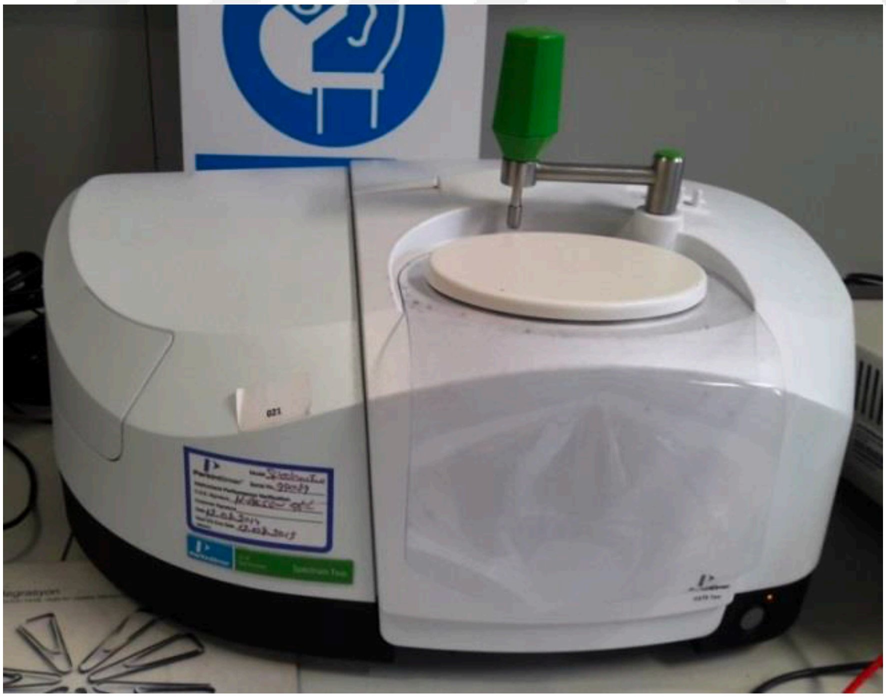


Figure 4.8 : Perkin Elmer FTIR Spectrum Two.

Figure 4.9 : Agilent 6850 GC-FID Device.

4.3 Method

4.3.1 Fabric pretreatment and the soiling procedure

The hydrophilicity of the fabrics was checked by dropping water. The blue fabric absorbed water faster than the beige fabric; this may be a result of the water repellent finish on the beige. Fabrics were washed with detergent and ironed. After processing, both fabrics had good absorbency.

The following fabric samples were prepared for this experiment:

Pieces of beige fabric, each of them approximately 5,5 g, cut square shaped.

Pieces of blue fabric, each of them approximately 5,5 g, cut square shaped.

Sosan oil has been used for staining samples by dripping 10, 5, 3, 2, and 1 drips of oil for each spot. In order to observe and compare their suitability for the experiment, a batch of samples was put in the oven (70 °C, for 30 min) and another batch was left to dry. The spread of 1 dripped sample was optimal for spectrophotometer evaluation and closer to real stain spread.

Each fabric samples have been stained by dripping oil: 4 drips on each corner and after they are cut to 4 pieces. Stains on corners were suitable for spectrophotometer.

Figure 4.10 : Oil drip through fabric check by weighing.

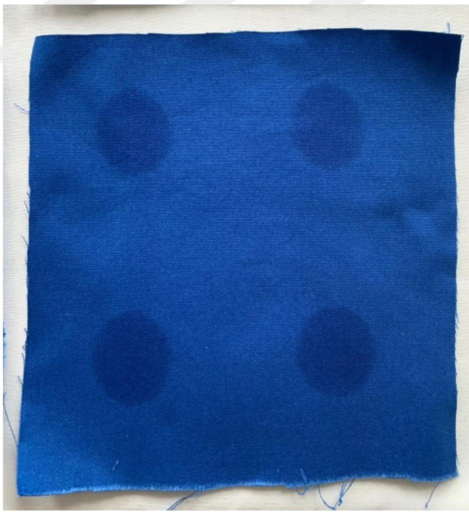


Figure 4.11 : Stained blue fabric before cut to 4 pieces.

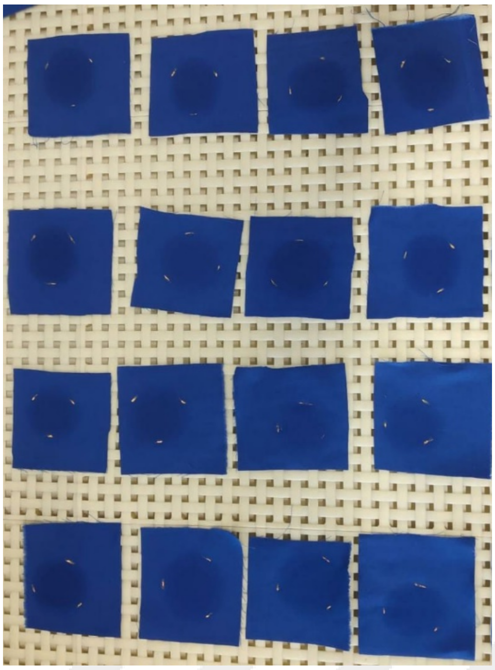


Figure 4.12 : Blue samples to be washed.

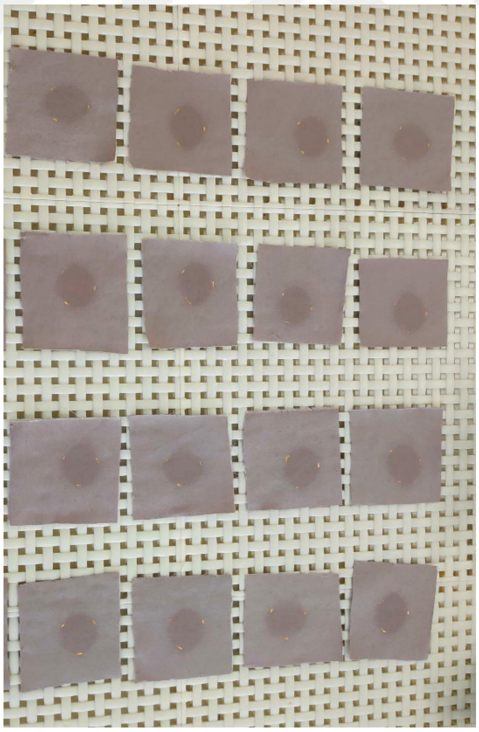


Figure 4.13 : Beige samples to be washed.

4.3.2 Drying procedure

After the fabrics were oiled, they were exposed to different drying methods. Considering the conditions that blue fabrics and beige fabrics may be exposed to during different production stages, 3 different drying methods were applied to each.

- Hand ironing process is done with the cotton fabric mode of the iron, applying heat and pressure for 30 seconds for each sample at the temperature 180°C-220°C.
- Steam ironing process is done with the cotton fabric mode of the iron, applying heat and pressure for 30 seconds for each sample at the temperature 180°C-220°C.
- Some of the samples were allowed to dry on their own by hanging them at room temperature for at least 24 hours.

4.3.3 Washing procedure

In the Gyrowash, the bath is adjusted to pH 10 by adding soda. A 1:20 liquor ratio was used. The oil remover solution was set to 2 g/l concentration.

Fabrics that have been oiled and dried by different methods are washed using a Gyrowash machine consisting of 8 tubes. Four samples of the same color fabric are placed in each tube. Only one surfactant was used in each tube. Thus, the washing performances of different surfactants were determined. Washing is carried out separately at 2 different temperatures: 40ºC and 60ºC. Washings take 45 minutes.

Figure 4.14 : Sample placement into the Gyrowash tubes.

Figure 4.15 : Gyrowash washing.

4.3.4 Examining the oil removal performance values

After the oiled fabrics are washed and dried, the oil removal performance is evaluated with a spectrophotometer device and soxhlet extraction device.

4.3.4.1 Spectrofotometer

The color values of fabric samples were assessed using a Datacolor 3890 spectrophotometer (Datacolor International, USA) under D65 illuminant conditions with a 10-degree angle standard observer. The measurements excluded the ultraviolet (UV) component and included the specular component. Each sample, folded twice, underwent four measurements with a 90° sample rotation before each reading, and the average of these four measurements was computed. After washing the greased fabrics and drying, the stain formation is evaluated with the spectrophotometer tool Datacolor 3890. ColorTools QC, as the color quality control software, is used and Standard KS, KSB and CIE outputs are examined. The differences between standard and batch X, Y, Z, L*, a*, b*, C*, h values are also evaluated and displayed as a table later.

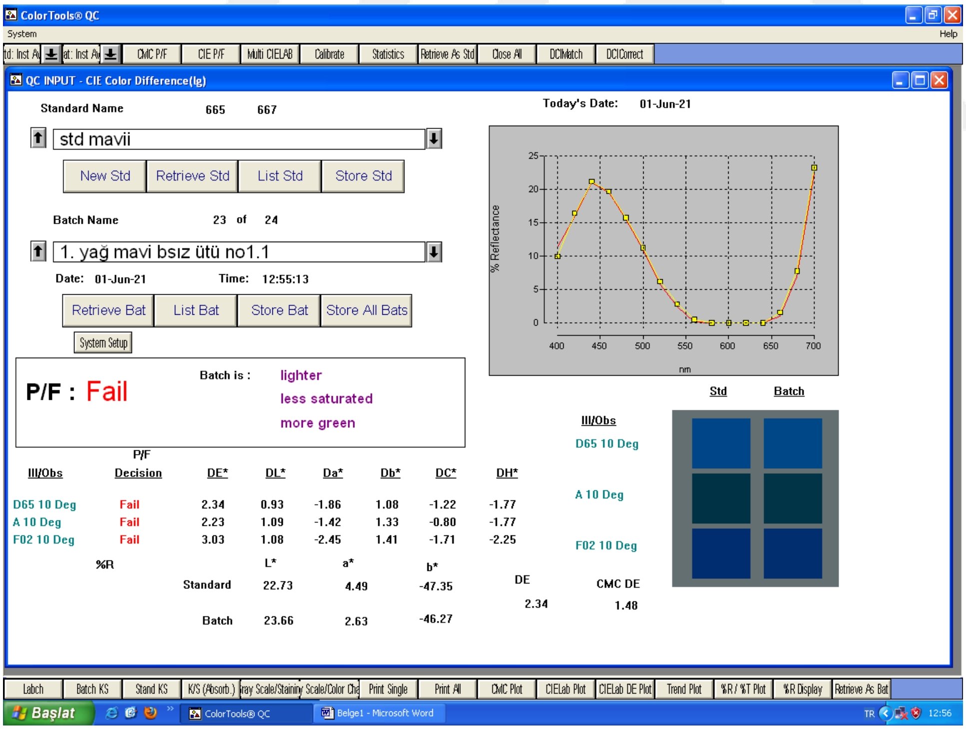


Figure 4.16 : ColorTools QC graphic.

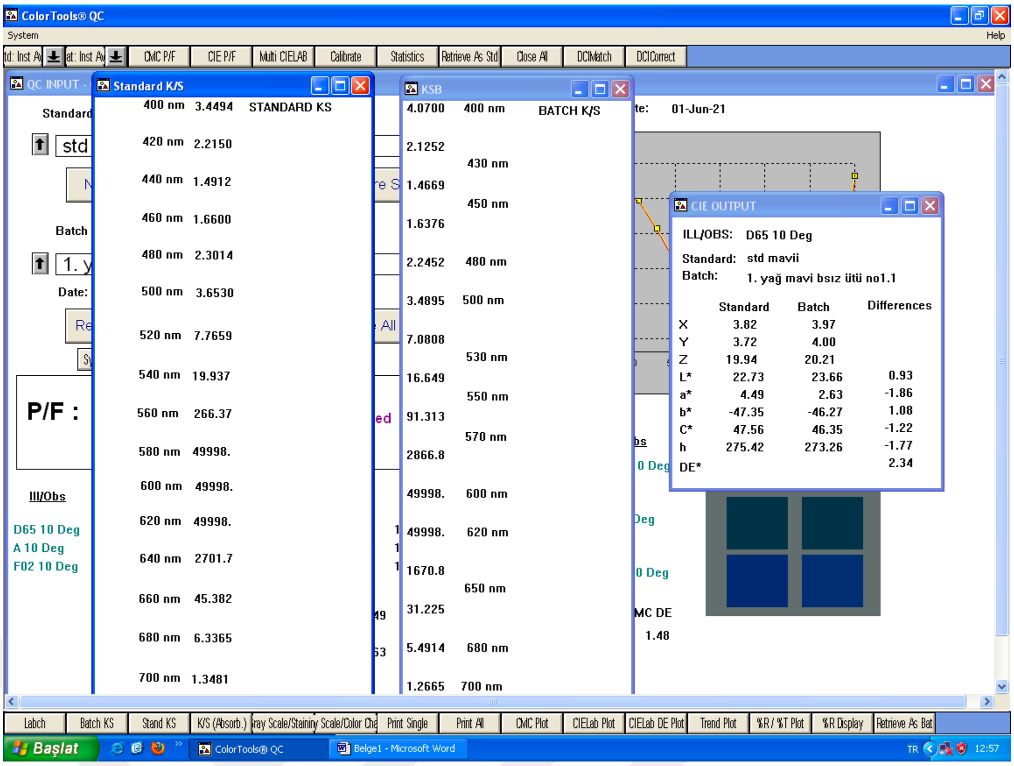


Figure 4.17 : ColorTools QC measured values

In Figure 4.16 and 4.17, the first batch of blue cotton fabric, soiled with Sosan Oil, subjected to hand ironing fixation with no steam, is shown as image from the ColorTools QC software. The evaluation is done, using the Instrument Average mode.

Finally, the oil removal percentage is calculated by the formula (4.1);

$$\text{Oil Removal (\%)} = \frac{Y_2 - Y_1}{Y - Y_1} \tag{4.1}$$

Y_1= tristimulus Y value of soiled fabric before washing.

Y_2= tristimulus Y value of soiled fabric after washing.

Y= tristimulus Y value of unsoiled fabric before washing.

4.3.4.2 Soxhlet extraction

Soxhlet extraction is a widely used method for extracting solid and liquid substances. It follows the principle of reversing the flow and siphoning the solvent, ensuring continued extraction of the required components from the material. When the liquid level of the solvent goes above the siphon of the Soxhlet extractor, the solvent will flow back into the round-bottom flask, and the siphon occurs. The Soxhlet extraction setup and apparatus are described in Figure 4.18.

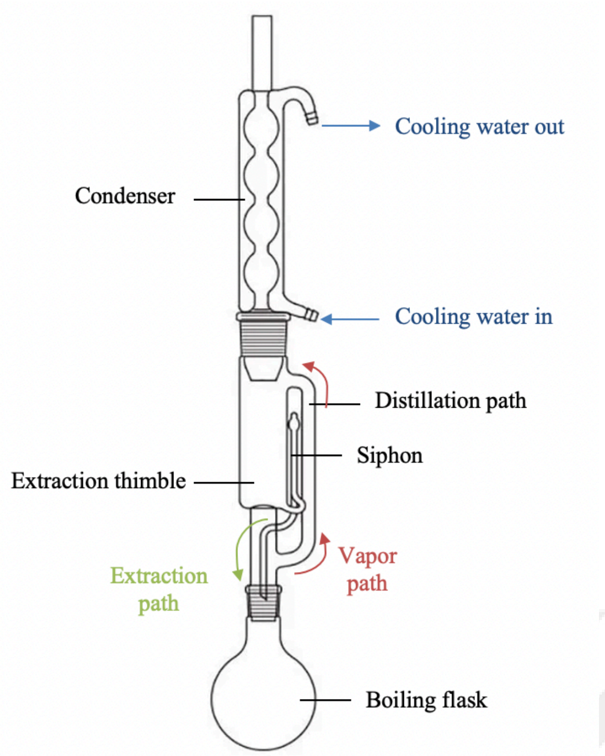


Figure 4.18 : Schematic of the Soxhlet extraction apparatus used to remove excess oil.

The sample is dried in a tared weighing container in an oven at 105 ± 3°C for 1 hour. Then it is cooled in a desiccator and weighed. This drying, cooling and weighing process is repeated until the change in the sample's mass in two successive weighings, which are carried out with a 30-minute gap, is within 0.01%. For the next part, the sample are placed in the Soxhlet device. The solvent is added in a way that it overflows, and about 25% extra solvent is added to ensure it doesn't evaporate quickly. The temperature is adjusted to 3 to 5 siphons per hour and samples are removed for at least 20 siphons. After extractions, the fabric sample is dried in open air and dried in an oven using the same procedure and cooled in a desiccator and weighed. Determine the mass of a weighing bottle to 0.001 g.

Soxhlet extraction was used for two purposes in this study. In its first application, the extractable substance on both fabrics used in the study was determined in accordance with the purpose of ASTM D2257-98 (reapproved 2012) Standard Test Method for Extractable Matter in Textiles, as described above. Using Equation 4.2, the amount of solvent extractable material was calculated for each sample.

$$S_d = \frac{W_1 - W_2}{W_1} \tag{4.2}$$

where:

S_d = Solvent extractable material from fabric.

W_1 = Oven-dried mass of specimen before solvent extraction, g,

W_2 = Oven-dried mass of specimen after solvent extraction,g.

Another purpose of using extraction is to calculate the oil removal performance of the chemical for each fabric sample oiled and washed with a chemical. It is extracted for the oil remaining on the washed fabric. This is the amount of oil that the chemical cannot remove. Using Equation 4.3, the oil removal percentage was calculated for each sample.

$$\text{Oil removal (\%)} = \left(1 - \frac{W_3 - W_4}{o}\right) * 100 \tag{4.3}$$

o = amount of oil added to the fabric, g.

W_3= Oven-dried mass of washed fabric before solvent extraction, g.

W_4= Oven-dried mass of washed fabric after solvent extraction, g.

However, extractable materials from the sample itself should be taken into account with equation 4.3. The equation can be updated as equation 4.4.

$$\text{Oil removal (\%)} = \left(1 - \frac{W_3 - W_4 - W_3 S_D}{o}\right) * 100 \tag{4.4}$$

5. RESULTS

5.1 Preliminary Experimental Results

Preliminary studies include testing the washing temperature and determining the oil removal performance of the chemicals included in the study at this temperature with a spectrophotometer, and how different drying methods (fixation) applied to the oiled fabric affect the oil removal performance. Table 5.1 and Table 5.2 give the oil removal percentages determined by spectrophotometer for blue and beige fabric, respectively.

Table 5.1 : Blue fabric spectrophotometer results at 40^{o}C.

Chemical No	Chemical Name	Trade Name	Oil Removal (%)			
			Steam Iron	Hand Iron	Hanging	Average
1	C11–C13-alcohol polyethylene glycol ethers (9 EO) (Branched)	Marlipal 3190	61.3	99.99	96.27	85.85
2	C11-alcohol polyalkylene glycol ethers (Alcohol-EO-PO-addition products)	Marlox 11027	39.89	64.90	35.81	46.87
3	Alcohols, C12-14 ethoxylated propoxylated (5EO-4PO)	Dehypon Ls54	48.13	39.73	51.72	46,52
4	C13-alcohol polyethylene glycol ethers (3 EO) (Branched)	Tridac Iso3	43.43	51.12	33.81	42,78
5	C12–C14-alcohol polyethylene glycol ethers (7 EO)	Lorodac 7/24	89.89	39.22	40.89	56.67
6	C11-alcohol polyalkylene glycol ethers (EO-PO addition)	Marlox 11009	42.70	54.21	65.77	54.22
7	C13-alcohol polyethylene glycol ethers (5 EO) (Branched)	Lutensol TO5	50.94	49.61	61.23	53.93
8	C12–C15-alcohol polyethylene glycol ethers (3 EO) (Branched)	Lialet 125/3	16.9	17.25	9.82	14.65
9	C12–C18-alcohol polyethylene glycol ethers (7 EO)	Novel 1218/7	38.95	45.69	33.05	39.23
10	C12–C14-alcohol polyethylene glycol ethers (6 EO)	Lorodac 6/24	45.32	37.84	36.02	39.73
11	C12–C14-alcohol polyethylene glycol ethers (3 EO)	Lorodac 3/24	42.13	40.59	33.69	38.80
12	C12–C14-alcohol polyethylene glycol ethers (5 EO)	Tianol Ls5	41.20	49.79	26.91	39.30

Considering the chemicals collectively, inconsistent results were obtained for beige and blue fabrics were evaluated based on their fixation degrees. For instance, Lorodac 7/24, which removes 89.89% of the oil in steam ironed blue fabric, has a low oil removal rate in hand ironed and hanging dried fabrics (39.22% and 40.89%, respectively). Marlox 11027 demonstrated its highest performance in washes in which both fabrics were hand ironed. Interestingly, among the chemicals, only Lutensol TO5 showed its best performance on hanging dried blue fabrics. Generally, it can be said that it is easier to remove oil at 40^{o}C from treated (steam iron or hand iron) blue fabric for most chemicals. However, this statement does not hold true for beige fabric.

Table 5.2 : Beige fabric spectrophotometer results at 40^{o}C.

Chemical No	Chemical Name	Trade Name	Steam Iron	Normal Iron	Hanging	Average
1	C11–C13-alcohol polyethylene glycol ethers (9 EO) (Branched)	Marlipal 3190	58.60	67.94	61.35	64.83
2	C11-alcohol polyalkylene glycol ethers (Alcohol-EO-PO-addition products)	Marlox 11027	53.63	72.26	54.61	66.05
3	Alcohols, C12-14 ethoxylated propoxylated (5EO-4PO)	Dehypon Ls54	65.64	67.67	62.81	66.99
4	C13-alcohol polyethylene glycol ethers (3 EO) (Branched)	Tridac Iso3	65.43	66.93	64.89	66.43
5	C12–C14-alcohol polyethylene glycol ethers (7 EO)	Lorodac 7/24	70.53	70.47	60.90	70.49
6	C11-alcohol polyalkylene glycol ethers (EO-PO addition)	Marlox 11009	53.04	60.64	58.24	57.31
7	C13-alcohol polyethylene glycol ethers (5 EO) (Branched)	Lutensol TO5	68.89	64.91	60.99	66.24
8	C12–C15-alcohol polyethylene glycol ethers (3 EO) (Branched)	Lialet 125/3	54.93	59.53	68.04	58.00
9	C12–C18-alcohol polyethylene glycol ethers (7 EO)	Novel 1218/7	63.53	66.93	73.14	65.79
10	C12–C14-alcohol polyethylene glycol ethers (6 EO)	Lorodac 6/24	44.27	65.37	68.44	58.34
11	C12–C14-alcohol polyethylene glycol ethers (3 EO)	Lorodac 3/24	71.54	68.14	59.62	69.28
12	C12–C14-alcohol polyethylene glycol ethers (5 EO)	Tianol Ls5	70.95	73.78	59.84	68.19

The important factor considered is the oil removal abilities of wetting agents for creating a surfactant recipe. Table 5.3 provides a comparison of the oil removal capabilities from blue fabric of different wetting agents. Although the chemicals listed in this table are not primarily intended for oil removal, they can still be helpful in the process. For comparison, hanging dried fabrics were taken into account. When it comes to removing oil from beige fabric, the wetting agents perform significantly better compared to their performance on blue fabric (34.46%), with an average of 63.71%. The difference in oil removal performance is particularly noticeable on the blue fabric, and the wetting agent with the chemical name C11-alcohol polyalkylene glycol ethers (EO-PO addition), also known as Marlox 11009, performs the best.

Table 5.3 : Oil removal performances of wetting agents determined by spectrophotometer.

Wetting Agent No	Chemical Name	Trade Name	Stain Removal (%) avg.
1	C13-alcohol polyethylene glycol ethers (3 EO) (Branched)	Tridac-Iso3	33.81
2	C12–C15-alcohol polyethylene glycol ethers (3 EO) (Branched)	Lialet 125-3	9.82
3	C11-alcohol polyalkylene glycol ethers (EO-PO addition)	Marlox 11009	65.77

When examining the blue fabric, it was observed that it was harder to remove oil from it. After Marlipal 3190, the best performers for all drying methods were Lutensol TO5 and Dehypon LS54. They both have similar carbon chain length and the same number of ethoxylates. Lutensol TO5 is alcohol ethoxylate, while Dehypon LS54 (alcohol ethoxylate-propoxhlate) is notable for its performance with its different structure. When aiming to create a surfactant mixture for removing oil, the use of surfactants with different structures provides a more effective result.

Table 5.4 : Oil removal percentages of chemicals in ironed and hanging dried blue fabrics.

Fixation	Trade Name	Oil Removal (%) avg.
Hand Ironing	Marlox 11009	54.21
Hand Ironing	Marlipal 3190	99.99
Hand Ironing	Dehypon LS54	39.73
Hanging	Marlox 11009	65.77
Hanging	Marlipal 3190	96.27
Hanging	Dehypon LS54	51.72

The chemicals compared in Table 5.4 are the three chemicals determined to be included in a surfactant recipe. Marlipal 3190 showed oil removal performance of 99.99% in hand ironing and 96.27% in hanging drying. For Marlipal 3190, which is a branched alcohol ethoxylated, the result is close to excellent in both drying types. The high degreasing performance of Marlipal 3190 is due to its high ethylene oxide number (9EO). Thus, it has a high HLB value and is expected to show good grease removal performance. Besides its superior performance, Marlipal 3190 has very high foam, which limits its use in industry.

The reasons for choosing Dehypon LS54 as the second surfactant are that it is an EO-PO derivative, has low foam and its HLB value is lower than marlipal 3190. This indicates that Dehypon LS54 is a suitable chemical for this oil, especially considering that HLB value of 10 is required to remove mineral oil. Dehypon LS54 showed a degreasing performance of 39.73% in hand ironing and 51.72% in hanging drying. The performance of Dehypon LS54 is higher in hang drying. For Dehypon LS54, it can be said that more fixed stains will be more difficult to remove. Fixing the stain negatively affected its performance. There are differences in the performance of Marlox 11009 in two different drying methods. Fixing the stain negatively affected its performance.

Considering that all 40^{o}C results were evaluated, some wetting agents significantly contributed to oil removal. Besides this, comparing the oil removal performances for different treated oils is not clear. On the blue fabric, the best oil removal was achieved when ironed with a steam iron, and on the beige fabric, the best oil removal was achieved on the fabric ironed with a hand iron.

It is obvious that the washing temperature remains below the cloud point (can be seen in Table 4.1) for most of the chemicals and they do not exhibit the best oil removal performance. For this reason, the study continued by washing at 60^{o}C.

5.2 Effect of Drying Method on Oil Removal Performance of Surfactants

After soiling, oily soil does not become fixed on the fabric left to hang dry; however, it is assumed that the soil becomes fixed when the fabric is ironed with a normal iron or a steam iron. The steam iron, with its steam, allows the oil to penetrate the fabric more deeply compared to a normal iron, causing the stain to become more firmly attached to the fabric.

Table 5.5 shows the variation of the values obtained from the spectrophotometer according to the methods by which the fabrics are treated after soiling. The standard sample is an unsoiled and untreated fabric, and when the Y value is accepted as 100, the Y value of the fixed fabrics is calculated proportionally. The Y value for blue fabric decreased more than for beige.

Table 5.5 : Spectrophotometer values of unsoiled and soiled treated with different methods.

Fabric	Blue Fabric				Beige Fabric			
	Tristimulus Y	L	a	b	Tristimulus Y	L	a	b
Standard sample	3.98 (100)	23.6	2,78	-46.35	25.95 (100)	57.99	5.86	16.89
Steam ironed unwashed fabric	2.4 (60.3)	17.58	9.17	-45.87	18.52 (71.4)	50.13	6.67	18.44
Normal ironed unwashed fabric	2.35 (59)	17.20	9.78	-45.96	18.45 (71.1)	50.04	6.55	18.84
Hanging dried unwashed fabric	2.25 (56.5)	16.69	10.48	-45.96	18 (69.4)	49.50	6.73	19.01

5.3 Spectrophotometer Results of Oil Removal Process at 60^{o}C

Table 5.6 and Figure 5.1 display the percentages of oil removal obtained from spectrophotometer results for each chemical used on the blue fabric. When the fabrics were left to hang dry after soiled, the average oil removal for all chemicals was 47.29%. However, when the fabrics were normal ironed or steam ironed after the oil soiling, the average oil removal for all chemicals was 42.67% and 43.58%, respectively. Oil soils were easier to remove when the fabrics were left to hang dry without any fixation, but there were no notable differences between the methods. The most effective chemical to remove oil from each of the different treated fabrics is to use Lutensol TO5. Lutensol TO5 is a chemical compound with the name C13-alcohol polyethylene glycol ethers (5 EO) (Branched). The chemical that has the lowest average oil removal rate is Marlox 11009, which is known as C11-alcohol polyalkylene glycol ethers (EO-PO addition). Marlox 11009 has the lowest percentage of effectiveness when used with steam ironed and hanging dried fabrics, but it is not the least effective when used with fabrics applied hand iron.

Table 5.6 : Blue fabric spectrophotometer results at 60^{o}C.

Chemical No	Chemical Name	Trade Name	Steam Iron	Normal Iron	Hanging	Average
1	C11–C13-alcohol polyethylene glycol ethers (9 EO) (Branched)	Marlipal 3190	48.87	52.14	56.61	52.54
2	C11-alcohol polyalkylene glycol ethers (Alcohol-EO-PO-addition products)	Marlox 11027	31.67	34.10	46.12	37.30
3	Alcohols, C12-14 ethoxylated propoxylated (5EO-4PO)	Dehypon Ls54	39.87	36.39	48.28	41.51
4	C13-alcohol polyethylene glycol ethers (3 EO) (Branched)	Tridac Iso3	35.21	44.50	41.38	40.36
5	C12–C14-alcohol polyethylene glycol ethers (7 EO)	Lorodac 7/24	43.41	45.41	45.69	44.84
6	C11-alcohol polyalkylene glycol ethers (EO-PO addition)	Marlox 11009	31.51	39.30	27.30	32.70
7	C13-alcohol polyethylene glycol ethers (5 EO) (Branched)	Lutensol TO5	74.44	58.26	69.11	67.27
8	C12–C15-alcohol polyethylene glycol ethers (3 EO) (Branched)	Lialet 125/3	37.62	37.16	45.98	40.25
9	C12–C18-alcohol polyethylene glycol ethers (7 EO)	Novel 1218/7	46.14	38.84	45.40	43.46
10	C12–C14-alcohol polyethylene glycol ethers (6 EO)	Lorodac 6/24	36.66	45.11	47.70	43.15
11	C12–C14-alcohol polyethylene glycol ethers (3 EO)	Lorodac 3/24	48.39	42.66	48.56	46.54
12	C12–C14-alcohol polyethylene glycol ethers (5 EO)	Tianol Ls5	49.20	38.23	45.40	44.27

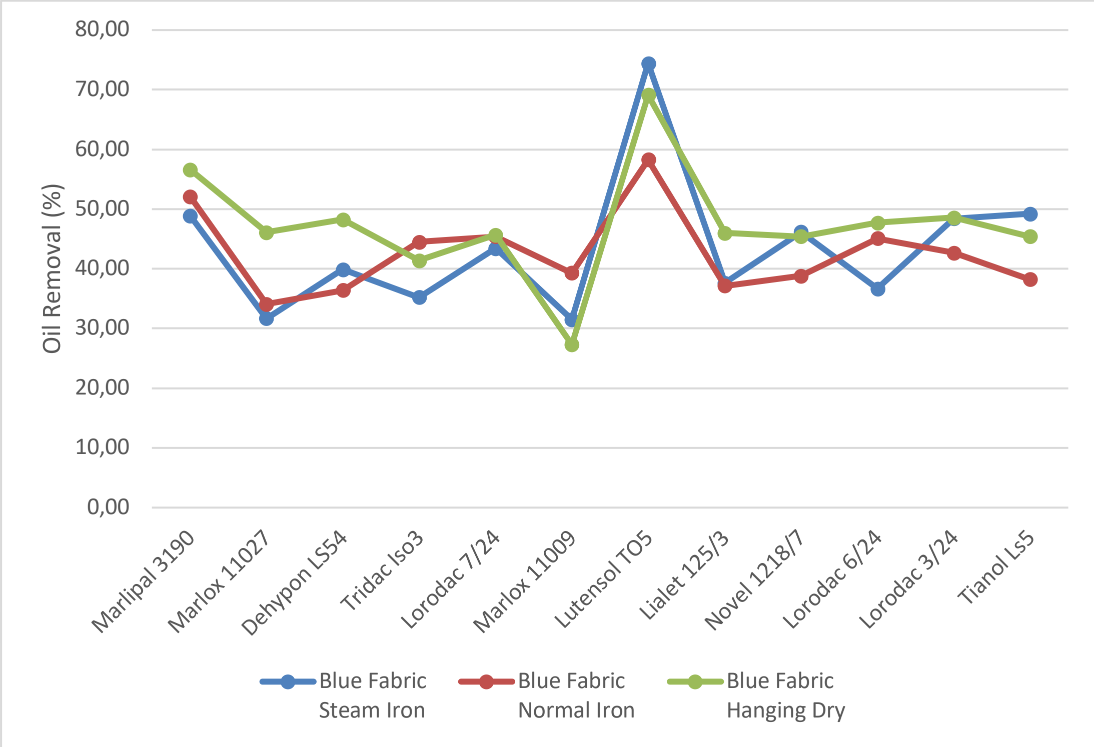


Figure 5.1 : Blue fabric spectrophotometer results at 60ºC.

Table 5.6 and Figure 5.2 displays the percentages of oil removal obtained from spectrophotometer results for each chemical used on the beige fabric.

When the fabrics were left to hang dry after soiled, the average oil removal for all chemicals was 73.53%. However, when the fabrics were normal ironed or steam ironed after soiling, the average oil removal for all chemicals was 69.30 and 62.77, respectively. Removing oil soils was easier when fabrics were left to hanging dry without any fixation. However, as fixation increased, removing oil soil became more difficult.

There are various chemicals that are effective in removing oil from different types of treated beige fabrics. Among them, Lorodac 3/24 shows the highest oil removal percentage of 71.52% when steam ironing is used on oiled fabric. Lutensol TO5 performs well with a percentage of 79.83% when normal ironing is applied, and Lorodac 7/24 achieves 80.89% when hanging dry is used. When considering all the processes, Lutensol TO5 proves to be the best with an average oil removal percentage of 75.91%. The chemical with the lowest average oil removal rate also on beige fabric is Marlox 11009, known as C11-alcohol polyalkylene glycol ethers (EO-PO addition). In contrast to the situation on the blue fabric, Marlox 11009 exhibited the lowest percentage oil removal of all drying methods on the beige fabric.

Table 5.7 : Beige fabric spectrophotometer results at 60°C.

Chemical No	Chemical Name	Trade Name	Steam Iron	Normal Iron	Hanging	Average
1	C11–C13-alcohol polyethylene glycol ethers (9 EO) (Branched)	Marlipal 3190	66.30	76.43	73.09	71.94
2	C11-alcohol polyalkylene glycol ethers (Alcohol-EO-PO-addition products)	Marlox 11027	58.32	55.55	65.22	59.70
3	Alcohols, C12-14 ethoxylated propoxylated (5EO-4PO)	Dehypon Ls54	53.30	61.99	68.81	61.36
4	C13-alcohol polyethylene glycol ethers (3 EO) (Branched)	Tridac Iso3	65.08	73.26	76.27	71.54
5	C12–C14-alcohol polyethylene glycol ethers (7 EO)	Lorodac 7/24	65.25	66.82	80.89	70.99
6	C11-alcohol polyalkylene glycol ethers (EO-PO addition)	Marlox 11009	45.12	60.09	63.55	56.25
7	C13-alcohol polyethylene glycol ethers (5 EO) (Branched)	Lutensol TO5	69.53	79.83	78.38	75.91
8	C12–C15-alcohol polyethylene glycol ethers (3 EO) (Branched)	Lialet 125/3	60.98	64.92	74.38	66.76
9	C12–C18-alcohol polyethylene glycol ethers (7 EO)	Novel 1218/7	71.36	74.59	76.30	74.08
10	C12–C14-alcohol polyethylene glycol ethers (6 EO)	Lorodac 6/24	58.86	72.19	74.82	68.62
11	C12–C14-alcohol polyethylene glycol ethers (3 EO)	Lorodac 3/24	71.52	77.26	77.02	75.27
12	C12–C14-alcohol polyethylene glycol ethers (5 EO)	Tianol Ls5	67.68	68.62	73.69	70.00

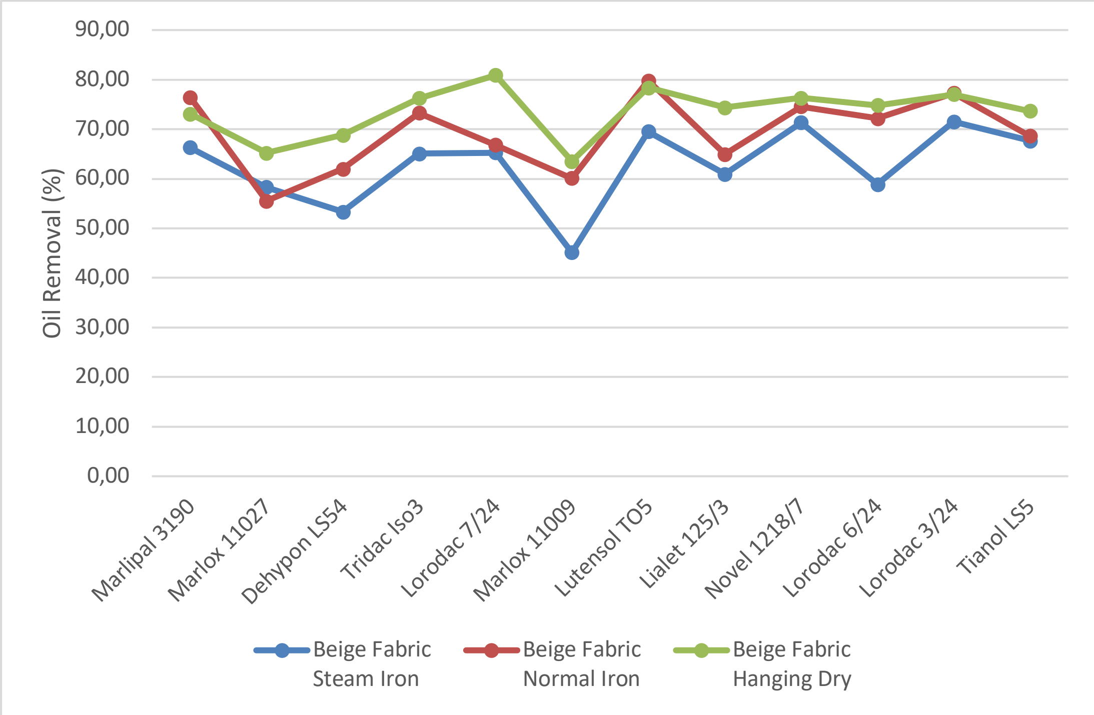


Figure 5.2 : Beige fabric spectrophotometer results at 60ºC.

When comparing the average oil removal values of each chemical for blue fabric and beige fabric, Figure 5.3 is obtained. It can be observed that the beige fabric has better oil removal performance than the blue fabric. According to the results obtained with the spectrophotometer, the lowest and highest values for the beige fabric are 59.70% and 75.91%, respectively. On the other hand, the values for the blue fabric range from 32.70% to 67.27%. These results indicate that the beige fabric shows a narrower range and higher values compared to the blue fabric.

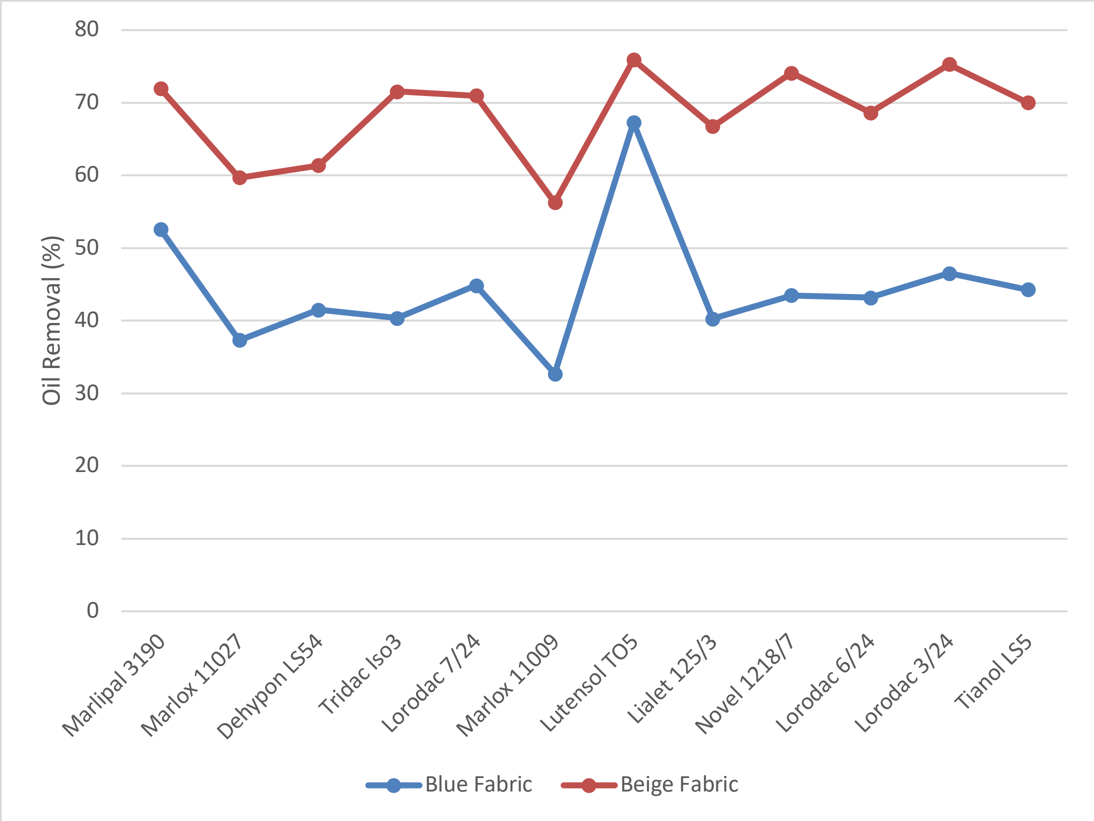
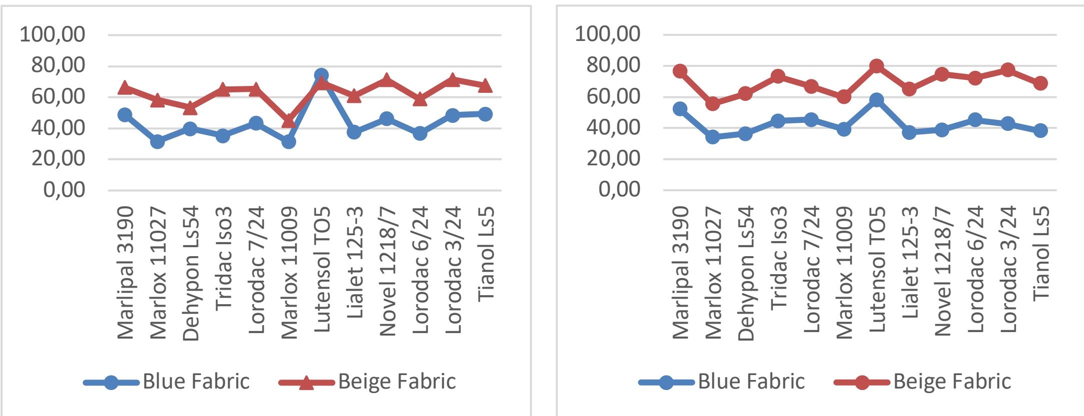


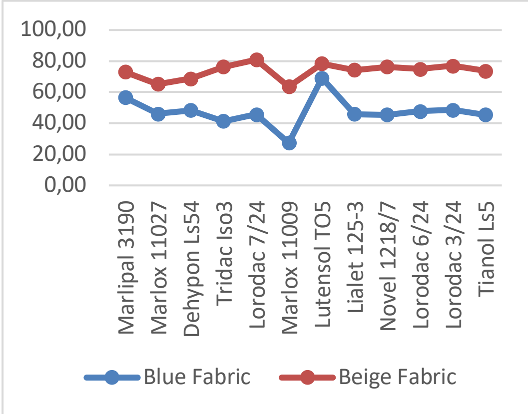
Figure 5.3 : Comparison of average oil removal percentages obtained by spectrophotometer for blue fabric and beige fabric.

For different drying methods of soiled fabric, the oil removal percentages of chemicals in blue and beige fabric were compared as shown in Figure 5.4.



a) Steam iron

b) Normal iron



c) Hanging dry

Figure 5.4 : Oil removal performances of chemicals for blue and beige fabric for each drying method: a) steam iron, b) hand iron, c) hanging dry.

5.4 Extraction Results of Oil Removal Process at 60ºC

Table 5.7 lists the oil removal percentages determined by extraction from blue and beige fabrics that were hanging dried and washed with chemicals. The chemical that has the highest percentage of oil removal is Lorodac 24/7, with 81.14% for blue fabric and 80% for beige fabric. The chemical that had the lowest percentage of oil removal was identified as Marlox 11009 for beige fabric, and Tridac ISO3 for blue fabric. The average percentage of oil removal from blue fabric is 54.14%, while the average percentage of oil removal from beige fabric is 57.31%. Although there are differences when considering the chemicals individually, the extraction method calculations indicate that similar amounts of oil were removed on average from both the blue fabric and the beige fabric.

Table 5.8 : Oil removal performances of chemicals determined by Soxhlet extraction for blue and beige fabric washed at 60ºC.

Chemical No	Chemical Name	Trade Name	Blue Fabric - Stain Removal % by extraction	Beige Fabric - Stain Removal % by extraction
1	C11–C13-alcohol polyethylene glycol ethers (9 EO) (Branched)	Marlipal 3190	60	72
2	C11-alcohol polyalkylene glycol ethers (Alcohol-EO-PO-addition products)	Marlox 11027	61	56
3	Alcohols, C12-14 ethoxylated propoxylated (5EO-4PO)	Dehypon Ls54	32	50

Table 5.8 (continued) : Oil removal performances of chemicals determined by Soxhlet extraction for blue and beige fabric washed at 60ºC.

Chemical No	Chemical Name	Trade Name	Blue Fabric - Stain Removal % by extraction	Beige Fabric - Stain Removal % by extraction
4	C13-alcohol polyethylene glycol ethers (3 EO) (Branched)	Tridac Iso3	16	50
5	C12–C14-alcohol polyethylene glycol ethers (7 EO)	Lorodac 7/24	81.14	80
6	C11-alcohol polyalkylene glycol ethers (EO-PO addition)	Marlox 11009	23.4	21.74
7	C13-alcohol polyethylene glycol ethers (5 EO) (Branched)	Lutensol TO5	61	72
8	C12–C15-alcohol polyethylene glycol ethers (3 EO) (Branched)	Lialet 125/3	9.80	39.13
9	C12–C18-alcohol polyethylene glycol ethers (7 EO)	Novel 1218/7	74	73
10	C12–C14-alcohol polyethylene glycol ethers (6 EO)	Lorodac 6/24	60	72
11	C12–C14-alcohol polyethylene glycol ethers (3 EO)	Lorodac 3/24	61	56
12	C12–C14-alcohol polyethylene glycol ethers (5 EO)	Tianol Ls5	32	50

Figure 5.5 shows a comparison of oil removal rates using extraction methods for each chemical on both blue fabric and beige fabric. When the graph is examined to make a comparison between the two fabrics, significant differences are observed for Tridac iso3 and Lialet 125/3. There is also a difference between Marlipal 3190 and Tianol LS5. Furthermore, the graph shows that the results for other chemicals on two different fabrics are compatible with each other.

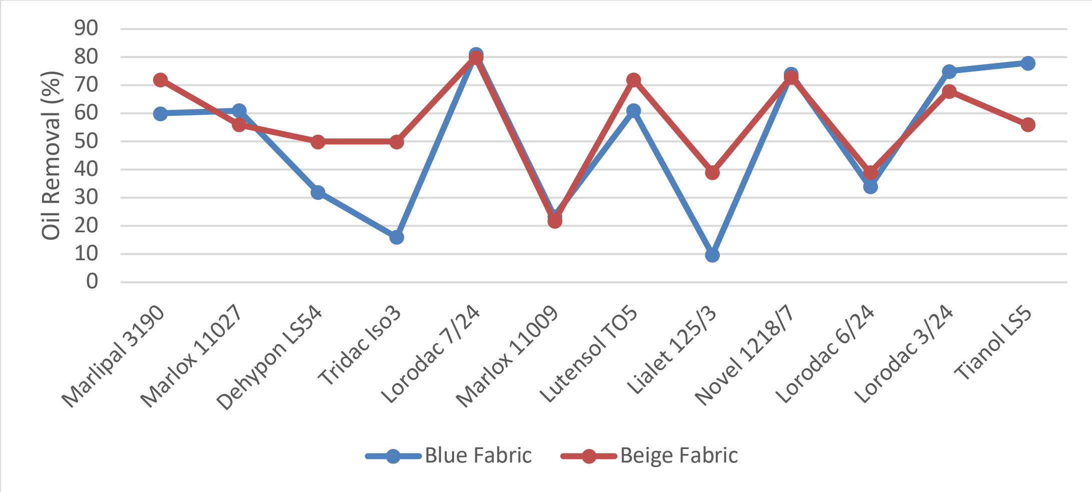


Figure 5.5 : Comparison of oil removal performances obtained by extraction.

5.5 Comparison of Oil Removal Performances Obtained from Extraction and Spectrophotometer

The findings of the oil removal rates for the blue fabric, obtained through spectrophotometer and extraction, are compared in Figure 5.6. These results are not consistent with each other. The reason behind this discrepancy is that the blue fabric changes color during the washing process. After the washing, a blue color is detected in the water used for washing.

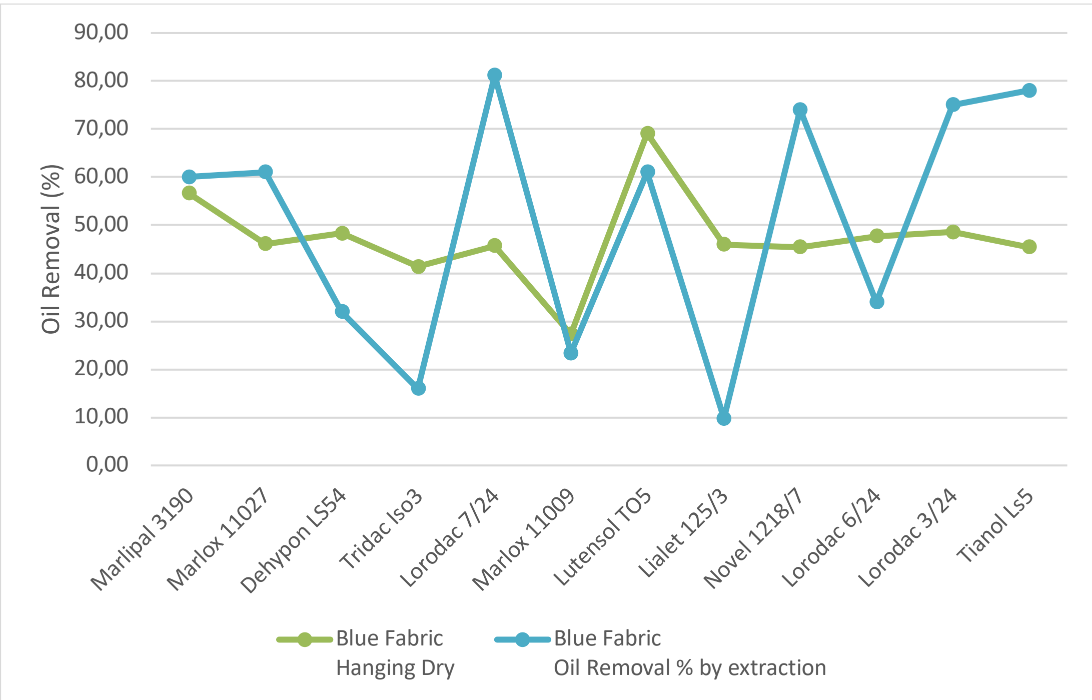


Figure 5.6 : Comparison of oil removal performances obtained from extraction and spectrophotometer for blue fabric.

Figure 5.7 shows the graph of oil removal percentages calculated in two different ways on beige fabric. For beige fabric, The oil removal percentages obtained through the spectrophotometer ranged from 56.25% to 71.71%, whereas the extraction method resulted in a range of 21.74% to 90.91%. While a much narrower range of results was obtained with the spectrophotometer, extraction gave a wider range of results.

In the beige fabric, the chemical with the lowest oil removal rate by both methods was determined as Marlox 11009, and while it was determined that it removed 56.25% oil on average by spectrophotometer, on the other hand, it was determined that it removed 21.74% oil by extraction.

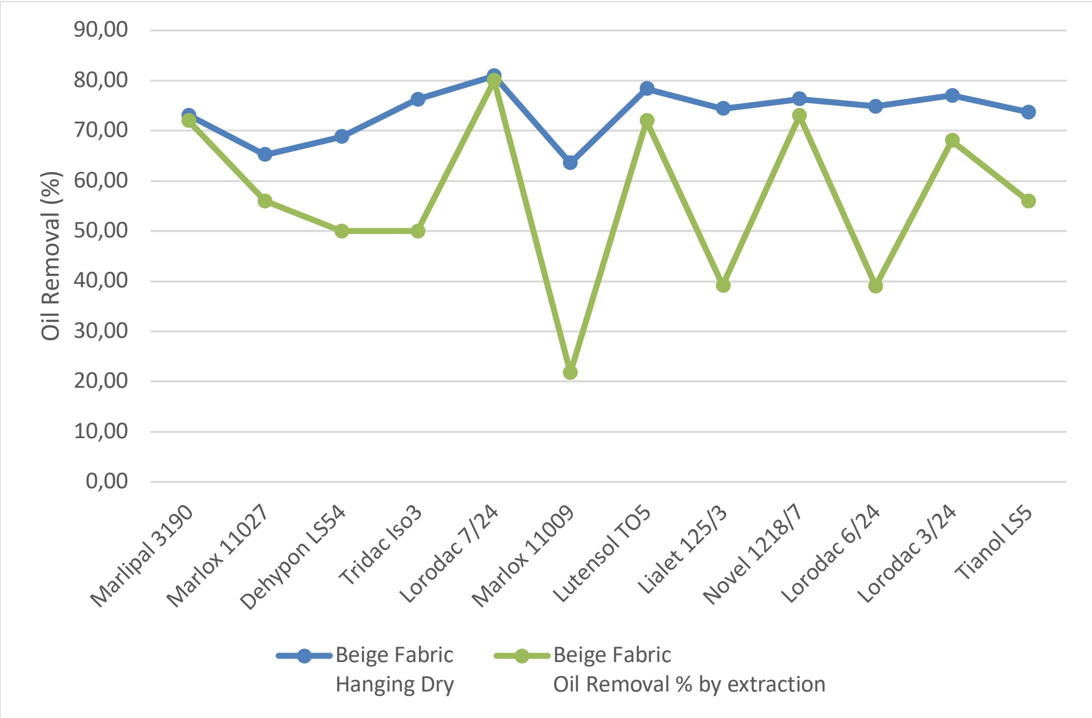


Figure 5.7 : Comparison of oil removal performances obtained from extraction and spectrophotometer for beige fabric.

5.6 The Relationship Between the Structures of Surfactants and Their Oil Removal Performance

When comparing Lorodac 7/24 (12-14 carbon) to Novel 1218-7 (12-18 carbon), which have the same ethoxylate number (7 EO) but different carbon distributions, the extraction results show that Lorodac 7/24 has better oil removal performance. However, when evaluating the spectrophotometer results, it is observed that Novel 1218-7 removes oil better than Lorodac 7/24 on beige fabrics ironed with steam iron and hand iron. The good oil removal performances of these two chemicals can be explained by the fact that ethylene oxide number 7 provides good hydrophilicity and enhances oil removal.

When examining chemicals with lower ethoxylate number (3 ethylene oxide), the best performance is achieved by Lorodac 3/24. The hydrophobic portion of Lorodac 3/24 is composed of linear chains consisting of 12, 13, and 14 carbons. Its HLB values are slightly higher than Lialet 125-3 and Tridac iso3, which have 3 ethylene oxides. The cloud point of Lorodac 3/24 corresponds to the exact washing temperature.

Tinaol LS5 and Dehypon LS54 have the same ethylene oxide number (5EO) and carbon chain (12-14 carbons). However, Dehypon ls54 contains 4 propylene oxides at the end. It is observed that Tinaol LS5 exhibits better oil removal performance. This is because the addition of PO makes the compound more hydrophobic, leading to a decrease in HLB. This negatively affects the oil removal performance.

Marlox 11027 and Marlox 11009 have the same carbon number and ethoxylate number but different PO numbers. Marlox 11009 has a higher PO content than Marlox 11027. Their HLB values are 11.2 and 9.4 for 11027 and 11009, respectively. Marlox 11027 demonstrates better oil removal performance.

In Figures 5.8 and 5.9, the oil removal performances of the chemicals are compared with the HLB value and cloud points. Among the chemicals with lower HLB values (between 8-9), Tridac Iso3 and Lialet 125-3 showed less oil removal, but surprisingly Lorodac 3/24 showed good oil removal performance. Although Lorodac 7/24 and Novel 1218/7, which have an HLB value of approximately 12, showed high oil removal performance, the performance of Lorodac 6/24, which has a very close HLB value (11.5), remained low. The oil removal performance for Marlipal 3190 with an HLB value of 13.2 is close to Lutensol TO5 with an HLB value of 10.5. In conclusion, this study shows that the HLB value alone cannot be decisive in evaluating the oil removal performance.

Marlox 11009, which has the lowest cloud point, showed low oil removal performance as expected. The cloud points of the four chemicals with the best degreasing performances, Lorodac 7/24, Novel 1218-7, Lorodac 3/24 and Lutensol TO5, are 57-59^{o}C, 48-59^{o}C, 60-62^{o}C and 66^{o}C, respectively. These values are close to the washing temperature (60^{o}C). Among other chemicals, it is noteworthy that Marlox 11027 shows high oil removal performance despite having a cloud point of 26-28^{o}C. This may indicate that Marlox 11027 works with an emulsification mechanism and that the phase inversion temperature of the system is higher, thus showing good oil removal performance at 60ºC.

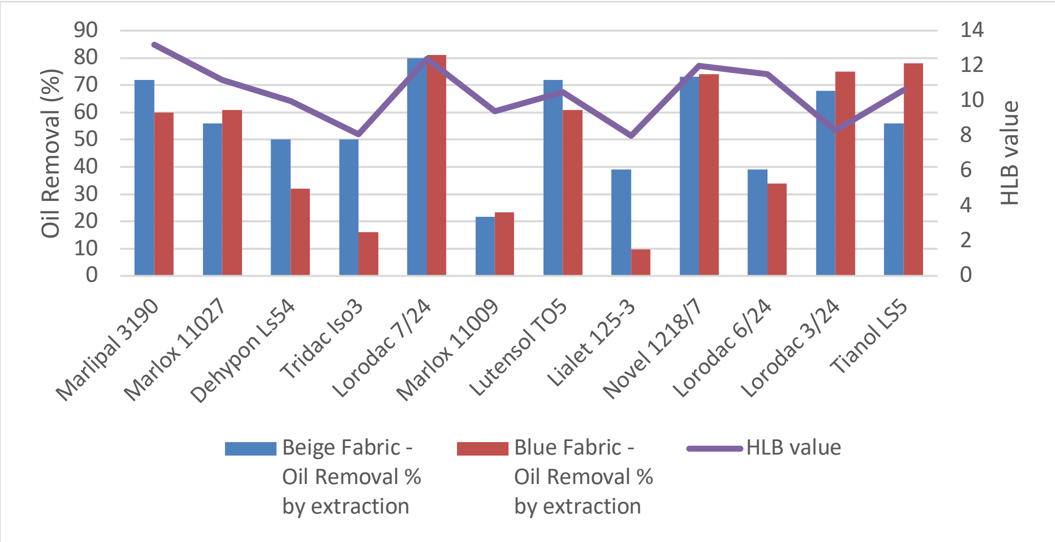


Figure 5.8 : Comparison of oil removal performances obtained from extraction with HLB values of chemicals.

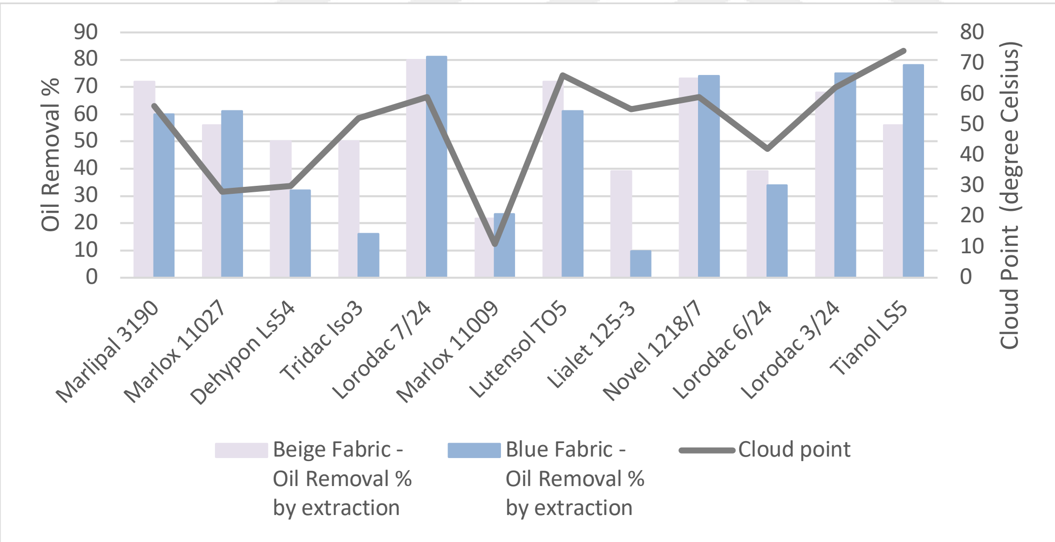


Figure 5.9 : Comparison of oil removal performances obtained from extraction with cloud point of chemicals.

5.7 Recipe for Oil Removal with Different Combinations of Surfactants

Different surfactants may exhibit synergistic effects when combined, leading to enhanced cleaning performance compared to using each surfactant individually. Each surfactant in the mixture may contribute specific properties that collectively result in improved wetting, emulsification, and overall oil removal performance.

It has been revealed that the fixation methods to which the oil is exposed affect the performance of removing the oil by chemicals. It shows that while the oil is removed with good performance by one chemical when it is not processed, the different components that emerge when the oil is exposed to heat can be removed better by another chemical.

While creating the formulations, chemicals with good performance were primarily taken into consideration. Chemicals with different ethoxylate numbers (3EO-5EO-7EO-9EO) and chemicals with different carbon numbers (from C11 to C18) were used together. The performance is improved because surfactants with different structures affect the carbon chain of the oil, which can vary in length. Table 5.9 shows the oil removal results of formulations determined by the determined extraction.

The results indicate that the performance of a single surfactant is surpassed. When examining the oil removal performance obtained through extraction: The highest oil removal obtained on the blue fabric belongs to Lorodac 7/24 with 81.14%, while the highest oil removal on the beige fabric belongs to Lorodac 7/24 with 80%. In the formulations, the highest rate was 92.37% on blue fabric and 96.15% on beige fabric.

Table 5.9 : Oil removal performances of formulation recipes determined by extraction.

Recipe No.	Recipe	Blue Fabric-Oil Removal (%)	Beige Fabric- Oil Removal (%)
1	Lorodac 3/24 +Tianol LS5+ Novel 1218/7	61.36	68.97
2	Marlox 11027+Lutensol TO5+Lorodac 7/24	91.07	90.91
3	Lorodac 3/24+Lutensol TO5+Marlipal 3190	92.37	96.15
4	Marlox 11009 +Lutensol TO5+ Lorodac 7/24	73.47	70.83
5	Marlox 11027+Lorodac 3/24 +Lorodac 7/24	74.07	73.91
6	Lutensol TO5+Lorodac 7/24+Novel 1218-7	83.42	85.19

Table 5.9 (continued) : Oil removal performances of formulation recipes determined by extraction.

Recipe No.	Recipe	Blue Fabric-Oil Removal (%)	Beige Fabric-Oil Removal (%)
7	Marlox 11027+Lorodac 7/24+Marlipal 3190	65.32	64
8	Marlox 11027+Lorodac 3/24+Marlipal 3190	58.75	88.46
9	Marlox 11027+Lutensol TO5+Novel 1218-7	92.24	95.83
10	Marlox 11027+Lutensol TO5+Marlipal 3190	68.78	56

The results of recipes 2, 3 and 9, which have the highest oil removal performance, were evaluated using a spectrophotometer and are shown in Table 5.10. Similar to the individual tests, the spectrophotometer findings for the blue fabric do not align with the extraction outcomes. Nevertheless, this method proves effective for the beige fabric and provides reliable results.

Table 5.10 : Oil removal performances of formulation recipes determined by spectrophotometer.

Recipe No.	Recipe	Blue Fabric-Oil Removal (%)	Beige Fabric- Oil Removal (%)
2	Marlox 11027+Lutensol TO5+Lorodac 7/24	70.16	89.77
3	Lorodac 3/24+Lutensol TO5+Marlipal 3190	66.47	98.19
9	Marlox 11027+Lutensol TO5+Novel 1218-7	73.51	92.3

6. CONCLUSION

According to the results obtained by extraction, the chemical with the best oil removal performance for beige and blue fabrics is Lorodac 7/24. This chemical has a linear hydrophobic chain with carbon numbers 12 and 14 and a hydrophilic part with 7 ethylene oxides. It is the ideal chemical to remove mineral oil from cotton fabric in an alkaline medium at 60^{o}C.

According to the results obtained with a spectrophotometer, 62.77% of the oil was removed from the beige fabric ironed with a steam iron, 69.30% from the fabric ironed normal iron, and 73.53% from the fabric dried by hanging. This indicates that as the fixation level increases, the removal of oil becomes more difficult due to the effects of heat and pressure. This effect is not observed only when the oil oxidizes, but rather because the oil penetrates the cotton structure more effectively through ironing.

When comparing the oil removal performances obtained by spectrophotometer and extraction, different results are obtained for the blue fabric and the beige fabric. It is determined that the beige fabric shows similar tendencies in terms of increase and decrease. However, for the blue fabric, the results are incompatible. This is because there is a loss during the washing of the blue fabric, which invalidates the oil removal performance determined by the spectrophotometer. For the beige fabric, usability is proven and the results are consistent.

Experiments were conducted with triple combinations to achieve higher oil removal performance. The highest oil removal obtained on the blue fabric belongs to Lorodac 7/24 with 81.14%, while the highest oil removal on the beige fabric belongs to Lorodac 7/24 with 80%. In the formulations, the highest rate was 92.37% on the blue fabric and 96.15% on the beige fabric. More oil removal was achieved with the recipe formed using three surfactants for both fabrics. The increase is more significant for the blue fabric. This suggests that using chemicals with different structures together in this triple combination improves the oil removal performance.

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