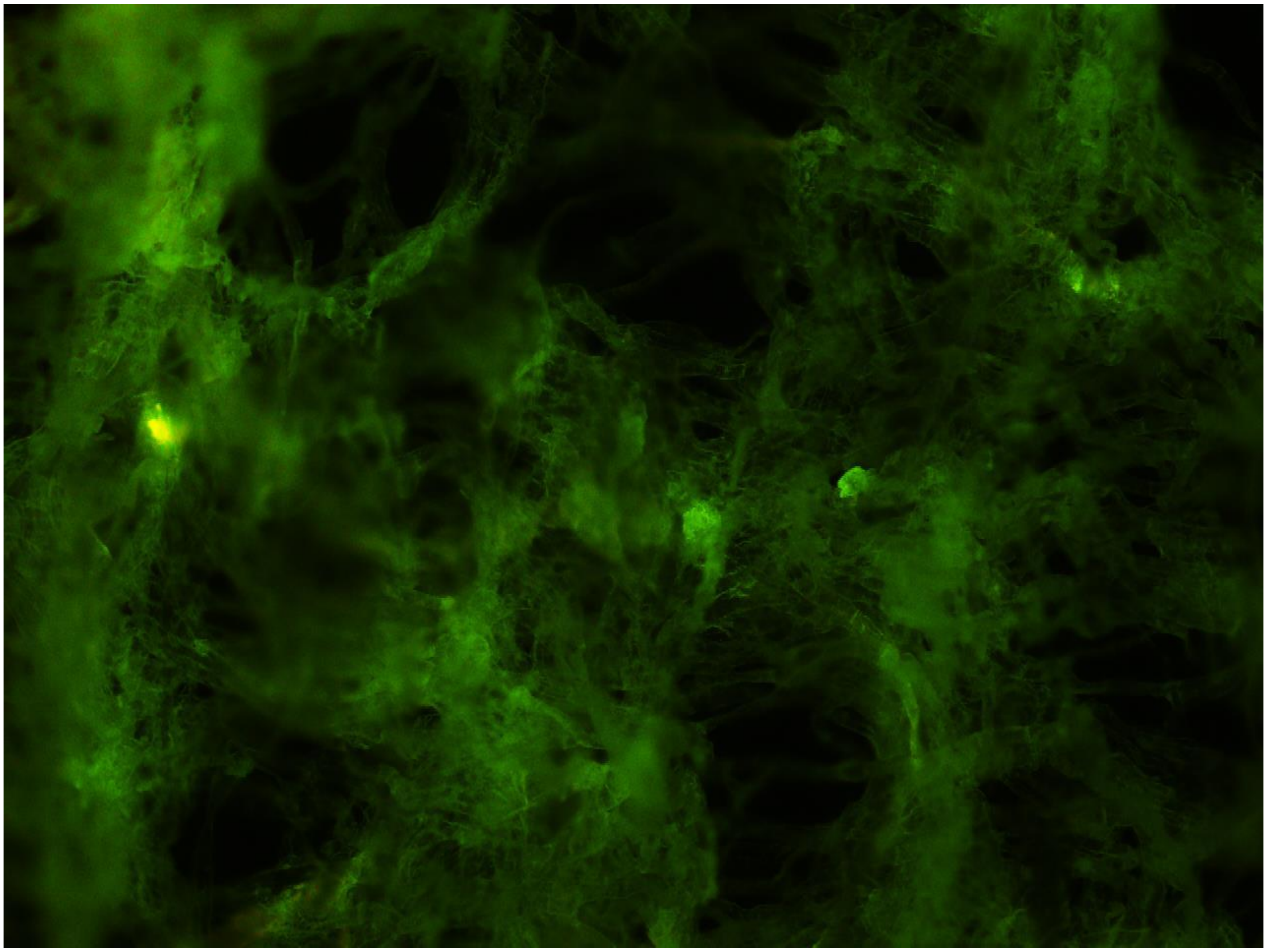

Solid Water in Oil Emulsions with phase transition stability

Bachelor of Science Thesis
Project performed at SCA Hygiene Products, Gothenburg

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

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Cover:
Picture of an emulsion coated on a handkerchief with 10 times enlargement. The picture was taken in UV-light and the water droplets in the emulsion contain fluorophore.

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ABSTRACT

When handkerchiefs and napkins are produced it is common that they are coated with a lotion. This lotion could be an emulsion which is most usually an oil in water emulsion or a water in oil emulsion. This is done to give the tissue product a desired effect upon use such as a softening or deliver of an active substance from the emulsion to the skin. For this thesis work the objectives have been to develop a water in oil emulsion where the continuous oil phase should be solid at room temperature but liquid close to and above skin temperature to facilitate the transfer of the discontinuous water phase to the skin to achieve for instance a cooling effect. The most effect would then be achieved with larger amount of water dispersed in the emulsion. The emulsion would be sufficiently stable to be heated to liquid when applied on the tissue and then when cooled down solidify on the product.

During the development of this emulsion, several types of oil phases have been made to find an oil phase that met the requirements. The requirements for the oil phase are that it should be solid at room temperature and liquid close to and above skin temperature. It should provide a dry, cooling feeling and not form prominent crystals that could destroy the water droplets in the emulsion. Different types of waxes were mixed in different quantities with the oils Mineral oil, Olive oil, 2-ethylhexyl palmitate and Isopropyl palmitate to find the most suitable oil phase. The mixture of Isopropyl palmitate and Syncrowax in the ratio 10-2 gave the most suitable oil phase according to the requirements.

Several emulsifications were made to achieve a stable emulsion that met the requirements for melting point and delivering of a cooling effect. Several factors were changed separately to achieve the result. These factors were; type of oil phase, oil-water-ratio, amount of surfactant/polymer, partly used separately and partly used mixed together in different ratios. When some of the emulsions with the desired melting point visually seemed stable they were observed in a microscope for further examination. The amount of water droplets in the emulsion, the size of the droplets and the variation of droplet size were examined. By doing this an indication of the emulsions stability could be obtained. The emulsions underwent a stability test where they were placed in an oven at 50°C where they were standing in various intervals to examine how they were affected by a longer time in heat. After several emulsifications the conclusion that the emulsion consisting of the oil phase with Isopropyl palmitate and Syncrowax in the ratio 10-2, the oil-water-ratio of 1-4 and the emulsifier amount of 3.85% of the total weight where 50% of the emulsifier was the polymer Cithrol DPHS-SO and 50% was the surfactant SPAN80 provided the most stable emulsion that also met the requirements for melting point.

Key words: Emulsions, W/O emulsions, emulsion coating, surfactants, surface active polymers, tissue products

Fasta Vatten i Oljaemulsioner med fasövergångsstabilitet

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SAMMANFATTNING

När näsdukar och servetter tillverkas är det vanligt att de beläggs med en lotion. Denna lotion kan vara en emulsion som oftast är en olja i vatten emulsion eller en vatten i olja emulsion. Detta görs för att papperprodukten ska få en önskad effekt vid användning så som mjukgörande eller en effekt orsakad av att en aktiv substans i emulsionen överförs till huden vid användning. För detta examensarbete har målet varit att ta fram en vatten i olja emulsion där den kontinueliga oljefasen skulle vara fast vid rumstemperatur men flytande vid och lite över hudtemperatur för att underlätta överföringen av den okontinerliga vattenfasen till huden. Tanken är att då den okontinuerliga fasen når huden ska detta ge t.ex en kylande effekt. Den största effekten skulle därmed fås med större antal vattendroppar i emulsionen. Emulsionen skulle vara såpass stabil att den klarade av att bli uppvärmd till vätskefas då den appliceras på papperprodukten och sedan svalna till fast fas på produkten.

Under framtagningen av denna emulsion har flera typer av oljefaser testats för att hitta en fas som uppfyller kraven. De krav som ställts på oljefasen är att den skulle vara fast vid rumstemperatur och flytande vid och precis över hudtemperatur. Den skulle även ge en torr, kylande känsla och inte bilda för framträdande kristaller som eventuellt skulle kunna förstöra emulsionens inneslutna vattendroppar. Olika typer av vax i olika mängder har blandats med Mineralolja, Olivolja, 2-ethylhexyl palmitate och Isopropyl palmitate för att finna den mest passande oljefasen. Slutsatsen från dessa beredningar är att blandningen Isopropyl palmitate och Syncrowax i förhållandet 10-2 gav den mest passande oljefasen utefter de krav som ställts.

Flera olika emulgeringar gjordes för att få fram en så stabil emulsion som möjligt som följer de krav på smältpunkt och leverans av kylande effekt som ställts. Flera olika faktorer ändrades var för sig för att nå resultatet. Dessa faktorer var; typ av oljefas, oljefas-vatten-mängd och mängd surfaktant/polymer, dels använda var för sig och dels blandade i olika mängder. Några till synes stabila emulsioner iaktogs i mikroskop för ytterligare undersökning. Antalet vattendroppar i emulsionen, storleken på dropparna och variationen av storleken på dropparna undersöktes. Genom att betrakta detta kunde även en indiktation om emulsionens stabilitet fås. Emulsionerna utsattes även för ett stabilitetstest där de placerades i en ugn på 50°C där de fick stå i olika intervaller för att se hur de påverkades av en längre tid i värme. Efter flera olika emulgeringar drogs slutsatsen att den emulsion som bestod av oljefasen med Isopropyl palmitate och Syncrowax i förhållandet 10-2, olja-vatten-förhållandet 1-4 och mängden emulgator på 3.85% av den totala vikten, varav 50% var polymeren Cithrol DPHS-SO och 50% var surfaktanten SPAN80 gav den mest stabila emulsionen som också uppfyllde kravet på smältpunkt.

Sökord: Emulsioner, W/O emulsioner, emulsionsbeläggning, surfaktanter, ytaktiva polymerer, pappersprodukter

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Julia Linse
Gothenburg 2016

CONTENT

1 INTRODUCTION

1.1 Background

The formation of an emulsion occurs when two seemingly immiscible phases are forced to mix. When this occurs, one of the phases encircles the other phase. An emulsifier is necessary to keep the emulsion stable which it does by acting at the interface between the phases. The encircling phase is called the continuous phase and the encircled phase is the discontinuous phase (Tadros 2013). When an emulsion is produced it is usually done by mixing the continuous phase and the emulsifier and then the discontinuous phase is poured slowly into the continuous one while it is being mixed with a high speed stirrer (Chappat 1994). The two most common types of emulsions are oil in water (O/W) emulsions and water in oil (W/O) emulsions (Scientific Spectator 2003).

Emulsions are widely used in different types of industries. The area of use can be everything from food industry to pharmacy, dermatological, cosmetic and tissue products industries (Chappat 1994) (Tadros 2013). Examples of emulsions that are common in food industries are milk, butter and margarine. Milk is an O/W emulsion and the substance that works as the emulsifier is Lecithin (Scientific Spectator 2003) (Tadros 2013) Common W/O emulsions in food industries are butter and margarine (McClements 2005). Dermatological and cosmetic applications of emulsions are e.g. hand creams, lotions, sunscreens and foundations. These applications can be made both as O/W emulsions and as W/O emulsions, the choice of emulsion type depends on the desired properties. When the water is the continuous phase, as it is in an O/W emulsion, an immediate feeling of hydration occurs when the product reaches the skin. W/O emulsions on the other hand are more effective in preventing the water loss from the skin since they form a protective film on the skin and this helps to achieve a longer lasting moisturizing effect. It is harder to make a stable W/O emulsion than a stable O/W emulsion because the amount of the discontinuous phase is often higher in a W/O emulsion than in an O/W emulsion but a W/O emulsion is more efficient than an O/W emulsion, in e.g. sunscreen, for a given concentration of an active substances (Friedman & Wang 2013).

Similar emulsions that are used in the dermatological and cosmetic industry can also be used in the production of tissue products such as napkins and handkerchiefs (Schuller 2016). In the tissue industry, napkins and handkerchiefs can be coated with emulsions to achieve various effects. The effects that would be desirable could be a softening effect or an effect caused by a transfer of an active substance from the discontinuous phase of the emulsion to the skin (Schuller 2016) (Chappat 1994).

1.2 Objectives

The objectives of this thesis work was to develop a water in oil emulsion where the continuous oil phase would be solid at room temperature to increase stability but liquid close to and above skin temperature to facilitate the transfer of the discontinuous water phase to the skin. The emulsion would have phase transition stability for it to be able to go from solid to liquid when it is applied on the tissue and after that go back to solid state, without causing phase separation.

2 THEORY

2.1 Emulsions

Emulsions are mixtures of two, or more, seemingly immiscible phases, usually liquids (Scientific Spectator 2003). When these two liquids are mixed one of the liquid phases act as the continuous phase in the emulsion which encircles the other liquid in the emulsion, the discontinuous phase (Tadros 2013). Several types of emulsions exists but the most common ones are oil in water emulsions (O/W emulsions) and water in oil emulsions (W/O emulsions) (Scientific Spectator 2003). To achieve a mixture of the immiscible liquids a third component is required, an emulsifier. The emulsion formation and stability is dependent on the choice of emulsifier. The most common substances used as emulsifiers are surfactants and surface active polymers. Mixtures of different types of surfactants and/or polymers can generate an even more effective emulsifier (Tadros 2013). In an emulsion system consisting of surfactant-oil-water, two independent variables need to be considered. These variables are the surfactant concentration and the oil-water-ratio (Morales Henríquez 2009). The formation of an emulsion is a nonspontaneous reaction and therefore energy is required to produce droplets of the discontinuous phase. The smaller droplets in the emulsion, the more energy and surfactant are required. Devices used to mix the emulsions are high speed stirrers such as e.g. an UltraTurrax or a Silversson Mixer (Tadros 2013). The most common application methods for coating on paper tissues are spray, weko, roll coating and slot die. When using spray and weko low viscosity of the emulsion is required but slot die do not manage to high viscosity either (Satas & Tracton 2001).

2.1.1 Breakdown processes of emulsions

Emulsions are thermodynamically unstable systems and the decrease of free energy is what's causing an emulsion to form. If the breakdown of an emulsion is a slow process it is however considered stable (Morales Henríquez 2009). When an emulsion is no longer stable several breakdown processes can occur depending on e.g. the particle size distribution of the dispersed phase or density differences between the discontinuous phase droplets and the continuous phase. The most common causes of emulsion breakdowns are creaming, sedimentation, flocculation, coalescence and phase inversion (Tadros 2013).

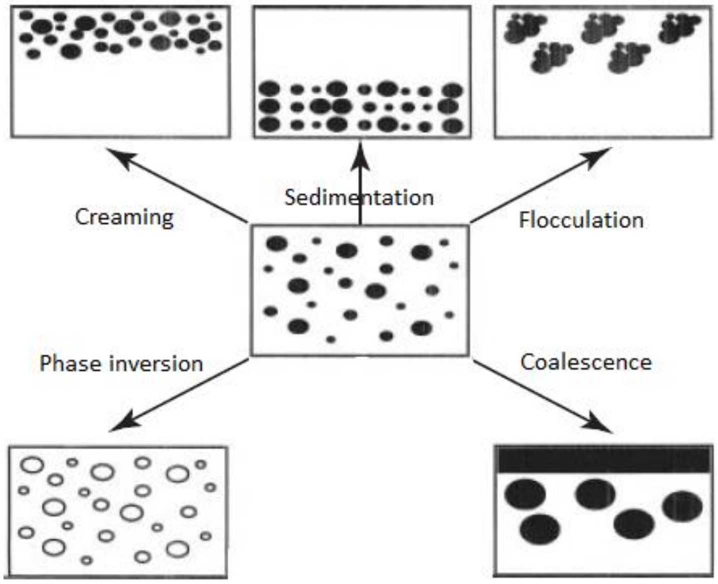


Figure 1 *Simplified picture of breakdown processes for emulsions (Tadros 2013)*

2.1.2 Creaming and sedimentation

Gravitational or centrifugal forces are the most usual causes for creaming and sedimentation to occur. Depending on the density of the discontinuous phase compared to the continuous phase the droplets will move towards the top or the bottom of the sample because of a concentration gradient being built up in the system. Creaming is the name of the occurrence when the discontinuous phase accumulates at the top of the sample and sedimentation is when it accumulates at the bottom of the sample (Tadros 2013).

2.1.3 Flocculation

The aggregation of droplets of the discontinuous phase, without any change in primary droplet size, is what's called flocculation. Van der Waals attraction between the droplets is what causing flocculation in all dispersed systems and depending on how strong the attraction is the capacity of the flocculation varies. When the Van der Waals attraction is weak it is not sufficient to repulse the droplets at a distance from each other and that's when flocculation occurs (Tadros 2013).

2.1.4 Coalescence

Coalescence is the occurrence when two or more droplets of the discontinuous phase form one bigger droplet with the purpose to lower the surface tension of the droplet. This is a result of a disruption in the liquid film enclosing the droplets. If this goes to the extreme it will cause a complete separation between the two phases (Tadros 2013).

2.1.5 Phase inversion

Phase inversion is when an exchange of the continuous and discontinuous phase occurs. An example of this is when a W/O emulsion change in time to become an O/W emulsion (Tadros 2013).

2.2 Surfactants

A surfactant is a surface active agent (Holmberg et al. 2004). It is characterized by its ability to adsorb to a surface or to an interface, which means that the surfactant accumulates at the interface (Tadros 2013), where the interface is a boundary between two immiscible phases. All surfactants are amphiphilic which means that they consist of at least two different parts, one hydrophilic and one hydrophobic (Holmberg et al. 2004).

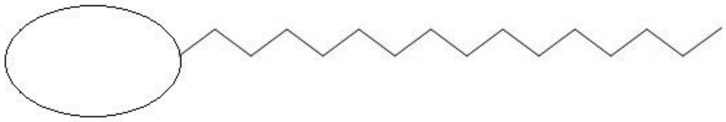


Figure 2 *Simplified picture of a surfactant*

When the interface is provided by surfactants a decrease of the surface tension occurs and this leads to a reduction in droplet size because the work to enlarge the interface decreases (Tadros 2013). A surfactant works well as an emulsifier in an emulsion because of its ability to decrease the surface tension and also its ability to decrease coalescence of dispersed droplets which both are properties that helps stabilizing the emulsion. A surfactant in an emulsion is active at the interface of two liquid phases but a surfactant in a suspension is active between a solid and a liquid phase providing e.g. solvent-borne paint and a surfactant in foam is active in the interface between a liquid and a gas phase providing e.g. shaving cream. This indicates that all interfaces are in some ways stabilized with surfactants. The tendency to accumulation is an important property of a surfactant, the higher ability the surfactant has to accumulate at a surface the more efficiency it has. The ability to form micelles is another important property of a surfactant. This occurs when unimers, which refers to free or unassociated surfactants, begin to aggregate in a solution. Micelle formation occurs to lower the free energy of the system by the unimer arranging its hydrophilic and hydrophobic parts adapted to the continuous and discontinuous phase. The critical micelle concentration, CMC, is the concentration at which unimers starts to form micelles. This often occurs at a relatively low concentration of surfactant and is an important feature (Holmberg et al. 2004). Below the CMC, a greater amount of surfactant will cause a lower surface tension but above the CMC, the surface tension remains constant regardless of the amount of surfactant added (Morales Henríquez 2009). There is not however any type of surfactant that is suitable to stabilize all types of mixtures, the choice of surfactant depends on the application. By studying surfactants geometrical aspects it can be stated that the surfactants best suited to prepare O/W emulsions are the surfactants with long, straight-chain aliphatic hydrocarbon tails. Surfactants that are best suited to prepare W/O emulsions are the ones that have highly branched hydrophobic tails (Holmberg et al. 2004).

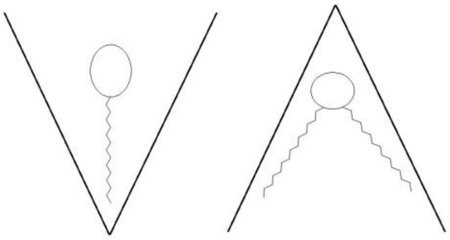


Figure 3 *Simplified pictures that show how the surfactants structure determines its behavior when forming micelles. The smaller part of the triangle will be the center of the micelle*

2.2.1 Types of surfactants

Surfactants are often divided into four different subgroups depending on their polar head group. These groups are anionics, cationics, non-ionics and zwitterionics (Holmberg et al. 2004).

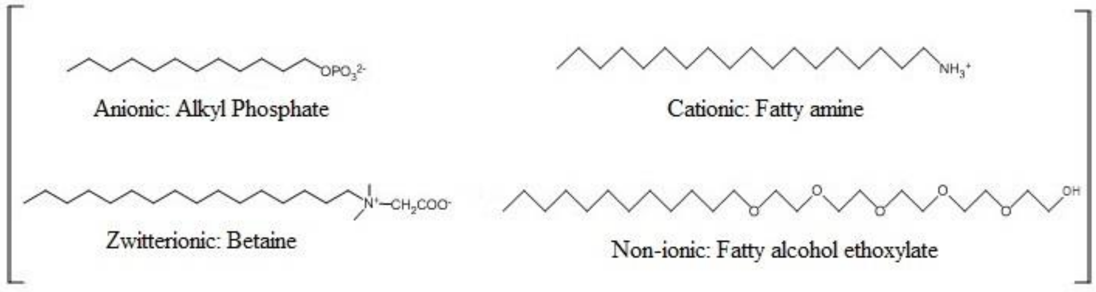


Figure 4 *Examples of different types of surfactants*

2.2.1.1 Anionics

Anionics are surfactants which have a negative charged head group. They are by far the largest group of surfactants. One of the major reasons that they are the most used group of surfactants is that they are easy and cheap to manufacture. In general anionics are not compatible with cationic surfactants but exceptions exist (Holmberg et al. 2004).

2.2.1.2 Cationics

Cationics are surfactants which have a positive charged head group. They are the third largest group of surfactants. Cationics that are hydrolytically stable have shown to be more toxic than the other types of surfactants. In general cationics are not compatible with anionic surfactants but exceptions exist (Holmberg et al. 2004).

2.2.1.3 Non-ionics

Non-ionics are surfactants which don’t have a charged head group. They are the second largest group of surfactants and because they don’t have any charge the non-ionic surfactants are not as affected by electrolytes as the ionic surfactants are (Holmberg et al. 2004). Non-ionic surfactants are the most effective emulsifiers that can be used to emulsify O/W and W/O emulsions (Tadros 2013). In general non-ionics are compatible with all other types of surfactants (Holmberg et al. 2004).

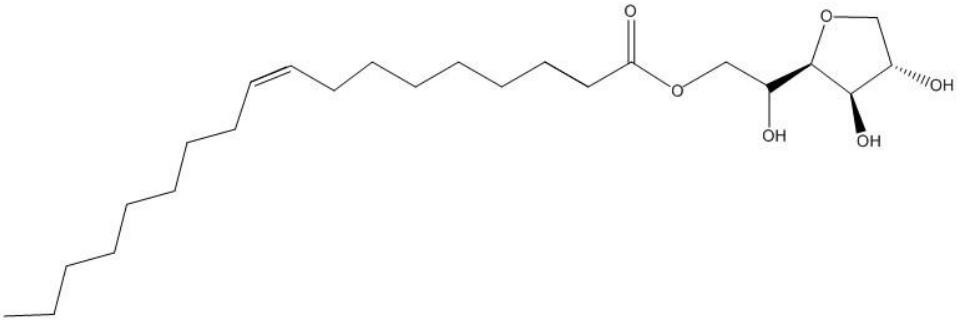


Figure 5 *SPAN80, example of a non-ionic surfactant*

2.2.1.4 Zwitterionics

Zwitterionics are surfactants which have both a positive and a negative charged head group. They are the smallest group of surfactants and this is probably due to their high cost. Zwitterionics are well suited for dermatological products since they show a very low skin irritation. Zwitterionic surfactants are generally stable in acidic and basic solutions and in general they are compatible with all other types of surfactants (Holmberg et al. 2004).

2.3 Surface active polymers

Surface active polymers are often called polymeric surfactants. The most common use for polymeric surfactants is for stabilization of dispersions or for controlling rheology properties (Holmberg et al. 2004). Polymeric surfactants are not as equally used as surfactants because of theirs high cost. They are more common for special application where cost is less of an issue, such as skin care products and cosmetics (Morales Henríquez 2009). Polymeric surfactants are generally more effective in stabilizing an emulsion than a surfactant is but their ability to produce small dispersed droplets of the discontinuous phase in the continuous phase is lower unless high energy is applied. Thus surface active polymers generally produce larger droplets than surfactants do and therefore often form emulsions with lower viscosity than emulsions with surfactants do (Tadros 2013). Polymeric surfactants can be divided into three main groups depending on its geometry. These groups are hydrophilic backbone polymer with hydrophobic side chains, hydrophobic backbone polymer with hydrophilic side chains and polymers with alternating hydrophilic and hydrophobic segments (Holmberg et al. 2004).

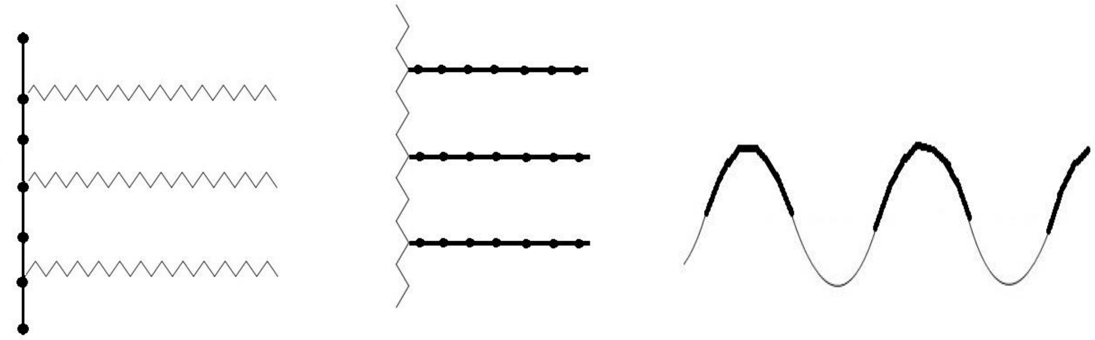


Figure 6 *From left: Hydrophilic backbone polymer with hydrophobic side chains, hydrophobic backbone polymer with hydrophilic side chains, polymer with alternating hydrophilic and hydrophobic segments*

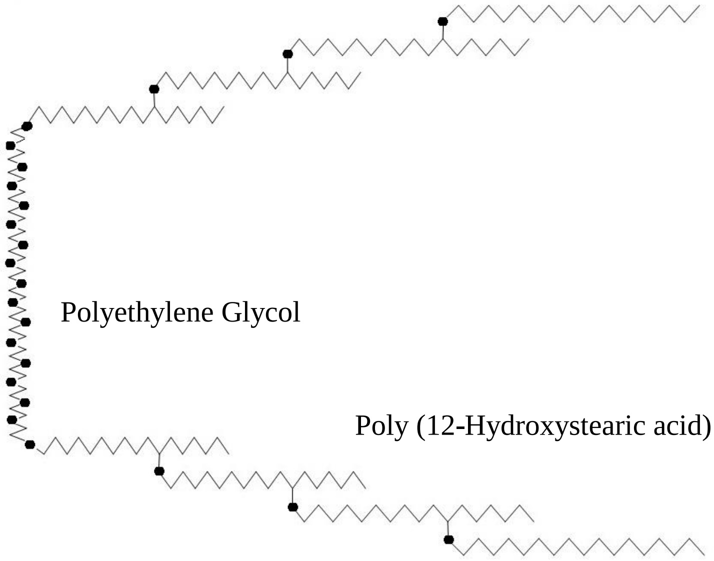


Figure 7 *Cithrol DPHS-SO, example of a surface active polymer with hydrophilic backbone and hydrophobic side chains*

2.4 The HLB system

HLB is an abbreviation for Hydrophilic-Lipophilic-Balance. The HLB system is designed as a guideline when choosing surfactant for an emulsion. It is used as a measurement of the surfactants affinity for the continuous and discontinuous phase (Morales Henríquez 2009). There are two different types of HLB systems, Griffins HLB system and Davies HLB system. The main difference between these two is that Griffins HLB system can only be used to calculate the HLB of non-ionic surfactants while Davies HLB system takes the charge of the surfactants polar head into account. Davies calculated the contributions from the polar head groups and assigned them HLB group numbers, listed in table 1. In Griffins HLB system, each surfactant is assigned a value from 0 to 20 depending on their proportion of hydrophilic and lipophilic molecules (Tadros 2013). In order for a surfactant to be suitable for an emulsion, its HLB value should be around ± 1 of the required HLB value of the oil (Scientific Spectator 2003).

$$\mathrm{HLB} = 20 * (\frac{\mathrm{M_h}}{\mathrm{M_t}})$$

Equation 1 *Theoretical formula for calculation of HLB values according to Griffins HLB system where M_h is the molar mass of the hydrophilic part of the surfactant and M_t is the total molar mass of the surfactant (Bingeman 2005)*

Table 1 *HLB group numbers according to Davies HLB system (Troy & Beringer 2006)*

Group	Group number
Hydrophilic groups	
-$SO_4^-Na^+$	38.7
-COO^-K^+	21.1
-COO^-Na^+	19.1
N (tertiary amine)	9.4
Ester (sorbitan ring)	6.8
Ester (free)	2.4
-COOH	2.1
Hydroxyl (free)	1.9
-O-	1.3
Hydroxyl (sorbitan ring)	0.5
Lipophilic groups	
-CH-	
-CH_2-	
-CH_3-	-0.475
=CH-	
Derived groups	
-(CH_2-CH_2-O)-	+0.33
-(CH_2-CH_2-CH_2-O)-	-0.15

$$\mathrm{HLB} = \sum(\text{Hydrophilic group numbers}) - \mathrm{m} * (\text{Group number}/{-\mathrm{CH_2}} - \text{group}) + 7$$

Equation 2 *Theoretical formula for calculation of HLB values according to Davies HLB system where m is the number of -CH_2-groups present in the surfactant (Troy & Beringer 2006).*

The surfactants that have longer hydrocarbon chains are more hydrophobic and therefore they have a lower HLB value. If the surfactant has more hydrophilic parts it is assigned a higher HLB value (Cray Valley 2010).

If a mixture of two or more different surfactant is used the HLB of the mixture can be calculated according to the following formula.

$$\mathrm{HLB} = \mathrm{x}_1 * \mathrm{HLB}_1 + \mathrm{x}_2 * \mathrm{HLB}_2 \ldots + \mathrm{x}_\mathrm{n} * \mathrm{HLB}_\mathrm{n}$$

Equation 3 *Theoretical formula for calculation of HLB values of a mixture of surfactants where n is the number of surfactants used and x is the percentage of each surfactant (Tadros 2013).*

The HLB range for different applications is listed below in table 2. From the table it can be stated that if the same oil is used to form a W/O emulsion and an O/W emulsion, a higher HLB value of the surfactant is required to form the O/W emulsion (Delta University 2014).

Table 2 *List of HLB ranges and their applications (Tadros 2013).*

HLB range	Application
3-6	W/O emulsions
7-9	Wetting agents
8-18	O/W emulsions
13-15	Detergents
15-18	Solubilizers

3 EXPERIMENTAL

3.1 Material

3.1.1 Chemicals

Oils: Mineral oil, 2-ethylhexyl palmitate, Isopropyl palmitate, Olive oil
Waxes: Cetiol, Tegosoft, Ceraphyl50, Ceraphyl424, Purester, Vaseline, Lipex102, Lipex512, Lipex BC, Akofine, Lipex CocoaSoft, Syncrowax, Akosoft
Surfactant: SPAN80
Polymer: Cithrol DPHS-SO
Fluorophore: Leucophor AF

Table 3 *The used waxes have tradenames which are explained in the table below*

Tradenames	Chemical names (INCI if chemical name is not available)
Cetiol	Tetradecylalcohol
Tegosoft	Tetradecylalcohol
Ceraphyl50	Myristyl Lactate
Ceraphyl424	Myristyl Myristate
Purester	Lauryl Laurate
Vaseline	Petroleum Jelly
Lipex102	Butyrospermum Parkii Butter
Lipex512	Butyrospermum Parkii Butter
Lipex BC	Hydrogenated Vegetable Oil
Akofine	Hydrogenated Vegetable Oil
Lipex CocoaSoft	Theobroma Cacao (Cocoa) Seed Butter
Syncrowax	Synthetic Beeswax
Akosoft	Hydrogenated Coco-glycerides

3.1.2 Apparatus

Stirrer: UltraTurrax IKA T25 digital
Microscopes: Nikon ECLIPSE Ni and Olympus BH2-UMA
Coating device: The roller part of a RK K LOX PROOFER

3.2 Methods

3.2.1 Oil phase preparation

Mineral oil, 2-ethylhexyl palmitate, Olive oil and Isopropyl palmitate were mixed separately with different types of waxes in different amounts to achieve a suitable oil phase for the W/O-emulsion. The requirement of the oil phase was that it had to be solid at room temperature to increase stability but liquid close to and above skin temperature to facilitate the transfer of the water phase to the skin while used in an emulsion. The melting range of the oil phase preparations were measured by putting the samples in a water bath of about 80°C with a thermometer in each sample.

3.2.2 Emulsification

The oil phase was first mixed with surfactant/polymer in a test tube for all emulsifications. Water was then poured into the test tube slowly by using a pipette while it was being stirred. All emulsions were stirred with an UltraTurrax device that operated at 20.000 rpm for 2 minutes each. One type of surfactant, a SPAN80, and one type of polymer, a Cithrol DPHS-SO, was used for the emulsifications. Several factors were changed separately to achieve the result. These factors were; type of oil phase, oil-water-ratio, amount of surfactant/polymer, partly used separately and partly used mixed together in different ratios. The melting ranges of the emulsions were measured by putting the test tubes in a water bath of about 80°C with a thermometer in each tube.

3.2.3 Microscopic observation

Some of the oil phase preparations and some of the emulsions with the desired melting point that visually seemed stable were observed in microscope for further examination. The microscopes used were Nikon ECLIPSE Ni and Olympus BH2-UMA. The oil phase structure and the amount of water droplets, the size of the droplets and the variation of droplet size were examined in the emulsions. In some of the emulsions Leucophor AF was added to the water phase for observations of the water droplets in the emulsion in UV-light.

3.2.4 Stability test

The emulsions underwent a stability test where they were placed in an oven at 50°C where they were standing for a week and were checked on every day to examine how they were affected by a longer time in heat.

3.2.5 Coating of emulsions on handkerchiefs

The emulsions were coated on handkerchiefs using the roller part of a RK K LOX PROOFER. The emulsions were poured on the roller and then rolled out on the handkerchiefs. The handkerchiefs were weighed before and after they got coated to determine how much emulsion that ended up on each. The area of the handkerchiefs used was 0.21*0.20m^2.

4 RESULTS AND DISCUSSION

4.1 Oil phase preparation

In the first oil phase preparations that were made different waxes in different quantities were mixed with 10g of Mineral oil.

Table 4 *Oil phase preparations*

Sample	Oil phase	Consistence	Melting range	Comment
1	Mineral oil 10g Cetiol 2g	Solid	25-29°C	
2	Mineral oil 10g Cetiol 4g	Solid	28-33°C	
3	Mineral oil 10g Cetiol 6g	Solid	32-37°C	Cooling effect? Forms a very sharp crystal structure that could cause phase separation by breaking the water droplets in the emulsion
4	Mineral oil 10g Tegosoft 2g	Solid	30-35°C	
5	Mineral oil 10g Tegosoft 4g	Solid	35-40°C	Cooling effect? Forms a very sharp crystal structure that could cause phase separation by breaking the water droplets in the emulsion
6	Mineral oil 10g Tegosoft 6g	Solid	40-45°C	Cooling effect? Forms a very sharp crystal structure that could cause phase separation by breaking the water droplets in the emulsion
7	Mineral oil 10g Ceraphyl50 2g	Liquid	-	
8	Mineral oil 10g Ceraphyl50 4g	Liquid	-	
9	Mineral oil 10g	Liquid	-	

	Ceraphyl50 6g			
10	Mineral oil 10g Ceraphyl424 2g	Solid	35-37°C	Forms a very sharp crystal structure that could cause phase separation and contains a warning symbol - will not be used
11	Mineral oil 10g Ceraphyl424 4g	Solid	38-39°C	
12	Mineral oil 10g Ceraphyl424 6g	Solid	40-45°C	
13	Mineral oil 10g Purester 2g	Liquid	-	
14	Mineral oil 10g Purester 4g	Liquid	-	
15	Mineral oil 10g Purester 6g	Liquid	-	

From the first oil phase preparation it was found that none of the Ceraphyl50 or the Purester preparations generated an oil phase that was solid at room temperature. Three more oil phase preparations were made with larger amount of wax and still 10g of Mineral oil.

Table 5 *Oil phase preparations*

Sample	Oil phase	Consistence	Melting range	Comment
1	Mineral oil 10g Purester 8g	Liquid	-	
2	Mineral oil 10g Purester 10g	Liquid	-	Small crystal structure at the bottom
3	Mineral oil 10g Purester 12g	Solid	Not determined	Forms a very sharp crystal structure that could cause phase separation by breaking the water droplets in the emulsion - will probably not be used because very large amount was needed

4	Mineral oil 10g Ceraphyl50 8g	Liquid	-	
5	Mineral oil 10g Ceraphyl50 10g	Liquid	-	
6	Mineral oil 10g Ceraphyl50 12g	Liquid	-	Does not give a solid mixture, could possibly be used in a three-component system

Ceraphyl50 has desired properties for the oil phase but does not solidify easy in a mixture with Mineral oil. A three-component system was tested with 2g of Ceraphyl50 added to samples of 2g, 4g and 6g of Cetiol, all samples mixed with 10g of Mineral oil. From the results from the first preparations of oil phases, see *table 4*, the conclusion was made that the preparation made with Cetiol and Tegosoft best met the requirements for the oil phase but they were not optimal since they formed a sharp crystal structure, visually observed, and further preparations were made.

Table 6 *Oil phase preparations*

Sample	Oil phase	Consistence	Melting range	Comment
1	Mineral oil 10g Cetiol 2g Ceraphyl50 2g	Solid	27-29°C	Forms a very sharp crystal structure – will not be further examined
2	Mineral oil 10g Cetiol 4g Ceraphyl50 2g	Solid	28-31°C	Forms a very sharp crystal structure – will not be further examined
3	Mineral oil 10g Cetiol 6g Ceraphyl50 2g	Solid	31-36°C	Forms a very sharp crystal structure – will not be further examined

The samples made with Mineral oil, Cetiol and Ceraphyl50 did not meet the requirements of the oil phase. They formed sharp crystals that might cause phase separation by breaking the water droplets when used in an emulsion, this was stated by visual observation, and the melting ranges were incorrect. More oil phase preparations were made to seek for a creamier consistence of the oil phase.

Table 7 *Oil phase preparations*

Sample	Oil phase	Consistence	Melting range	Comment
1	Mineral oil 10g Vaseline 2g	Liquid	-	
2	Mineral oil 10g Vaseline 4g	Liquid	-	
3	Mineral oil 10g Vaseline 6g	Liquid	-	
4	Mineral oil 10g Lipex102 2g	Liquid	-	
5	Mineral oil 10g Lipex102 4g	Liquid	-	
6	Mineral oil 10g Lipex 102 6g	Liquid	-	
7	Mineral oil 10g Lipex 512 2g	Liquid	-	
8	Mineral oil 10g Lipex 512 4g	Liquid	-	
9	Mineral oil 10g Lipex512 6g	Liquid	-	
10	Mineral oil 10g Akofine 2g	Solid	34-36°C	Does not form as prominent crystals as the rest of the solid oil phases - creamier consistence. Dry feeling?
11	Mineral oil 10g Akofine 4g	Solid	36-39°C	Does not form as prominent crystals as the rest of the solid oil phases - creamier consistence. Dry feeling?
12	Mineral oil 10g Akofine 6g	Solid	39-44°C	Does not form as prominent crystals as the rest of the solid oil phases - creamier consistence. Dry feeling?
13	Mineral oil 10g	Liquid	-	

	Lipex BC 2g			
14	Mineral oil 10g Lipex BC 4g	Liquid	-	
15	Mineral oil 10g Lipex BC 6g	Liquid	-	Highly viscous, does not form as prominent crystals as the rest of the solid oil phases
16	Mineral oil 10g Lipex CocoaSoft 2g	Liquid	-	
17	Mineral oil 10g Lipex CocoaSoft 4g	Liquid	-	
18	Mineral oil 10g Lipex CocoaSoft 6g	Liquid	-	

From the preparations, see table 6, the samples containing Akofine best met the requirements for the oil phase and Akofine was further examined. A three-component system was tested with 2g Akofine mixed with 1g Tegosoft and 10g Mineral oil in one sample and with 2g Tegosoft and 10g Mineral oil in another. The cooling effect of Tegosoft is desired and the samples containing Akofine contributed to a creamy and dry consistence of the oil phase, that's why these waxes were tested in a three-component system.

Table 8 *Oil phase preparations*

Sample	Oil phase	Consistence	Melting range	Comment
1	Mineral oil 10g Akofine 2g Tegosoft 1g	Solid	32-37°C	
2	Mineral oil 10g Akofine 2g Tegosoft 2g	Solid	30-35°C	

The oil phase preparations from *table 7 and 8* were examined in an Olympus BH2-UMA microscope. From the observation in microscope it could be stated that the preparations were not as homogenous as was desired. The samples containing Tegosoft contributed to a sharp crystal structure and the samples with Akofine showed a grainy structure. Further oil phase preparations were made to find a suitable oil phase. This time 10g of Mineral oil was mixed with different amounts of Syncrowax.

Table 9 *Oil phase preparations*

Sample	Oil phase	Consistence	Melting range	Comment
1	Mineral oil 10g Syncrowax 1g	Solid	27-32°C	Does not form prominent crystals - creamier consistence
2	Mineral oil 10g Syncrowax 2g	Solid	35-40°C	Does not form prominent crystals - creamier consistence
3	Mineral oil 10g Syncrowax 3g	Solid	36-42°C	Does not form prominent crystals - creamier consistence

The same amounts of Syncrowax were also mixed with 10g 2-ethylhexyl palmitate instead of Mineral oil.

Table 10 *Oil phase preparations*

Sample	Oil phase	Consistence	Melting range	Comment
1	2-ethylhexyl palmitate 10g Syncrowax 1g	Solid	25-30°C	Almost liquid at room temperature. Melting range refers to when the mixture is completely fluent. Does not form prominent crystals - creamier consistence
2	2-ethylhexyl palmitate 10g Syncrowax 2g	Solid	27-32°C	Does not form prominent crystals - creamier consistence
3	2-ethylhexyl palmitate 10g Syncrowax 3g	Solid	28-33°C	Does not form prominent crystals - creamier consistence

The preparations with Syncrowax, see *table 9 and 10*, showed useful results and a three-component system was tested with Syncrowax and Akofine. This system was tested because the preparations with Akofine were not as oily on the skin as the rest of the oil phase preparations and both Akofine and Syncrowax contributed to a creamier consistence of the oil phases.

Table 11 *Oil phase preparations*

Sample	Oil phase	Consistence	Melting range	Comment
1	Mineral oil 10g Syncrowax 1g Akofine 1g	Solid	27-32°C	

The same three-component system was tested but with 10g of 2-ethylhexyl palmitate instead of 10g Mineral oil.

Table 12 *Oil phase preparations*

Sample	Oil phase	Consistence	Melting range	Comment
1	2-ethylhexyl palmitate 10g Syncrowax 1g Akofine 1g	Solid	25-30°C	

The preparations from *table 11 and 12* had a good creamy consistence but the melting range was a bit low. Further preparations were made but limited access to 2-ethylhexyl palmitate oil led to oil phase preparations with Isopropyl palmitate instead of 2-ethylhexyl palmitate because they have similar properties. This time 5g of Isopropyl palmitate was mixed with different amounts of Syncrowax.

Table 13 *Oil phase preparations*

Sample	Oil phase	Consistence	Melting range	Comment
1	Isopropyl palmitate 5g Syncrowax 0.5g	Solid	25-27°C	Almost liquid at room temperature
2	Isopropyl palmitate 5g Syncrowax 1g	Solid	26-28°C	Almost liquid at room temperature
3	Isopropyl palmitate 5g Syncrowax 1.5g	Solid	27-29°C	

1g of Tegosoft was added to each sample to examine if the melting range could be raised.

Table 14 *Oil phase preparations*

Sample	Oil phase	Consistence	Melting range	Comment
1	Isopropyl palmitate 5g Syncrowax 0.5g Tegosoft 1g	Solid	25-27°C	Almost liquid at room temperature but slightly firmer than without Tegosoft
2	Isopropyl palmitate 5g Syncrowax 1g Tegosoft 1g	Solid	26-28°C	Almost liquid at room temperature but slightly firmer than without Tegosoft
3	Isopropyl palmitate 5g Syncrowax 1.5g Tegosoft 1g	Solid	28-30°C	

Further 1g more of Tegosoft was added to the samples.

Table 15 *Oil phase preparations*

Sample	Oil phase	Consistence	Melting range	Comment
1	Isopropyl palmitate 5g Syncrowax 0.5g Tegosoft 2g	Solid	25-27°C	
2	Isopropyl palmitate 5g Syncrowax 1g Tegosoft 2g	Solid	26-28°C	
3	Isopropyl palmitate 5g Syncrowax 1.5g Tegosoft 2g	Solid	28-31°C	

The conclusion made from this oil phase preparation was that Tegosoft did not contribute to a raise in melting range in this mixture.

Two equal oil phase preparations were made, with 5g 2-ethylhexyl palmitate and 1g Syncrowax, but they were cooled down at different rates. One of the samples cooled down slowly at room temperature and the other sample was placed in a freezer for a rapid cooling. This was done to examine if the cooling rate were crucial for formation of crystals in the samples. The oil phase crystals were analyzed using an Olympus BH2-UMA microscope.

Table 16 *Oil phase preparations with different cooling rate*

Sample	Oil phase	Consistence	Cooling rate	Comment
1	2-ethylhexyl palmitate 5g Syncrowax 1g	Solid	Slow	Formed more crystals
2	2-ethylhexyl palmitate 5g Syncrowax 1g	Solid	Rapid	Formed less crystals

The conclusion that the sample that was cooled down rapidly had formed least crystals was made. This is desirable because large crystals can destroy the water droplets formation when used in an emulsion.

Another examination with different cooling ratios was made with two samples. This time Isopropyl palmitate was used as the oil and Syncrowax and Akofine used as the type of waxes. One sample contained only Syncrowax as the type of wax and the other sample contained both Syncrowax and Akofine. This was done to examine how much Akofine contributes to crystal formation in the oil phase and also if the sample with Akofine could be less grainy if it was cooled down rapidly.

Table 17 *Oil phase preparations with different cooling rate*

Sample	Oil phase	Consistence	Cooling rate	Comment
1	Isopropyl palmitate 5g Syncrowax 0.5g Akofine 0.5g	Solid	Rapid	Forms more crystals than the sample without Akofine, but less than the samples that was cooled down slowly
2	Isopropyl palmitate 5g Syncrowax 0.5g	Solid	Rapid	Almost completely homogeneous

The conclusion from this oil phase preparations is that the oil phases does not form as much crystals when it is cooled down rapidly as it does when it is cooled down slowly. The sample that contained Akofine had formed more crystals than the samples without, but fewer crystals than the samples with Akofine that had cooled down at room temperature.

To examine if the addition of polymer/surfactant affect the melting point of the oil phases, two oil phase preparations were made with each 5g Isopropyl palmitate and 1g Syncrowax, one of these contained the surfactant SPAN80 and one the polymer Cithrol DPHS-SO. The amount of surfactant/polymer added was 3.85w% of the total weight.

Table 18 *Oil phase preparations with added surfactant/polymer*

Sample	Oil phase	Consistence	Melting range	Comment
1	Isopropyl palmitate 5g Syncrowax 1g	Solid	24-27°C	0.24g Cithrol DPHS-SO was added (3.85w %).
2	Isopropyl palmitate 5g Syncrowax 1g	Solid	25-28°C	0.24g SPAN80 was added (3.85w %).

The conclusion from this preparation is that the addition of polymer/surfactant to the oil phase does not affect the melting range of the preparations, but it does affect the melting range when used in an emulsion, see emulsifications results.

More oil phase preparations were made but this time with 5g of Olive oil in each sample. This was done to examine if some of the waxes that didn't solidify in the other oils might would in this one.

Table 19 *Oil phase preparations*

Sample	Oil phase	Consistence	Melting range	Comment
1	Olive oil 5g Lipex CocoaSoft 1g	Liquid	-	
2	Olive oil 5g Lipex CocoaSoft 2g	Liquid	-	
3	Olive oil 5g Lipex CocoaSoft 3g	Liquid	-	
4	Olive oil 5g Akofine 1g	Solid		Smooth consistence
5	Olive oil 5g Akofine 2g	Solid		Smooth consistence
6	Olive oil 5g Akofine 3g	Solid		Smooth consistence
7	Olive oil 5g Syncrowax 0.5g	Solid		Smooth consistence
8	Olive oil 5g Syncrowax1g	Solid		Smooth consistence
9	Olive oil 5g Syncrowax 1.5g	Solid		Smooth consistence
10	Olive oil 5g Tegosoft 1g	Solid		Prominent crystals
11	Olive oil 5g Tegosoft 2g	Solid		Prominent crystals

12	Olive oil 5g Tegosoft 3g	Solid		Prominent crystals
13	Olive oil 5g Purester 1g	Liquid	-	
14	Olive oil 5g Purester 2g	Liquid	-	
15	Olive oil 5g Purester 3g	Liquid	-	

The Lipex CocoaSoft didn’t solidify in the Olive oil with the used amounts. Higher amount of Lipex CocoaSoft were added to examine if that would make the solution solid.

Table 20 *Oil phase preparations*

Sample	Oil phase	Consistence	Melting range	Comment
1	Olive oil 5g Lipex CocoaSoft 4g			
2	Olive oil 5g Lipex CocoaSoft 5g			
3	Olive oil 5g Lipex CocoaSoft 6g			Partly crystallized

The oil phase preparations made with Olive oil did not show useful results and were not further investigated. The oil phase that best met the requirements after all oil phase preparations was the one with Isopropyl palmitate and Syncrowax used in the ratio 10-2.

4.2 Emulsification

The purpose of the first emulsification was to find a suitable oil-water-ratio. Three emulsions with constant amount of surfactant and different oil-water-ratio were made. The same oil-water-ratios were used with a constant amount of surfactant/polymer. The amount of surfactant/polymer was 3 w% of the weight of the oil phase. The first emulsifications were performed at room temperature.

Table 21 *Emulsifications with different oil-water-ratio and SPAN80 as the emulsifier*

Sample	Oil phase	Water	SPAN80	Comment
1	Mineral oil 12g	6g	0.36g	O-W-ratio: 2-1, turbid mixture but a visible separation at the top of the sample after one day
2	Mineral oil 12g	12g	0.36g	O-W-ratio: 1-1, turbid mixture but a visible separation at the top and bottom of the sample

				after one day
3	Mineral oil 12g	18g	0.36g	O-W-ratio: 2-3, turbid mixture but a visible small separation at the top of the sample after one day. After three days an obvious separation

Table 22 *Emulsifications with different oil-water-ratio and Cithrol DPHS-SO as the emulsifier*

Sample	Oil phase	Water	Cithrol DPHS-SO	Comment
1	Mineral oil 12g	6g	0.36g	O-W-ratio: 1-2, obvious separation at the top of the sample after one day
2	Mineral oil 12g	12g	0.36g	O-W-ratio: 1-1, obvious separation at the top of the sample but a little less than sample 1 after one day
3	Mineral oil 12g	18g	0.36g	O-W-ratio: 2-3, separation at the top of the sample but a lot less than the two other samples after one day

To examine which phase that had separated from the emulsions a control was made by pipetting some of the separated liquid on the top and on the bottom of the test tubes and drop it in a beaker of water. By doing this it could be determined that the separated phase at the top was oil and the phase at the bottom was water.

The most stable emulsions from the first emulsifications were achieved from the oil-water-ratio 2-3 for both the surfactant and the polymer. That ratio was used for the emulsions that followed but then with different combinations of surfactant and polymer used together. The surfactant/polymer amount was still 3w% of the weight of the oil phase. For this emulsification, and the rest that follows, the oil and water were heated to 60°C before they were mixed to facilitate the emulsification.

Table 23 *Emulsifications with surfactant and polymer used together in different ratios as the emulsifier*

Sample	1	2	3	4	5
Cithrol DPHS-SO	0g	0.075g	0.15g	0.225g	0.3g
SPAN80	0.3g	0.225g	0.15g	0.075g	0g
Oil phase	Mineral oil 12g	Mineral oil 12g	Mineral oil 12g	Mineral oil 12g	Mineral oil 12g
Water	18g	18g	18g	18g	18g
Comment	0% polymer,	25% polymer,	50% polymer,	75% polymer,	100% polymer,

	100% surfactant. Turbid mixture but a visible small separation at the top and bottom of the sample after two day	75% surfactant. Obvious separation at the bottom of the sample after two days	50% surfactant. Small separation at both the bottom and top of the sample after two days	25% surfactant. Much more stable than the other samples, after two days no visually separation had occurred, after five days just a small separation occurred on the top of the sample	0% surfactant. Obvious separation on the bottom of the sample after two days

The conclusions made from this emulsification were that the amount of surfactant/polymer had to be increased to form a stable emulsion. With the oil-water-ratio used the amount of surfactant/polymer was just 1w% of the total weight. The following emulsifications were performed with the same oil-water-ratio but with different amount of surfactant/polymer, this time used by separately.

Table 24 *Emulsifications with different amounts of surfactant*

Sample	Oil phase	Water	SPAN80	Comment
1	Mineral oil 10g	15g	0.5g	The amount of SPAN80 was 1.95w% of the total weight. After one day the emulsion was stable
2	Mineral oil 10g	15g	1g	The amount of SPAN80 was 3.85w% of the total weight. After two days the sample with 4w% SPAN80 shows a slightly better result than the other samples
3	Mineral oil 10g	15g	1.5g	The amount of SPAN80 was 5.65w% of the total weight. After one day the emulsion was stable

Table 25 *Emulsifications with different amounts of polymer*

Sample	Oil phase	Water	Cithrol DPHS-SO	Comment
1	Mineral oil 10g	15g	0.5g	The amount of Cithrol DPHS-SO was 1.95w% of the total

				weight. After one day the emulsion was stable
2	Mineral oil 10g	15g	1g	The amount of Cithrol DPHS-SO was 3.85w% of the total weight. After two days the sample with 4w% Cithrol DPHS-SO shows a slightly better result than the other samples
3	Mineral oil 10g	15g	1.5g	The amount of Cithrol DPHS-SO was 5.65w% of the total weight. After one day the emulsion was stable

All emulsions were visually stable after one day but after two days some separation had occurred at the top of every sample except the ones with 3.85w% of surfactant/polymer. The phase that had separated from the emulsions was oil. The oil had probably separated from the emulsion because the amount of added water was not enough to fill the amount of oil that was used with water droplets, which means sedimentation in the oil phase might have occurred. This means that the whole emulsion probably had gone through creaming or flocculation. That’s why the following emulsifications were made to test different amounts of water but with a constant amount of emulsifier at 3.85w%, consisting of surfactant/polymer.

Table 26 *Emulsifications with different oil-water-ratio and SPAN80 as the emulsifier*

Sample	Oil phase	Water	SPAN80	Comment
1	Mineral oil 5g	10g	0.6g	O-W-ratio: 1-2, very small separation of oil at the top of the sample after one day
2	Mineral oil 5g	12.5g	0.7g	O-W-ratio: 2-5, visually stable after one day

Table 27 *Emulsifications with different oil-water-ratio and Cithrol DPHS-SO as the emulsifier*

Sample	Oil phase	Water	Cithrol DPHS-SO	Comment
1	Mineral oil 5g	10g	0.6g	O-W-ratio: 1-2, very small separation of oil at the top of the sample after one day
2	Mineral oil 5g	12.5g	0.7g	O-W-ratio: 2-5, visually stable after one day

The oil-water-ratio that contributed to the most stable emulsions was the 2-5 ratio. That ratio was used with the oil phase preparation t of 10g Mineral oil and 2g Syncrowax. The surfactant level was still at 3.85w% of the total weight and the surfactant and polymer were used separately.

Table 28 *Emulsification with wax added to the oil phase with SPAN80 as the emulsifier*

Sample	Oil phase	Water	SPAN80	Comment
1	Mineral oil 8.33g Syncrowax 1.67g	25g	1.4g	Stable after four days. Heated to 60°C – still solid

Table 29 *Emulsification with wax added to the oil phase with Cithrol DPHS-SO as the emulsifier*

Sample	Oil phase	Water	Cithrol DPHS-SO	Comment
1	Mineral oil 8.33g Syncrowax 1.67g	25g	1.4g	Stable after four days. Liquid when heated to 50-55°C

The emulsions high viscosity might cause problems when they are applied on the tissue and that's why the Mineral oil was replaced with 2-ethylhexyl palmitate in four emulsifications and Olive oil in four other emulsifications to examine if the change of oil would lead to a decrease in viscosity. The oil-water-ratios that were tested in these emulsifications were 1-2 and 2-5 and the amount of surfactant/polymer was 3.85w% of the total weight, used separately.

Table 30 *Emulsifications with different oil-water-ratio and SPAN80 as the emulsifier*

Sample	Oil phase	Water	SPAN80	Comment
1	2-ethylhexyl palmitate 10g	20g	1.2g	O-W-ratio: 1-2, Not stable after two days
2	2-ethylhexyl palmitate 10g	25g	1.4g	O-W-ratio: 2-5, Not stable after two days

Table 31 *Emulsifications with different oil-water-ratio and Cithrol DPHS-SO as the emulsifier*

Sample	Oil phase	Water	Cithrol DPHS-SO	Comment
3	2-ethylhexyl palmitate 10g	20g	1.2g	O-W-ratio: 1-2, Stable after five days and liquid at room temperature
4	2-ethylhexyl palmitate 10g	25g	1.4g	O-W-ratio: 2-5, Stable after five days and liquid at room temperature

Table 32 *Emulsifications with different oil-water-ratio and SPAN80 as the emulsifier*

Sample	Oil phase	Water	SPAN80	Comment
1	Olive oil 10g	20g	1.2g	O-W-ratio: 1-2, Not stable after two days
2	Olive oil 10g	25g	1.4g	O-W-ratio: 2-5, Not stable after two days

Table 33 *Emulsifications with different oil-water-ratio and Cithrol DPHS-SO as the emulsifier*

Sample	Oil phase	Water	Cithrol DPHS-SO	Comment
3	Olive oil 10g	20g	1.2g	O-W-ratio: 1-2, Stable after five days and liquid at room temperature
4	Olive oil 10g	25g	1.4g	O-W-ratio: 2-5, Stable after five days and liquid at room temperature

Since the requirement of the emulsion is that it should be solid at room temperature an emulsification was done with a mixture of 2-ethylhexyl palmitate and Syncrowax used as the oil phase. The oil-water-ratio used was 2-5 and the surfactant/polymer amount was 3.85w% of the total weight, used separately.

Table 34 *Emulsification with wax added to the oil phase and SPAN80 used as the emulsifier*

Sample	Oil phase	Water	SPAN80	Comment
1	2-ethylhexyl palmitate 8.33g Syncrowax 1.67g	25g	1.4g	Stable after four days. Heated to 60°C – still solid

Table 35 *Emulsification with wax added to the oil phase and Cithrol DPHS-SO as the emulsifier*

Sample	Oil phase	Water	Cithrol DPHS-SO	Comment
1	2-ethylhexyl palmitate 8.33g Syncrowax 1.67g	25g	1.4g	Stable after four days. Liquid when heated to 45-50°C

Limited access to 2-ethylhexyl palmitate led to emulsification with Isopropyl palmitate instead of 2-ethylhexyl palmitate because they have similar properties. The oil-water ratio was still 2-5 and the amount of surfactant/polymer was 3.85w% of the total weight, used separately.

Table 36 *Emulsification with SPAN80 as the emulsifier*

Sample	Oil Phase	Water	SPAN80	Comment
1	Isopropyl palmitate 10g	25g	1.4g	Separation of oil at the top of the sample after one day

Table 37 *Emulsification with Cithrol DPHS-SO as the emulsifier*

Sample	Oil phase	Water	Cithrol DPHS-SO	Comment
1	Isopropyl palmitate 10g	25g	1.4g	Stable after one day

An emulsification was done with a mixture of Isopropyl palmitate and Syncrowax used as the oil phase, since that combination had showed best results from the oil phase preparations. The oil-water-ratio used was 2-5 and the surfactant/polymer amount was 3.85w% of the total weight, used separately.

Table 38 *Emulsification with wax added to the oil phase and with SPAN80 used as the emulsifier*

Sample	Oil phase	Water	SPAN80	Comment
1	Isopropyl palmitate 8.33g Syncrowax 1.67g	25g	1.4g	Liquid when heated to 50°C but still highly viscous

Table 39 *Emulsification with wax added to the oil phase and with Cithrol DPHS-SO used as the emulsifier*

Sample	Oil phase	Water	Cithrol DPHS-SO	Comment
1	Isopropyl palmitate 8.33g Syncrowax 1.67g	25g	1.4g	Liquid when heated to 27-30°C

From the previous emulsifications it can be stated that the emulsions with polymer have a lower viscosity than the emulsions with surfactant. The emulsions with polymer have shown desirable properties, such as solid consistence at room temperature and liquid consistence when heated. The sought for emulsion should be liquid close to and above skin temperature which is 35-40°C and that’s a bit higher than what the emulsions with polymer have shown. Three emulsifications were made with a larger amount of wax in the oil phase, 3-10 wax-oil-ratios, and with different amount of polymer in each sample to examine how these changes affect the emulsions viscosity. The oil-water ratio was still 2-5. Directly when an emulsion was prepared it was placed in a fridge because rapid cooling had shown better results in the oil phase preparations. The oil phase preparations where cooled down in a freezer but that will cause the water droplets in the emulsions to solidify, which is not desirable.

Table 40 *Emulsifications with different amount of Cithrol DPHS-SO as the emulsifier*

Sample	Oil phase	Water	Cithrol DPHS-SO	Comment
1	Isopropyl palmitate 7.7g Syncrowax 2.3g	25g	0.7g	2w% polymer of the total weight
2	Isopropyl palmitate 7.7g Syncrowax 2.3g	25g	1.05g	2.9w% polymer of the total weight
3	Isopropyl palmitate 7.7g Syncrowax 2.3g	25g	1.4g	3.85w% polymer of the total weight

Table 41 *Emulsifications with different amount of Cithrol DPHS-SO as the emulsifier*

Sample	Oil phase	Water	Cithrol DPHS-SO	Comment
1	Isopropyl palmitate 8.33g Syncrowax 1.67g	25g	0.7g	2w% polymer of the total weight
2	Isopropyl palmitate 8.33 Syncrowax 1.67g	25g	1.05g	2.9w% polymer of the total weight
3	Isopropyl palmitate 8.33g Syncrowax 1.67g	25g	1.4g	3.85w% polymer of the total weight

It was still difficult to distinguish the water droplets in the emulsion so a new emulsification was made. The surfactant and the polymer were used together to examine if a mixture of those two would lead to an emulsion with higher melting range. In the water a substance with fluorescent properties, Leucophor AF, was added in order to be able to see the water droplets when the emulsion was examined in a

Nikon ECLIPSE Ni microscope with UV-light. The total amount of surfactant/polymer in the emulsions was 3.85w% of the total weight, the amount of wax in the oil phase had a wax-oil-ratio of 2-10 and the oil-water-ratio was 2-5.

Table 42 *Emulsifications with surfactant and polymer used together in different ratios as the emulsifier*

Sample	1	2	3
Cithrol DPHS-SO	0.35g	0.7g	1.05g
SPAN80	1.05g	0.7g	0.35g
Oil phase	Isopropyl palmitate 8.33g Syncrowax 1.67g	Isopropyl palmitate 8.33g Syncrowax 1.67g	Isopropyl palmitate 8.33g Syncrowax 1.67g
Water	25g	25g	25g
Comment	25% polymer, 75% surfactant. Liquid when heated to 40-45°C	50% polymer, 50% surfactant. Liquid when heated to 35-40°C	75% polymer, 25% surfactant. Liquid when heated to 30-35°C

The conclusion from the emulsification seen in *table 42* is that higher amount of SPAN80 as the surfactant increases the melting range.

An emulsification was done to examine the optimal amount of oil-water-ratio in the system with the oil phase consisting of Isopropyl palmitate and Syncrowax in the ratio 10-2 and with the surfactant amount at 3.85w% of the total weight, used separately.

Table 43 *Emulsifications with different oil-water-ratios and with SPAN80 used as the emulsifier*

Sample	Oil phase	Water	SPAN80	Comment
1	Isopropyl palmitate 4.17g Syncrowax 0.83g	10g	0.6g	O-W-ratio 1-2, heated to 60°C – still solid
2	Isopropyl palmitate 8.33g Syncrowax 1.67g	12.5g	0.7g	O-W-ratio 2-5, heated to 60°C – still solid
3	Isopropyl palmitate 8.33g Syncrowax 1.67g	15g	0.8g	O-W-ratio 1-3, heated to 60°C – still solid
4	Isopropyl palmitate 8.33g	17.5g	0.9g	O-W-ratio 2-7, heated to 60°C – still solid

	Syncrowax 1.67g			

Table 44 *Emulsifications with different oil-water-ratios and with Cithrol DPHS-SO used as the emulsifier*

Sample	Oil phase	Water	Cithrol DPHS-SO	Comment
1	Isopropyl palmitate 4.17g Syncrowax 0.83g	10g	0.6g	O-W-ratio 1-2, liquid when heated to 25-30°C
2	Isopropyl palmitate 8.33 Syncrowax 1.67g	12.5g	0.7g	O-W-ratio 2-5, liquid when heated to 30-35°C
3	Isopropyl palmitate 8.33g Syncrowax 1.67g	15g	0.8g	O-W-ratio 1-3, liquid when heated to 35-40°C
4	Isopropyl palmitate 8.33g Syncrowax 1.67g	17.5g	0.9g	O-W-ratio 2-7, liquid when heated to 40-45°C

The conclusions made from the emulsifications in *table 44* were that higher amount of water will lead to a higher melting range of the emulsion. Since the emulsions with the oil-water-ratio 2-7 were stable they were further examined because a higher amount of water in the emulsion will lead to a greater cooling effect of the emulsion.

All emulsions that have been made that contained Syncrowax were stable at room temperature without any signs of separation. The reason of this might be that Syncrowax in itself has emulsifying properties.

The emulsions from table 41underwent a stability test where they were placed in an oven at 50°C for 24 hours to examine how they were affected by a longer time in heat. All of the emulsions that only contained SPAN80 as emulsifier had started to separate a bit at the top of the sample. The samples with mixes of SPAN80 and Cithrol DPHS-SO and the ones with only Cihrol DPHS-SO were still stable after 24 hours. It could also be stated that the emulsions with larger amount of water hade higher viscosity and higher amount of SPAN80 in the mixture also led to higher viscosity. New emulsifications were made with mixtures of SPAN80 and Citrol DPHS-SO but this time with a higher water amount, the oil phase-water-ratio of 2-7. The oil used was Isopropyl palmitate and the wax was Syncrowax, used in the wax-oil-ratio 2-10. The amount of surfactant/polymer-mixture was 3.85w% of the total weight. The water phase contained Leucophor AF.

Table 45 *Emulsifications with surfactant and polymer used together in different ratios as the emulsifier*

Sample	1	2	3
Cithrol DPHS-SO	0.225g	0.45g	0.675g
SPAN80	0.675g	0.45g	0.225g
Oil phase	Isopropyl palmitate 4.17g Syncrowax 0.83g	Isopropyl palmitate 4.17g Syncrowax 0.83g	Isopropyl palmitate 4.17g Syncrowax 0.83g
Water	17.5g	17.5g	17.5g
Comment	25% polymer, 75% surfactant.	50% polymer, 50% surfactant.	75% polymer, 25% surfactant.

Emulsifications with Akosoft used as the oil phase were done. Akosoft was used as the only component in one emulsification, because it had desirable properties on its own, and in another emulsification it was mixed with Syncrowax to examine how the addition would affect the emulsion. The oil-water-ratio used for the emulsions were 2- 7 and the amount of surfactant/polymer were 3.85w% of the total weight, used separately.

Table 46 *Emulsifications with wax added to the oil phase and with SPAN80 used as the emulsifier*

Sample	Oil phase	Water	SPAN80	Comment
1	Akosoft 5g	17.5g	0.9g	Did not form W/O emulsion.
2	Akosoft 4.2g Syncrowax 0.8g	17.5g	0.9g	Forms unstable emulsion, water separates out from the emulsion when heated to 35°C.

Table 47 *Emulsifications with wax added to the oil phase and with Cithrol DPHS-SO used as the emulsifier*

Sample	Oil phase	Water	Cithrol DPHS-SO	Comment
1	Akosoft 5g	17.5g	0.9g	Liquid when heated to 27-33°C
2	Akosoft 4.2g Syncrowax 0.8g	17.5g	0.9g	Not liquid when heated to 55°C

The emulsifications with Akosoft used as the oil phase did not show useful results and further emulsifications with that oil phase was not made.

From previous emulsifications it has shown that the emulsions containing polymer and the oil-water-ratio 2-7 provides the best result that meets the requirements for the emulsion. The oil-water-ratio 2-7 has previously been the used as the ratio with the highest amount of water. Further emulsifications were made with the ratio1-1 water used as the lowest amount of water in the emulsions and the oil-water-ratio of 1-4 used as the highest. The oil phase contained Isopropyl palmitate and Syncrowax in the ratio 10-2 and mixes of Cithrol DPHS-SO and SPAN80 were examined. The total amount of surfactant/polymer was 3.85 w% of the total weight. One emulsification was done with 100% Cithrol DPHS-SO as the emulsifier; this was not done for SPAN80 because emulsions with SPAN80 used on its own had previously showed not to be stable. The water phase contained Leucophor AF.

Table 48 *Emulsifications with surfactant and polymer used together in different ratios as the emulsifier and with an oil-water-ratio of 1-1*

Sample	1	2	3	4
Cithrol DPHS-SO	1g	0.75g	0.50g	0.25g
SPAN80	0g	0.25g	0.50g	0.75g
Oil phase	Isopropyl palmitate 10.4g Syncrowax 2.1g	Isopropyl palmitate 10.4g Syncrowax 2.1g	Isopropyl palmitate 10.4g Syncrowax 2.1g	Isopropyl palmitate 10.4g Syncrowax 2.1g
Water	12.5g	12.5g	12.5g	12.5g
Comment	100% polymer, 0% surfactant. Stable after three days in an oven at 50°C	75% polymer, 25% surfactant. Stable after three days in an oven at 50°C	50 % polymer, 50% surfactant. Stable after three days in an oven at 50°C	25% polymer, 75% surfactant. Stable after three days in an oven at 50°C

Table 49 *Emulsifications with surfactant and polymer used together in different ratios as the emulsifier and with an oil-water-ratio of 1-4*

Sample	1	2	3	4
Cithrol DPHS-SO	1g	0.75g	0.50g	0.25g
SPAN80	0g	0.25g	0.50g	0.75g
Oil phase	Isopropyl palmitate 4.2g Syncrowax 0.8g	Isopropyl palmitate 4.2g Syncrowax 0.8g	Isopropyl palmitate 4.2g Syncrowax 0.8g	Isopropyl palmitate 4.2g Syncrowax 0.8g
Water	20g	20g	20g	20g
Comment	100% polymer, 0% surfactant. Stable after	75% polymer, 25% surfactant. Stable after	50 % polymer, 50% surfactant. Stable after	25% polymer, 75% surfactant. Stable after

	four days in an oven at 50°C	seven days in an oven at 50°C	seven days in an oven at 50°C	seven days in an oven at 50°C

The emulsions from 47 and 48 were placed in an oven at 50°C for a week. They were checked every day to see if they still were stable. All emulsions were stable after two day and a clear difference in viscosity between the samples with high and low water amount was noted, were the samples with higher amount of water had higher viscosity but all samples were liquid at 50°C. After four days some separation at the top of the test tube had occurred on the samples with the oil-water-ratio 1-1. The samples which were stable after four days were all of the samples with an oil-water-ratio of 1-4. After seven days three emulsions were still stable, all of the emulsions with the oil-water-ratio 1-4 except the one with 100% polymer as the emulsifier.

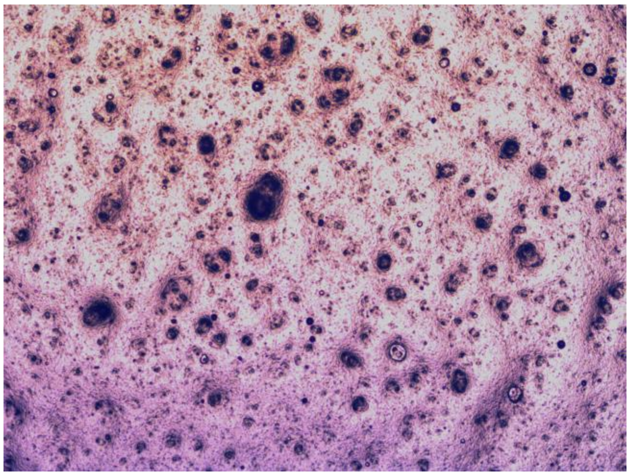
The emulsifications with Cithrol DPHS-SO as the emulsifier had previously showed better results than the ones with SPAN80 as the emulsifier. An examination of the HLB-dependence was done where an emulsification was done with SPAN80 mixed with TWEEN80 to achieve the same HLB value as Cithrol DPHS-SO has. SPAN80 has a HLB value of 4.3 and TWEEN80 has a HLB value of 15. The HLB value was calculated as follows.

$$(4.3_{HLB\ SPAN80} * 0.89) + (15_{HLB\ TWEEN80} * 0.11) = 5.477 \approx 5.5$$

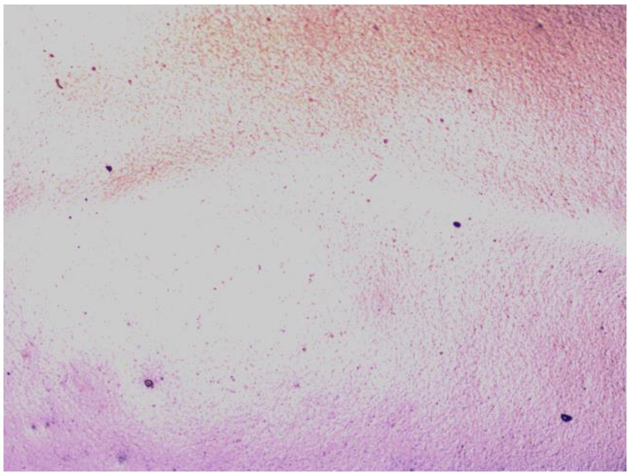
Equation 4 *Calculation of the HLB value of the surfactant mixture*

89w% SPAN80 was mixed with 11w% TWEEN80 to achieve the HLB value of 5.5, which is the HLB value of Cithrol DPHS-SO. This was done for examination if the required HLB value of the oil might be closer to the HLB value of the polymer and therefore make those emulsions more stable. The emulsification sample with the surfactant mixture was compared with an emulsification with 100% polymer as the emulsifier. Both of the comparing samples were placed in an oven at 50°C for one day. The sample with polymer as the emulsifier was still stable after one day in the oven while the sample with the surfactant mixture was not. Some separation had occurred at the top of the sample. The conclusion from this examination was that it wasn’t the HLB value of the polymer that made the emulsions with polymer as the emulsifier more stable, it was probably the structure of the polymer.

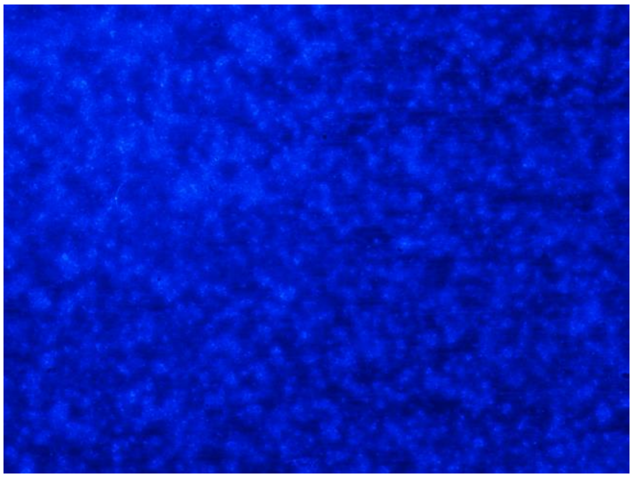
4.3 Microscopic observation



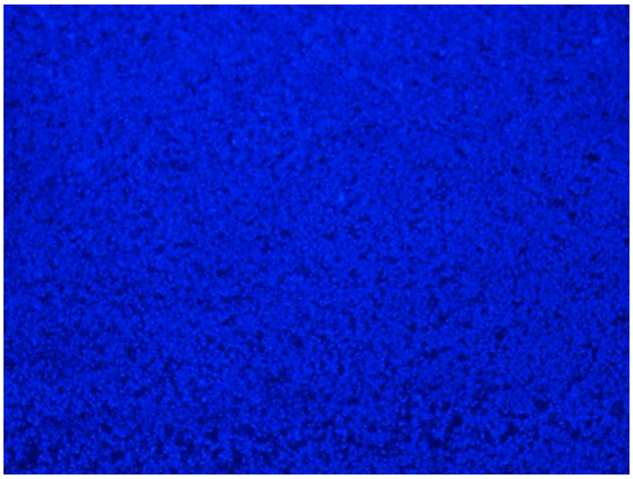
Picture 1 *Oil phase preparation consisting of 10g 2-ethylhexyl palmitate, 1g Akofine and 1g Syncrowax, observed in an Olympus BH2-UMA with four times enlargement*



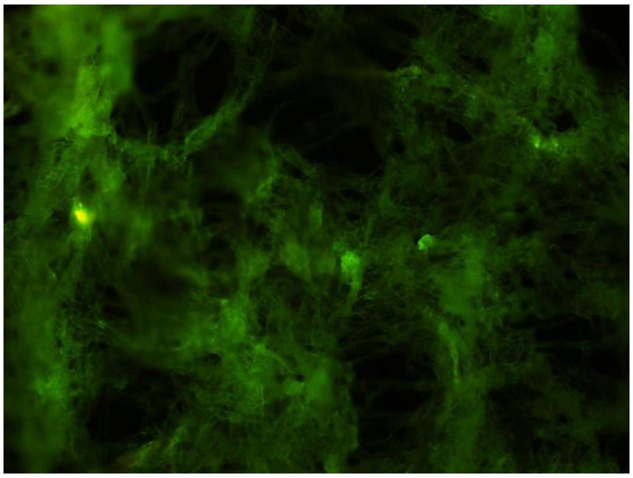
Picture 2 *Oil phase preparation consisting of 10g Isopropyl palmitate and 2g Syncrowax, observed in an Olympus BH2-UMA with four times enlargement*



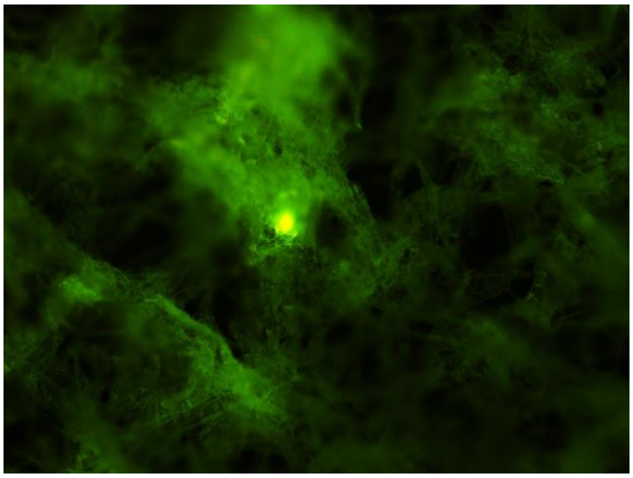
Picture 3 *Emulsion with the oil phase consisting of Isopropyl palmitate and Syncrowax in the ratio 10-2, the oil-water-ratio of 1-1 and the emulsifier amount was 3.85w% of the total weight. The emulsifier used consisted of 100% Cithrol DPHS-SO. The water droplets in the emulsions contained the fluorophore Leucophor AF. The emulsion was observed in UV-light with a Nikon ECLIPSE Ni microscope with four times enlargement*



Picture 4 *Emulsion with the oil phase consisting of Isopropyl palmitate and Syncrowax in the ratio 10-2, the oil-water-ratio of 1-4 and the emulsifier amount was 3.85w% of the total weight. The emulsifier used consisted of 100% Cithrol DPHS-SO. The water droplets in the emulsions contained the fluorophore Leucophor AF. The emulsion was observed in UV-light with a Nikon ECLIPSE Ni microscope with four times enlargement*

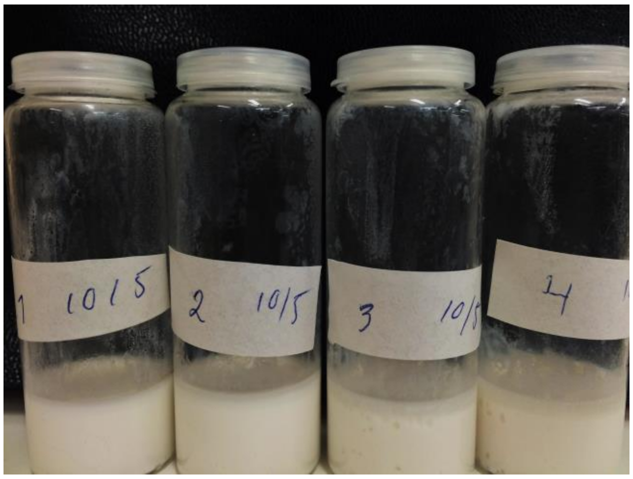


Picture 5 *Emulsion coated on handkerchief with emulsion with the oil phase consisting of Isopropyl palmitate and Syncrowax in the ratio 10-2, the oil-water-ratio of 1-2 and the emulsifier amount was 3.85w% of the total weight. The emulsifier used consisted of 100% SPAN80. The water droplets in the emulsions contained the Fluorophore Leucophor AF. The emulsion was observed in UV-light with a Nikon ECLIPSE Ni microscope with ten times enlargement*

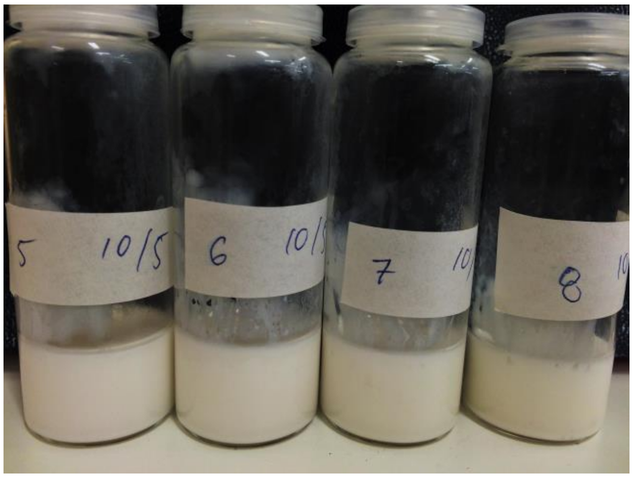


Picture 6 *Emulsion coated on handkerchief with emulsion with the oil phase consisting of Isopropyl palmitate and Syncrowax in the ratio 10-2, the oil-water-ratio of 1-2 and the emulsifier amount was 3.85w% of the total weight. The emulsifier used consisted of 100% SPAN80. The water droplets in the emulsions contained the Fluorophore Leucophor AF. The emulsion was observed in UV-light with a Nikon ECLIPSE Ni microscope with ten times enlargement*

4.4 Stability test



Picture 7 *Emulsions from table 47 with an oil-water-ratio of 1-1 and 3.85w% emulsifier of the total weight, some separation could be seen at the top of each sample after four days in an oven at 50*°C



Picture 8 *Emulsions from table 49 with an oil-water-ratio of 1-4 and 3.85w% emulsifier of the total weight, some separation could be seen on the top of sample 5 after seven days*

4.5 Coating of emulsions on handkerchiefs

Three emulsions were used to coat handkerchiefs; five handkerchiefs were coated with each emulsion. The emulsions used can be seen in table 42, emulsion 1 consists of 25% polymer, 75% surfactant, emulsion 2 consists of 50% polymer, 50% surfactant and emulsion 3 consists of 75% polymer, 25% surfactant. The total amount of surfactant/polymer in the emulsions was 3.85w% of the total weight, the amount of wax in the oil phase had a wax-oil-ratio of 2-10 and the oil-water-ratio was 2-5. The oil used was Isopropyl palmitate, the wax was Syncrowax and the water phase had 0.2w% Leucophor AF added to be able to observe the water droplets with a Nikon ECLIPSE Ni microscope in UV-light.

Table 50 *Coating of emulsions on handkerchiefs*

Emulsion 1	
Handkercheif number	Weight of emulsion on handkerchief
1.1	0.079g
1.2	0.106g
1.3	0.221g
1.4	0.140g
1.5	0.15g

Table 51 *Coating of emulsions on handkerchiefs*

Emulsion 2	
Handkercheif number	Weight of emulsion on handkerchief
2.1	0.17g
2.2	0.14g
2.3	0.16g
2.4	0.14g
2.5	0.31g

Table 52 *Coating of emulsions on handkerchiefs*

Emulsion 3	
Handkercheif number	Weight of emulsion on handkerchief
3.1	0.2g
3.2	0.25g
3.3	0.29g
3.4	0.21g
3.5	0.26g

5 CONCLUSIONS

The objectives of this thesis work was to develop a water in oil emulsion where the continuous oil phase would be solid at room temperature to increase stability but liquid close to and above skin temperature to facilitate the transfer of the discontinuous water phase to the skin. The conclusion from the oil phase preparations was that the oil phases that formed sharp crystal structure would not be suitable to use in an emulsion since these sharp crystals might destroy the water droplets in an emulsion. After several preparations a suitable oil phase preparation was found consisting of Isopropyl palmitate and Syncrowax in the ratio 10-2. This oil phase had a creamy consistence and did not form sharp crystals.

Conclusions made from the emulsifications was that the emulsions that contained the surfactant SPAN80 as the emulsifier had higher viscosity and increased melting range compared to the emulsions with the polymer Cithrol DPHS-SO. A further conclusion which also refers to the viscosity of the emulsions was that higher water amount in the emulsions led to higher viscosity and increased melting range of the emulsion. The emulsions with only SPAN80 as the emulsifier were not as stable as the ones with only Cithrol DPHS-SO but the most stable emulsions were the ones made with mixtures of them both as the emulsifier. The objectives of the emulsion was that it would have phase transition stability for it to be able to go from solid to liquid when it was applied on the tissue and after that go back to solid state, without causing phase separation. This was fulfilled with the emulsion that consisted of the oil phase Isopropyl palmitate and Syncrowax in the ratio 10-2, the oil-water-ratio 1-4 and the emulsifier amount of 3.85w% of the total weight, where 50% of the emulsifier was Cithrol DPHS-SO and 50% was the surfactant SPAN80.

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