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Comparison of two sizes of B mixers in the production of make-up foundation emulsions

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Lumene skin care and make-up emulsions are core technologies manufactured in the Espoo factory. The objective of this thesis was to validate the different size of reactor, than normally used, for the manufacturing of the make-up foundations. Also the theory of colloidal chemistry and the viscosity measurements are expressed in this thesis.

The devices used in manufacturing emulsions are validated B-mixers with effective homogenizers Make-up foundations were manufactured with B 600 before, but now all foundations must be manufactured with a smaller B 250 kg. Therefore test batches must had been manufactured couple of different ways. The test batches included three products. Two of those were silicone based water-in-silicone emulsion foundations and one was an oil-in-water emulsion. The tests performed in the laboratory were viscosity and stability tests and Lumiziser analysis.

This test series shows that it is safe to change the manufacture from a bigger reactor to smaller one using the same or almost same instructions. The main concern about this particular scaling down was the new homogenizer of B250, but the results shows that the product and the manufacture are similar and as good in both cases. The objective was achieved and the foundations are manufactured now in smaller reactor.

Keywords	emulsion, production, cosmetics, foundation, B

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Lumenen ihon hoito- ja meikkivoide-emulsiot ovat keskeisiä tuotteita, joita valmistetaan Espoon kosmetiikkatehtaalla. Insinöörityön tavoitteena oli validoida erikokoinen reaktori, mitä yleensä käytetään, meikkivoiteiden tuotantoon. Lisäksi työssä on kirjallisuusosa, jossa on käsitelty emulsio- ja viskoteettiteoriaa.

Valmistukseen käytetään validoituja B-reaktoreita, joissa on tehokas homogenaattori. Meikkivoiteet valmistettiin aikaisemmin 600 kilon B-reaktorissa, mutta nykyään meikkivoiteet valmistetaan pienemmässä 250 kilon laitteessa. Tästä syystä B250:lla valmistettiin koe-eriä parilla eri tavalla kolmesta eri tuotteesta. Kaksi näistä tuotteista on silikonipohjaisia meikkivoiteita ja yksi perinteisempi öljy-vedessä emulsio. Koe-erien massat tutkittiin laboratoriossa, kokeina viskositeetti, säilyvyystestit ja Lumiziser-analyysi.

Nämä koe-erät ja niistä tehdyt kokeet osoittivat, että pienemmällä tuotantolaitteella on turvallista tehdä meikkivoide-emulsioita noudattaen melkein samoja työohjeita kuin isommalla laitteella. Vaikka oli epäilys, että B250:n homogenaattori olisi huonompi tehoiltaan kuin B600:n vastaava osa, niin tuotteiden laadussa ei huomattu juurikaan eroa. Tavoite saavutettiin hyvin ja tuotanto on siirretty pienempään reaktoriin.

Avainsanat	emulsio, tuotanto, kosmetiikka, meikkivoide, B

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Appendix 3. Final manufacturing instruction of C Foundation

LIST OF ABBREVIATIONS

B250	250 kg B-reactor
B600	600 kg B-reactor
HLB	Hydrophilic/lipophilic balance

1 Introduction

Lumene is a Finnish cosmetic company based in Kauklahti, Espoo. High quality skincare and make-up products are manufactured also in the Espoo factory with approximately 250 employees. Cosmetic emulsions like skin care products and make-up foundations are the core of Lumene’s business; thus the technology and procedure of production are validated to reach high quality and optimal performance.

Emulsions are basic forms of Lumene’s products and the technology of developing and manufacturing of emulsions are introduced in this thesis. Scaling between two sizes of B manufacturing mixers is validated by producing test batches of make-up foundations and analysing the products in the laboratory.

2 Theory of cosmetic emulsion technology

2.1 Theory of emulsion

The oil-water emulsion technology is one of the most important aspects of the surface and colloidal chemistry. Oil is not soluble in water and vice versa, and the essential subject is based on the fact that oil and water do not mix together if shaken. Oil breaks into small drops (about few millimeters in diameter), but these drops join together rather quickly and return to their original state. [1. pp. 211]

A colloid, in chemistry, is a mixture in which one substance of microscopically dispersed insoluble particles is suspended throughout another substance. Ideal colloidal systems are composed of two phases, the dispersed phase and continuous phase. The theory of colloid is mostly based on ideal two-phase systems, but in practise it is rarely true. Colloidal systems are multi-component in nature where small amounts of other components have significant effects on colloidal stability and properties. [2. pp. 67]

A dispersion is a system in which particles are dispersed in a continuous phase of a different composition (or state). In emulsion, very fine droplets of liquid are dispersed in a second liquid. These two liquids are partially or totally immiscible. To produce stable emulsions, a surface-active agent must also be present. Surfactants promote emulsion stability by adsorbing to liquid-liquid interface and reducing the surface tension. Also some form of mechanical agitation is needed to form emulsion.

The two emulsion phases are referred to as”oil” (lipophilic) phase (can also be silicone) and the ”water” (hydrophilic) phase forming two possible emulsion types: water-in-oil (W/O) emulsion and oil-in-water (O/W) emulsion.

Generally speaking the continuous phase is in excess. If you have an equal amount of both phases, it depends on the surfactant and on the method of formation which type of emulsion you get, W/O or O/W. It also is possible to distinguish the O/W from W/O in several different ways. Generally, the O/W emulsions are easy to disperse to water and can be coloured by water-soluble dyes and exhibit a higher electrical conductivity than W/O emulsions. [2. pp. 90]

2.2 Surfactants and emulsifiers

All molecules (such us soaps, surfactants, detergents) reduce surface tension when they are dissolved in water. It means that surface active substances adsorb at the surface and reduce surface tension. This also happens in the oil-water interface and the tension between oil and water will be reduced when a surfactant is added. [1. pp. 65]

An important characteristic of surfactants is solubility in water. Solubility is dependent on the alkyl group as well as on the polar group. Polarity of the molecules means difference on electronegativity between the bonded atoms.

Oil and water can be dispersed with the help of suitable emulsifiers (surfactants) to give emulsions. Interfacial tension (IFT) between oil and water is high, app. 50 mN/m, which leads to formation of large oil drops. By adding suitable emulsifiers, the value of IFT can be reduced to very low values (even less than 1 mN/m). That means that oil drops are smaller and remain for a dispersed longer time (even years). Stability and the characteristics of these emulsions are related to the area of applications. [1. pp. 211]

In cosmetic formulations, surfactants can act as detergents for cleansing, as wetting agents for better spreadability, as foaming agents, as emulsifiers to create stable mixtures of oil and water, as condition agents and as solubilisizers.

Some commonly used emulsifiers in skin care are glyceryl stearate, PEG-100 stearate, stearyl alcohol, cetyl alcohol, laureth-23, steareth alcohol, cetyl/PEG/PPG 10 dimethicone, and stearic acid.
Emulsifiers have a hydrophilic head and a lipophilic tail (Figure 1). The hydrophilic head clings onto the water phase of an emulsion, and the lipophilic tails creates a ball around the oil-phase ingredients. [3]

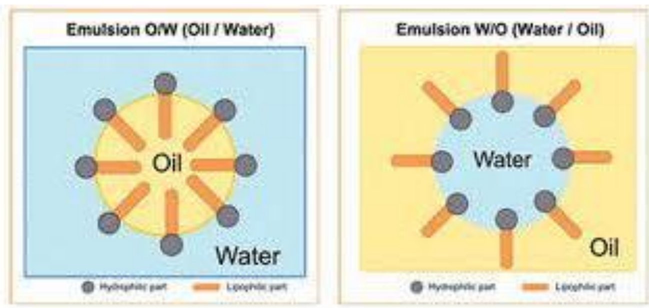


Figure 1. Positions of the molecules in the water and oil phase. (http://www.skin-hairactives.com/cosmetic-emulsifier-1173753.html)

Hundreds of many types of surfactants are available for stabilising the emulsion. The common method of choosing the optimum one is the use of HLB (hydrophilic/lipophilic balance) value. The HBL scale is running from 1 to 20. The lower value promoting W/O emulsion and higher value surfactants produce O/W emulsions. There are many techniques to determine the HBL value of the surfactant, but the most common method is using this relationship:

$$\text{HBL value} = 20 * \left[1 - \frac{S}{A}\right],$$

where S is the saponification number of the ester, and A is the acid number of the recovered acid.

This relationship is only applicable for certain type of non-ionic surfactants. There is no universal method available for determining the HBL values for all types of surfactants. [2. pp. 90]

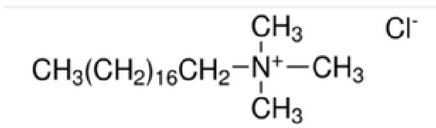
Surfactants can be grouped into four main chemical/structure categories based upon the ionic nature they contain. These categories are listed below:

- Anionic (negative charge)
- Cationic (posive charge)
- Nonionic (no charge)
- Amphotetic (capable both positive and negative charge, or no charge)

Anionic surfactants are typically used in cleansing formulations because they are excellent detergents, providing both foam and detergency. The most commonly used product type is alkyl sulfate. A common example is sodium lauryl sulfate (SLS):

$$CH_3\text{-}(CH_2)_{11}\text{-}OSO_3\text{-}Na$$

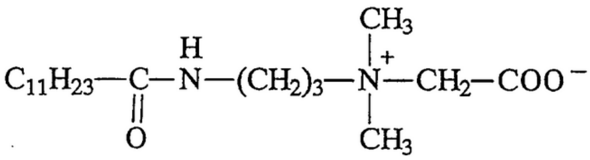
Cationic surfactants are effective conditioners, with some foaming. They are also irritating to skin and eyes at very low levels compared to other surfactants. For example, stearyl trimethyl ammonium chloride:



Noninonic surfactants are mild but low foaming surfactants. They are sued commonly to making emulsions. An example of nonionic surfactant is Laureth 12:

$$CH_3\text{-}(CH_2)_{11}\text{-}O\text{-}(CH_2CH_2O)_{12}H$$

Amphoteric surfactants also function as detergents, but they have somewhat different chemical structures and properties. These materials are less irritating and are used as primary detergents in mild formulations such as baby shampoos. Example of lauryl betaine is given below:



[9. pp. 111]

Using blends of non-ionic surfactants gives more effective promotion to emulsions and forms more stable systems. Blends offers the higher packing density of the surfactants molecules at the oil/water interface. [2. pp. 90]

Silicone-based emulsifiers provide the same benefits as W/O emulsifiers, but without disadvantages such as greasy feel, manufacturing-required heating/cooling, waxes for stability and limited flexibility in formulations. Silicone-based emulsifiers have high molecular weight but still remain as liquid at room temperature, because of the flexible Si-O bond. Organic W/O emulsifiers with high molecular weight are usually waxes; therefore heating is necessary during the manufacturing. Silicone-based emulsifiers also succeed in W/O emulsions due to the combination of high molecular weight and flexibility.

Silicone emulsifiers are typically used in colour cosmetic applications. Volatile silicone oils are commonly used in foundations; thus the silicone-based emulsifiers are the best option to create stable emulsion. W/Si foundations are longer-lasting as they are more resistant to wash-off than O/W systems. [4]

3 Viscosity

3.1 Theory of viscosity measuring

Viscosity is the measure of the internal friction of a fluid. This friction becomes apparent when layer of fluid in made to move in relation of another layer. The greater the friction the greater amount force is required to cause the movement and this is called *shear*. Shearing occurs for example during mixing, pouring and spreading. Highly viscous fluids therefore require more force than less viscous materials.

Isaac Newton defined the viscosity represented in Figure 2. Two parallel planes of fluid of equal area (A) are separated by distance (dx) and are moving in the same direction at different velocities (V1 and V2).

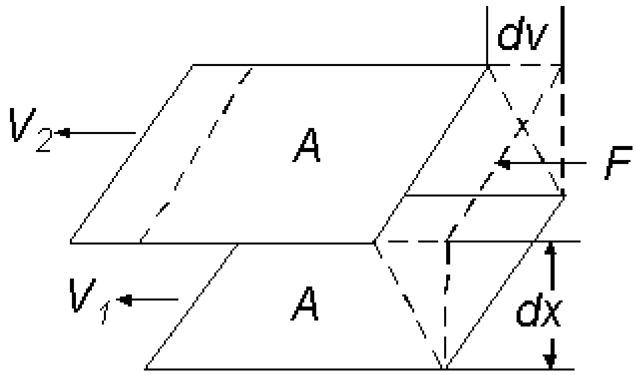


Figure 2. Isaac Newton's model of viscosity

Formula can be expressed as follows:

$$\frac{F}{A} = \eta \frac{dv}{dx}$$

where η is constant for given material and called viscosity. The velocity gradient $\frac{dv}{dx}$ is a measure of the speed, at which the intermediate layers move with respect to each other. This is also called shear rate (S). It is unit of measure is called reciprocal second (sec^{-1}).

The term $\frac{F}{A}$ is the force per unit area to produce the shearing action. It is also called shear stress (F') with unit dunes per square centimetre. With these simplified terms, viscosity can be defined by following formula:

$$\eta = \frac{F'}{A}$$

The fundamental unit of viscosity measurement is the poise. A material requiring a shear stress rate of one dyne per square centimetre to produce a shear rate of one reciprocal second has a viscosity of one poise, or 100 centipoise. Viscosity can also be expressed in Pascal-seconds (Pa·s) or milli-Pascal-seconds (mPa·s). One Pascal-second is equal to ten poise and one milli-Pascal-second is equal to one poise.

The properties of the sample affect the results of the viscosity measurements. The conditions of the measuring circumstance has to be always the same; thus the results are comparable. Temperature, shear rate, measuring time and size of the measuring spindle are the factors that should be considered. [10]

This Isaac Newton theory is about absolute viscosity with unit poise. Kinematic viscosity has unit Stokes (St) or Centistokes (cSt) which are as SI units m^2/s and mm^2/s. [11.pp. 5]

3.2 Brookfield viscometer

In Lumene laboratory viscosity is measured with Brookfield LV 2 -viscometer (Figure 3.).

Figure 3. Brookfield DV2 Viscometer in Lumene R&D laboratory

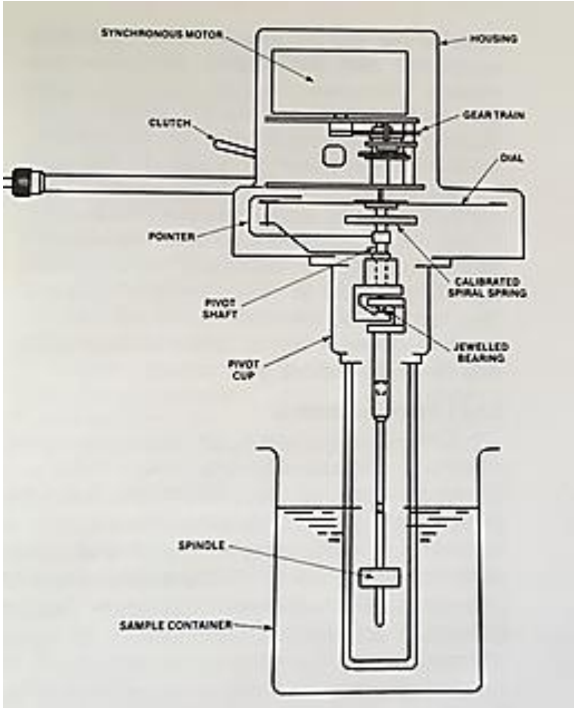


Figure 4. Brookfield viscosimeter. [11]

The Brookfield viscometer (Figure 4) measures the torque required to rotate an immersed element (the spindle) in a fluid (Figure 5 and Figure 6). The spindle is driven by a synchronous motor through a calibrated spring. The deflection of the spring is indicated by a digital display. The given viscosity or resistance to flow (indicated by the degree to which the spring winds up) is proportional to the spindle's speed of rotation and is related to the spindle's size and shape. The drag will increase as the spindle size and/or rotational speed increase. It follows that for a given spindle geometry and speed, an increase in viscosity will be indicated by an increase in the deflection of the spring. The synchronous drive motor and multiple-speed transmission are located at the top of the instrument inside the housing to which the name plate is attached. The main case of the viscometer contains a calibrated beryllium-copper spring, one end of which is attached to the pivot shaft; the other end is connected directly to the dial. The dial is driven by the transmission and in turn drives the pivot shaft through the calibrated spring. [10.pp.7-8]

Figure 5. Spindels used in emulsion measurement

Figure 6. Spindels

4 Lumene foundations

4.1 Formulas and ingredients

In this thesis, the manufacturing comparison focuses on two types of Lumene foundations. Lumene also manufactures other cosmetic skin care emulsions using B reactors. The most selling make-up foundations are water-in-silicone-based formulas, which are cold-process produced with quite an easy and simple formula with silicone and water, the silicone based emulsifier and active ingredients and surface treated pigments. These foundations are A Foundation and C foundation.

Other type of formula is B Foundation which is oil-in-water emulsion that is manufactured traditionally by combining the water and oil-phases at 75-80 degrees celcius.

These three foundations contain both a silicone-based and an organic emulsifier. A Foundation and C Foundations are silicone-based formulas with a silicone-based emulsifier, and B Foundation has a combination of two organic emulsifiers.

A Foundation has a silicone emulsifier with inci name *Polyglyceryl-4 Isostearate (and) Cetyl PEG/PPG-10/1 Dimethicone (and) Hexyl Laurate*. It is emulsifier for W/O creams and lotions with excellent heat and freeze/thaw stability. It can be formulated with all kinds of cosmetic oils. It has a high compatibility with active ingredients, and it can be used as an emulsifier for sun protection preparations with high content of organic and/or physical UV filters.

C Foundation has a silicone emulsifier with inci name *Lauryl PEG-10 Tris(Trimethylsiloxy)silylethyl Dimethicone.* This is a non-diluted and low viscosity silicone surfactant. It is designed to produce stable water-in- silicone emulsions and water-in-oil emulsions with light sensory.

B Foundation has an emulsifier with inci name *PEG-100 Stearate (and) Glyceryl Stearate*. This stearate is designed for use in oil/water emulsions which are either acidic or contain electrolytes

B foundation also has another emulsifier with inci name *Cetyl Alcohol (and) Glyceryl Stearate (and) PEG-75 Stearate (and) Ceteth-20 (and) Steareth-20*. It has strong emulsifying and stabilizing properties and is used for difficult formulations. It also has an excellent stability and presence of liquid crystals.

The formulas of the foundations are a commercial secret and have been developed in the Lumene Research and Development Laboratory. In tables 1-3 are shown trade names, inci-names and percentages of the ingredients. There are also the phases with letters to guide the manufacturing. After each table there are general manufacturing instructions how to prepare the formula in the laboratory or in the production. The accurate and final production instructions are in appendices 1-3.

Table 1 A Foundation formula

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Table 2. C Foundation ingredients and inci names

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Table 3 B Foundation ingredients and inci-names

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4.2 Research and development of cosmetic products

Developing a new colour cosmetic product starts from the proposal of the marketing team. The R&D chemist evaluates the ingredients that meet the wanted marketing claims and properties, and formulates the product according to that. The laboratory technician prepares the formula on a laboratory scale as many times as is needed with certain modifications. Samples are tested and approved by the marketing team. The approved formula is tested in the laboratory. Stability tests, microbiological challenge-tests, skin irritation patch-tests and possible SPF- and UVA-tests are performed from the R&D-versions. The chart in Figure 7. shows well how the evaluating and troubleshooting of emulsion formulation goes in the R&D procedure.

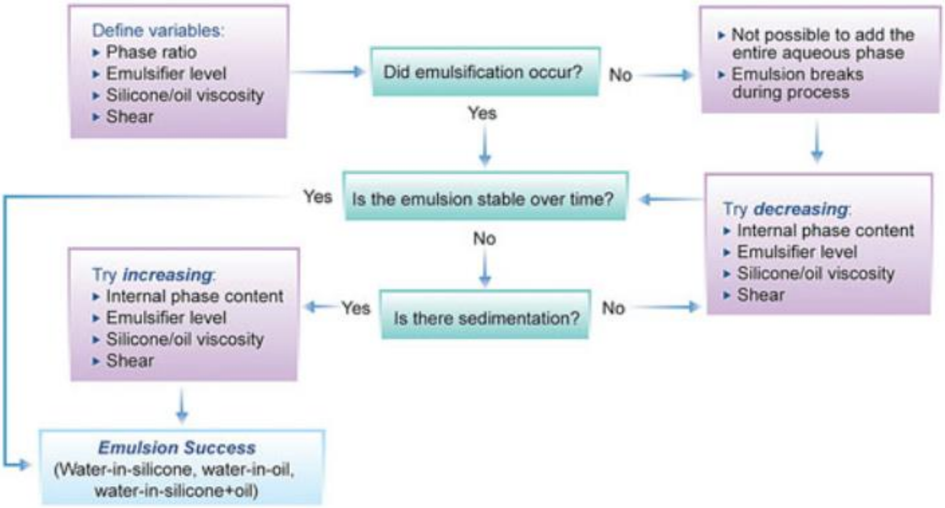

Figure 7. Evaluating the W/S process. (http://www.cosmeticsandtoiletries.com/formulating/function/feelenhancer/Silicone-Emulsifiers-and-Formulation-Techniques-for-Stable-Aesthetic-Products-230040831.html?prodrefresh=y)

The first step towards production with new approved formula is to prepare the pilot scale batch with B reactor sized 10 kg. This device is applicable in the laboratory. This procedure gives approximately directial idea how the formula behaves on an industrial scale. According to that, the manufacturing instruction to manufacturing worker is prepared. The first batch in the production is the most critical point of the new product.

4.3 Bulk manufacture scale up

Formulating a product in the laboratory that perfectly meets the brief of the marketing team is great, but then it would be better if the formula can be successfully repeated in the production scale. There are many steps to consider before the perfect laboratory formulated product is ready for the packaging line. The formulator and her/his experience of the production, and methods of manufacturing are generally main issues which impact to success.

The first critical point is the formulator. Ensuring the formulator has experience of a production environment and the equipment is the most important aspect to ensure so that there are no unrealistic proposals for formulation methodology. All formulators should be encouraged to train and even work in the production in their early lab career. By seeing first hand how for example processes, handling considerations, timing, equipment and limitations differ between the laboratory and production gives comprehensive picture of the whole process and of formulating the products as easily as possible from the production point of view.

Understanding the production equipment prevents many scale-up issues from the beginning. A typical example can be a formulation with two separate phases prepared during the process, where the formulator has not considered the possible size, weight, heating and handling restrictions in production. Processes that have 3-4 different phases or premixes can be simple in the laboratory, but very complex logistically in production. Full or at least basic understanding of production vessels, incorporation, mixing rates, mixing methods, heating and cooling and controls (like pH) is vital to economic and succesful scale-up.

Ingredient corporation often vary between laboratory and production. In the laboratory all the ingredients are added ”over the side”, but in production there are many ways for incorporation. Sometimes ingredients are pumped in to the main vessel under the surface, sometimes added onto the vortex of the homogenizer. Such variations and addition rates can affect the behavior of certain ingredients and how they disperse. Powders are a good example, in the laboratory is easy to handle 20 g of lightweight powder, but in production 2000 kg of the same powder is incredibly different.

Speeds, methods and rates often vary between laboratory and production. Mixing, over all, determines the final aesthetic and the stability of the product. Successful emulation and scale-up of mixing methods between laboratory and production means replicated rheology and also stability. If the homogenization rate in the laboratory is not the same as in production, the product will be different. The differences in emulsion aesthetics may not be detectable immediately, but emulsion could be prone ultimate instability if the droplet size is not as expected. Microscopy is very useful for investigating the droplet size and for comparing between laboratory and production output in mixing perspective. Microscopy will reveal insufficient (or over) mixing, so the appearance and viscosity readings are not quite right.

Heating and cooling are procedures that typically are critical points scaling up from laboratory to production. The key difference between these two is without doubt time. In the laboratory, a phase containing waxes and butters may take 5 minutes to heat to 75°C and melt to be a uniform liquid. In production environment, it could easily take an hour and larger pieces of waxes could be harder to melt down and maybe require a higher temperature. Also the heating of the whole batch within a large vessel takes much more time in the production environment than in the laboratory and it is important to understand the impact on the ingredients of longer exposure time. Cooling takes also longer time in production than in the laboratory. It is vital to understand these differences in processes, because the impact to viscosity, stability and structure can be significant.

There are some recommendations and tips for successful scale-up. An ideal situation would be to have a hands-on formulator with experience of the production environment and effective communication about methodology, issues and opportunities with process engineers/workers. This inclusion also promotes a more seamless transfer from the laboratory to production. Pilot scale batches made together with the formulator and the engineer/manufacture worker are the best way to validate the process and aid the smooth process from the laboratory to production. Flexibility of methodology decreases the risks of problems.

Successful scale-up from the laboratory to production scale is not always a smooth process, but there are many considerations and steps that can be adopted to reduce issues. [5]

5 Manufacturing and equipment of cosmetic emulsions

5.1 B technology

B universal homogeniser mixer is for production of cosmetics and pharmaceutical products, such as cosmetic creams, gel products, mascara and make up foundations. In Lumene production B mixers are used particularly for this use.
The equipment has pressure and vacuum resistant boilers with double jackets, homogenisers (Figure 9.), anchor stirrers and is available for pilot plants and production plants of capacities between 10 to 10 000 litres. [6]

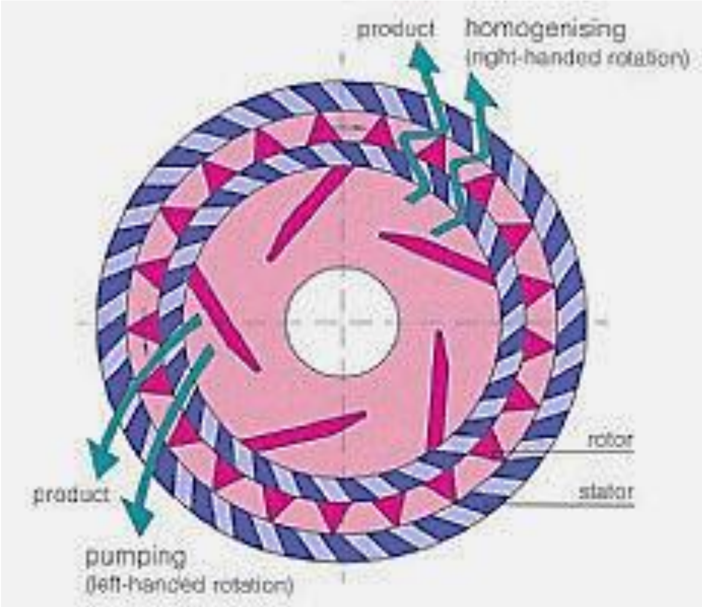

Figure 9. Patented homogeniser with intensive shear "homogeniser" mode or low-shear "pump" mode, simply achieved by switching the direction of rotation and its special geometry. [6]

In this thesis, two sizes of B mixers are compared. B 600 kg (B600) is normally used in the manufacture of Lumene foundations, but now it is investigated whether B 250 kg (B250) is as effective and equal to B600 and could production be transfer to smaller B mixer. B250 has also been used before in foundation and make-up production, but the homogenizer has been un-effective for proper emulsification. The homogenizer device is fixed the tests must be done to ensure the high quality also in B250 like it is in B600.

6 Comparison of two size of B reactors

6.1 Problem

Foundations are usually manufactured in B reactor volume of 600 kg. In the future that bigger reactor is needed to dedicate to FDA products; thus the foundations are wanted to produce in smaller reactor whose volume is 250 kg. This smaller B have had problems with the power of the homogenizer, swirl hasn't been strong enough and the quality of the foundations couldn't be quaranteed. After installing new rotator to B 250 kg still has weaker shwirl than B 600kg. The procedure needs to be validated to make sure that foundations are as stable and good quality as made in the bigger B 600 kg reactor.

Lumene manufactures two types of foundation emulsions.

B foundation is quite traditional water-in-oil emulsion with *Cetyl Alcohol (and) Glyceryl Stearate (and) PEG-75 Stearate (and) Ceteth-20 (and) Steareth-20* and *PEG-100 Stearate (and) Glyceryl Stearate* as emulsifiers. The water phase is prepared (in 80 degrees) in the B reactor and the pigments are disperged in to it. The oil phase is melted (80 degrees) and mixed separately in the heatable container with mixer. Both phases are mixed together in 80 degrees and homogenised vigorously.

A and Beauty serum foundations are water-in-silicone emulsions manufactured in room temperature. A foundation contains * as emulsifier and C foundation" formulating aid". Both of these products, actually very different textured, foundations are produced quite similar way. The silicone phase in mixed in B reactor and the water phase separately in the barrel. The water phase is soaked through the rotator to the silicone phase and after vigorous homogenization the emulsion is formed.

C foundation also contains *Polyglyceryl-3 Diisostearate* as another emulsifier designed for cold-process formulas.

A foundation is very thick and mousse-like emulsion; the texture is achieved by all means of *Dimethicone/Divinyldimethicone/Silsesquioxane Crosspolymer* which is a high performing hybrid elastomer powder consisting of interlacing polymer networks of polydimethylsiloxane and polymethylsilsesquioxane. [7]
The texture of this raw material is quite demanding because it is very light, styrofoam like subtance. It is added to the ready-made emulsion with homogenizing, but the problem is that the material tends to float on the surface of the emulsion and does not mix to the emulsion without help of the manufacture worker.

6.2 Testing plan

All three foundations were made in the production following the instructions made to B 600 kg and doubling the homogenization times of instructions. B Foundation was also manufactured by fixing the homogenization times. This way it was possible to determine whether the homogenizer/rotator is as effective as in B 600kg and if the homogenization times needed to be fixed and increased.

Every test batch was investigated immediately by checking them with a microscope, viscosity, pH (only B foundation) and centrifuge. All stability tests described below were performed and results were analysed.

In practice doubling homogenization times were not necessary at every point of manufacturing because the manufacturing time would have become too long. Table 4. shows actual homogenization times and are easy to compare at one glance.

Table 4. Homogenization times

B Foundation Oil-in-water emulsion	**phase A**	**phase B**	**phase C**	**phase D**	**phase E**	**phase F**
Batch 1	40 min	While combin-ing	-	12 min	15 min	20 min
Batch 2	80 min	While combin-ing	-	24 min	30 min	40 min
Batch 3	40 min	While combin-ing	-	24 min	15 min	30 min

A Foundation Water-in-silicone emulsion	**phase A**	**phase B**	**phase C**	**phase D**	**phase E**

Batch 1	48 min	35 min	20 min	36 min	1 min
Batch 2	62 min	70 min	20 min	57 min	1 min
C Foundation Water-in-silicone emulsion	**phase A**	**phase B**	**phase C**	**phase D**	**phase E**
Batch 1	7 min	25 min	5 min	5 min	5 min
Batch 2	14 min	50 min	10 min	10 min	10 min

7 Stability tests

The degree of stability of any emulsion is related to the rate of coagulation of two drops (O/W, oil drops; W/O, water drops):

Oil drop + Oil drop → Time--→ One oil drop

The length of time is the degree of emulsion stability. It means that two oil drops in O/W emulsion come closer together to form bigger drops. The repulsion forces are smaller than attraction forces. [1.pp.235.]

In the test series in this thesis, the stability tests were based on Lumene's Standard Of Prosedure (SOP) which is used in R&D laboratory daily basis.

The samples are stored in the stability test jar (PP-plastic, 180 ml) for three (3) months in the dark room temperature (+25-25 C), heat cabin (+38-42 C), refrigerator (+4-8 C) and freezer (-18-22 C). Every jar is tagged by a testing circumstance, trial code and product name.

During the test samples in every circumstance are checked every month comparing it to the room temperature sample. Before analyzing the temperature of the samples should be set in the room temperature.

The tests that are included are listed below:

- Appearance, color
- Odour

- pH (only water-in-oil or oil-in-water emulsions)
- Separation
- Structure, Microscope
- Viscosity

In addition, there are some other stress tests that can be executed on to the samples. *The Shoukel test* is performed in the tube with 30g sample. Sample is set in the refrigerator overnight and the next morning sample is removed between heat cabin (+45C) and refrigerator in every hour until 4 heat cabin-refrigerator cycles are accomplished. After that the sample is let to balance at room temperature overnight and is compared to non-stressed sample by following tests:

- Appearance
- Odour
- Separation
- Structure, Microscope

The K-test is also a stress test where the 30 g sample in the tube is first refrigerated for 24 hours, melted and then stored in the heat cabin for another 24 hours. After the temperature is balanced in room temperature, it is centrifuged for 10 min 4000 rpm and the following tests are performed:

- Appearance
- Odour
- Separation
- Structure, microscope

The Freeze/Melt –test in performed also in the tube with a 30 g of sample by freezing it first at -18-24°C for 24 hours. After that sample is melted to room temperature. Then the cycle is repeated 5 times and following the features are checked:

- Appearance
- Odour
- Separation
- Structure, microscope

Lumisizer/instability index is measured with Lumisizer (Figure 10). This piece of equipment is a temperature controlled dispersion/stability analyzer for the comprehensive characterization of emulsions and suspensions. Lumisizer instantaneously measures the extinction of transmitted light across the entire length of sample. Separation, sedimentation or consolidation are directly measured by the Lumisizer. These instruments employ the technology, which allows you to obtain space- and time-resolved extinction profiles over the entire sample length of up to 12 different samples simoultaneously. Near infrared light (I_0) illuminates the entire sample cell, the transmitted light I is detected and transmission is converted I_0/I. [8]

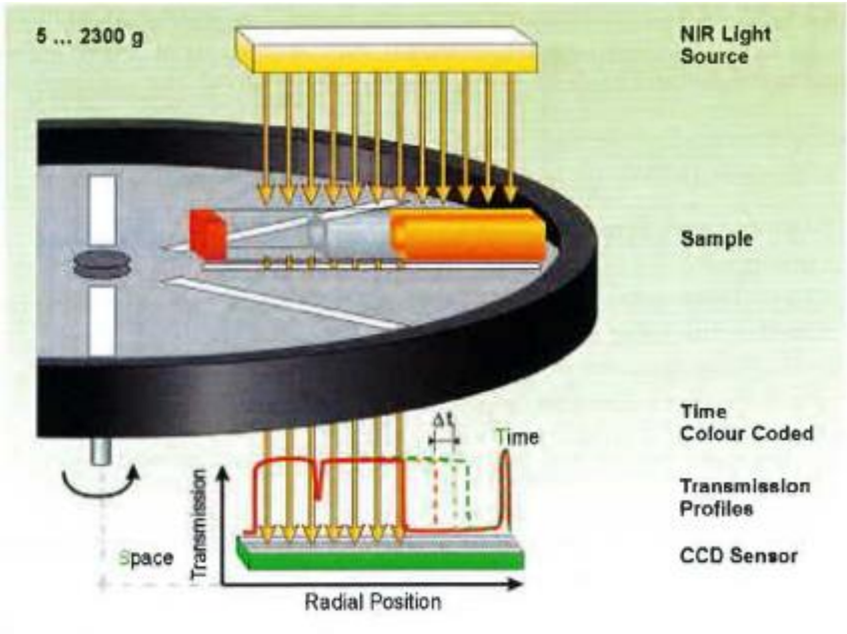

Figure 10. Measurement principles of Lumiziser-technology

8 Results of the analysis of test batches

The most important feature to monitor is viscosity. The behavior of viscosity imparts the stability of longer period. Test batch results are always compared to those of the original bulk manufactured with B600. The products that are already in the stores and which consumers have used have been manufactured with B600; thus now when the production is moved to a smaller mixer (B250), the quality and properties should be the same as when manufactured with B600. All test batches are manufactured with B250. The difference between every batch is the homogenization time (table 4).

8.1 The C Foundation

The viscosity of the C Foundation was measured with Brookfield DV 2 viscometer by using spindle 3, with speed 10 and measuring 1 minute. The unit of the results are cPa (centipoises). This formula is very thin and liquid; thus the spindle is bigger.

Table 5. Viscosity results of C foundation

	TO	6°C 1m	6°C 2m	6°C 3m	RT 1 m	RT 2m	RT 3m	40°C 1m	40°C 2m	40°C 3m
By original manuf. Instruction	2500	2880	2890	2820	3050	2870	2820	3130	3060	3010
By original manuf. Instruction but homog,times x2	3080	3720	3550	3600	3870	3780	3640	3970	3820	3700
Batch manufactured with B600	2380	2990	2690	2650	3290	2800	2770	3890	3150	3090

The C Foundation was easiest formula to manufacture. No heating was needed and all ingredients were very easy to add by the manufacturing worker. As we can see in these results, by increasing the homogenizing time, the thicker bulk was achieved. The batch made by following the original instructions was pretty much comparable with the bulk made by B600. The conclusion from this finding foundation is that the manufacturing instructions or homogenizing times do not need to be changed for manufacturing with B250.

The Lumiziser curves in Figures 11-13 shows the separation rates during centrifuging the sample in 40 degrees 21 hours.

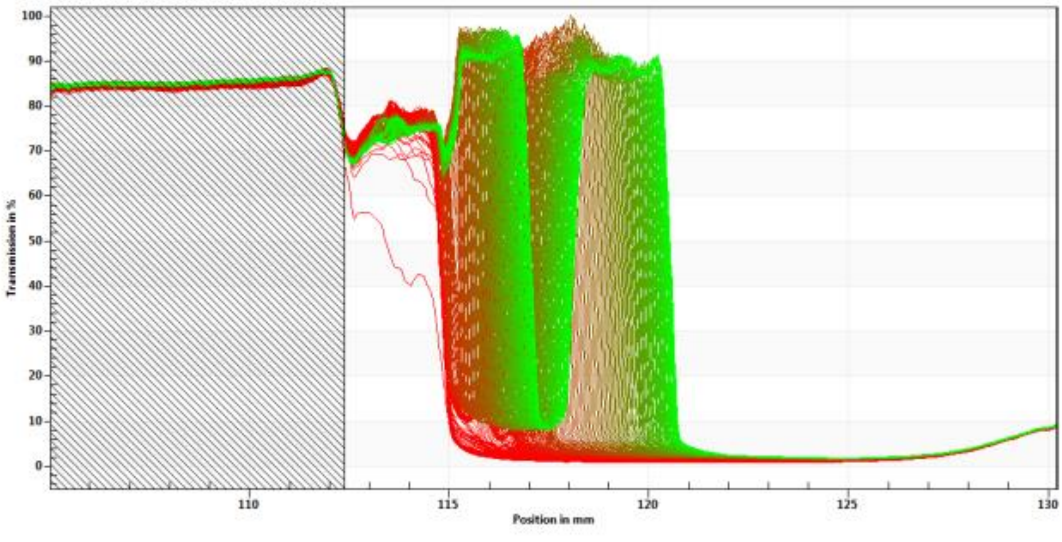

Figure 11. Lumiziser curve of the C Foundation manufactured by original instruction.

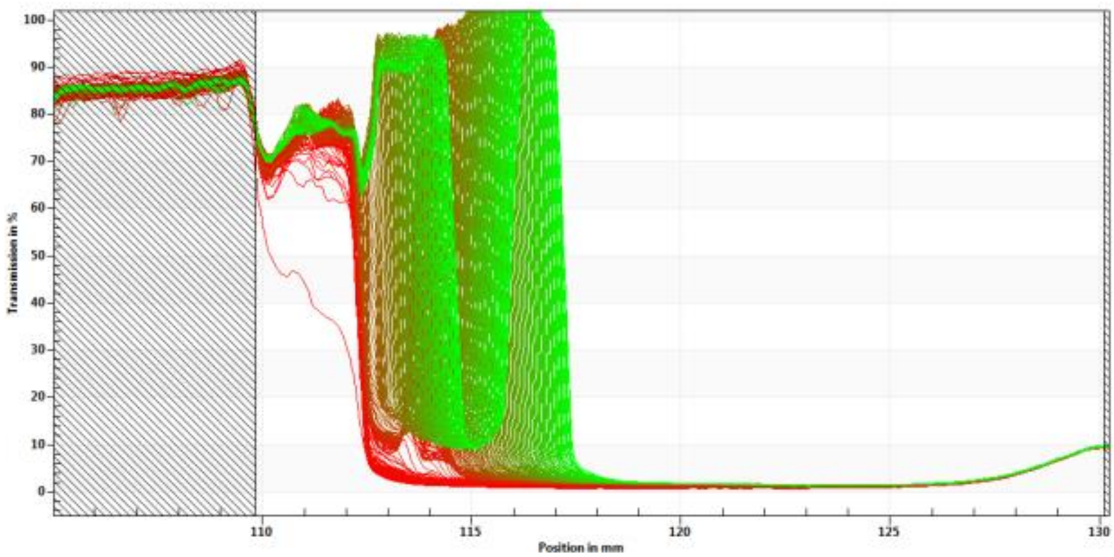

Figure 12. Lumiziser curve of the C Foundation manufactured by doubling the homogenization times.

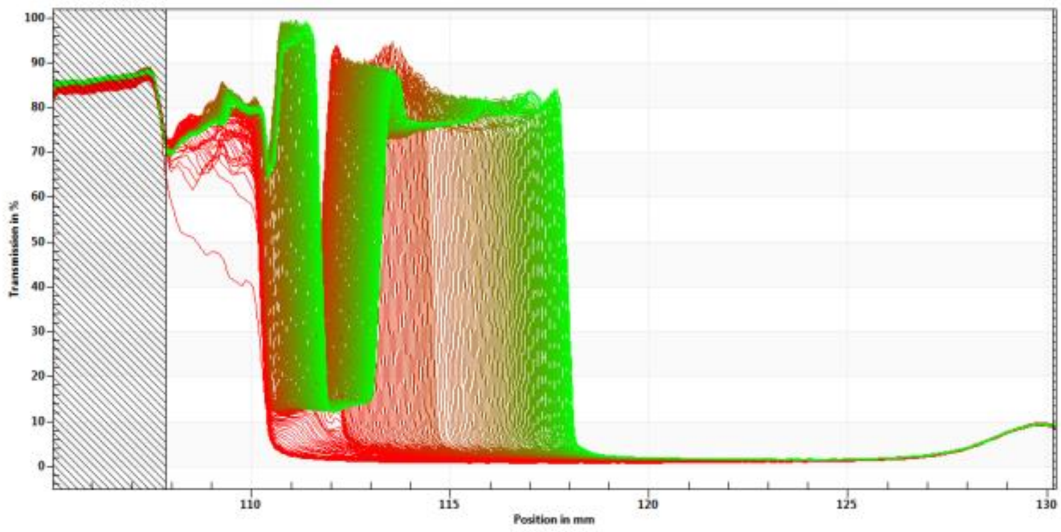

Figure 13. Lumiziser curve of the C Foundation manufactured by B600.

Also, the results for the other stability tests (K-test, Shoukel, Freeze/melt, centrifuge) were comparable to those of B600 bulk. These features are investigated by approximating the product in the tube.

8.2 The A Foundation

The viscosity of the A Foundation is measured with Brookfield DV 2 viscometer by using Spindle 6, with speed 10 and measuring for 1 minute. The unit of the results are cPa (centipoises). The A Foundation is very thick emulsion; therefore the spindle used was smaller.

Table 6. Viscosities of A foundation

	TO	6°C 1m	6°C 2m	6°C 3m	RT 1 m	RT 2m	RT 3m	40°C 1m	40°C 2m	40°C 3m
By original manuf. Instruction	62300	59700	60900	60500	59200	59500	58000	59000	50300	56400
By original manuf. Instruction but homog,times x2	70600	64700	65100	65700	68100	63700	64100	62100	64000	61200
Batch manufactured with B600	62600	63400	64800	60800	68300	66500	62400	64400	59000	58700

All test batches were quite easy to manufacture in B250.The A Foundation was the most demanding formula because of one ingredient. This raw material is very foam like, very light ingredient, which does not sink under the bulk surface; therefore the manual paddling is required. Luckily, the manufacturing worker invented a method where then is no need to manual work. The raw material was ground with the Ystral mixer and then added to the bulk throughout the circulation of the homogenization.
The batch made by following the original instructions was is pretty much comparable with the bulk made by B600. The conclusion from this findings is that the manufacturing instructions or homogenizing times don't need to change for manufacturing with B250.

Lumiziser analysis was performed by centrifuging sample in 40 degrees 21 hours.

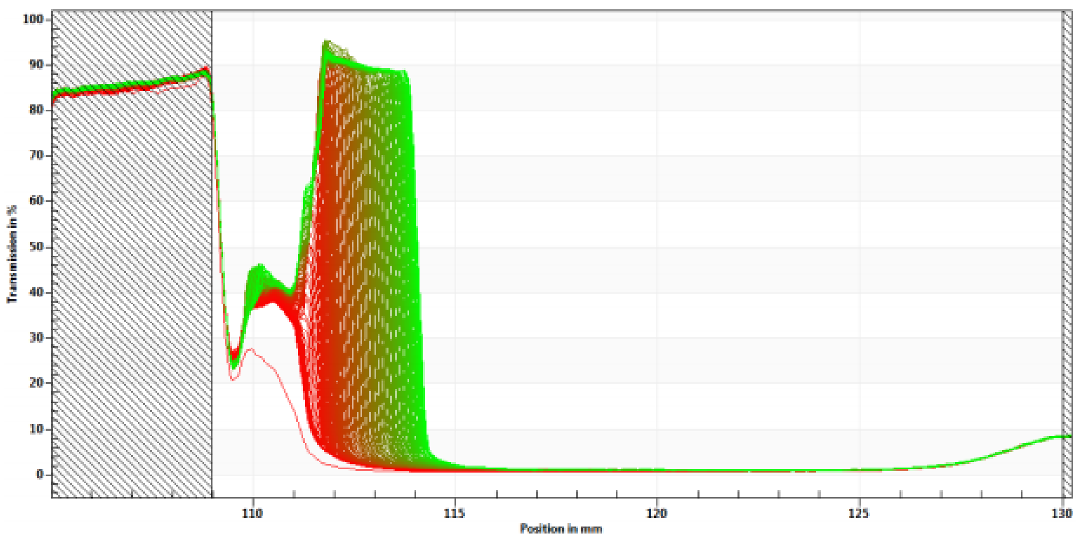

Figure 14. Lumiziser curve of the A Foundation manufactured according to original instruction.

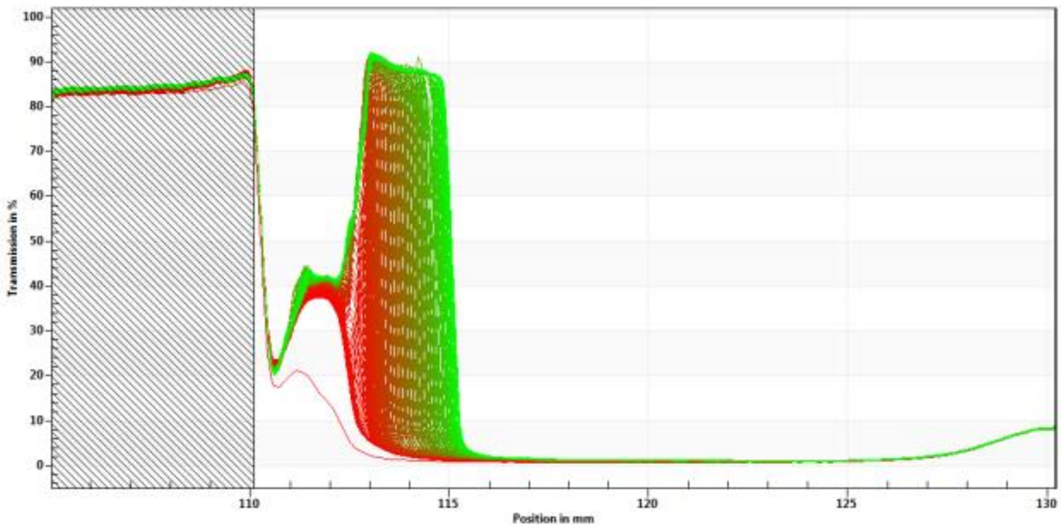

Figure 15. Lumiziser curve of the A Foundation manufactured by doubling the homogenization times.

Also, the results of the other stability tests (K-test, Shoukel, Freeze/melt, centrifuge) were comparable to those of B600 bulk.

8.3 The B Foundation

The viscosity of the B Foundation was measured with the Brookfield DV 2 viscometer by using Spindle 5, at speed 10 and measuring for 1 minute. The unit of the results are cPa (centipoises). The B foundation is quite a light emulsion. Table 7 presents the results.

Table 7. Viscosity results of B foundation

	TO	6°C 1m	6°C 2m	6°C 3m	RT 1 m	RT 2m	RT 3m	40°C 1m	40°C 2m	40°C 3m
By original manuf. Instruction	17900	12600	12800	11500	11000	11000	9960	12600	10700	8720
By original manuf. Instruction but homog,times x2	19100	14000	12400	10700	11800	11600	10700	11400	11400	9400
By original manuf. Instruction but fixed homog.times	18200	13900	11300	12000	13100	11500	11300	13100	10000	10400
Batch manufactured with B600	13400	12000	11200	13000	11900	10700	10100	12800	12400	10500

The B Foundation was manufactured in 3 different ways. Two batches like with the other foundations, and one batch with fixed homogenization times, which means that times are something between the manufacturing introduction and doubled homogenization times. Regarding the viscosity results for this batch, it was closest to B600 manufactured batch.

Lumiziser curves displayed in Figures 16-18.

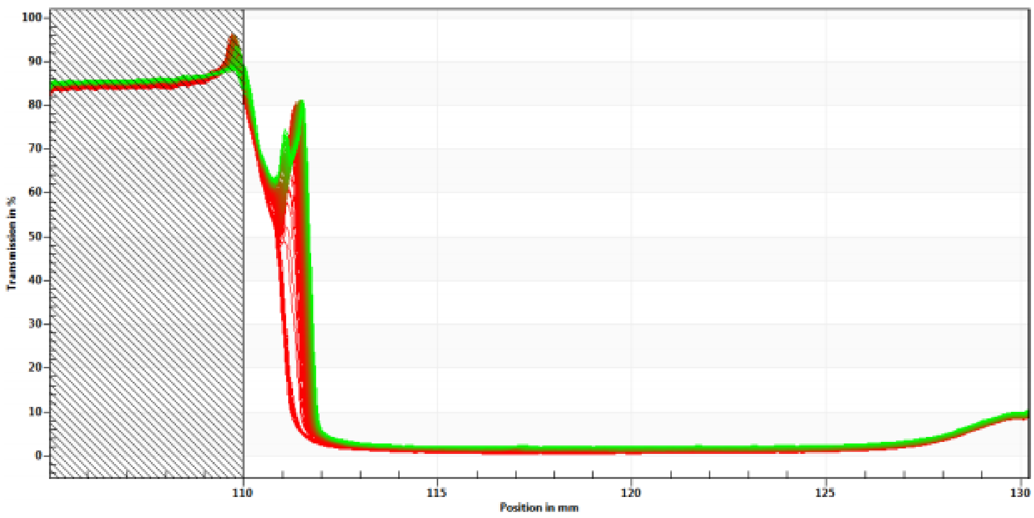

Figure 16. Lumiziser curve of the B Foundation manufactured according original instruction.

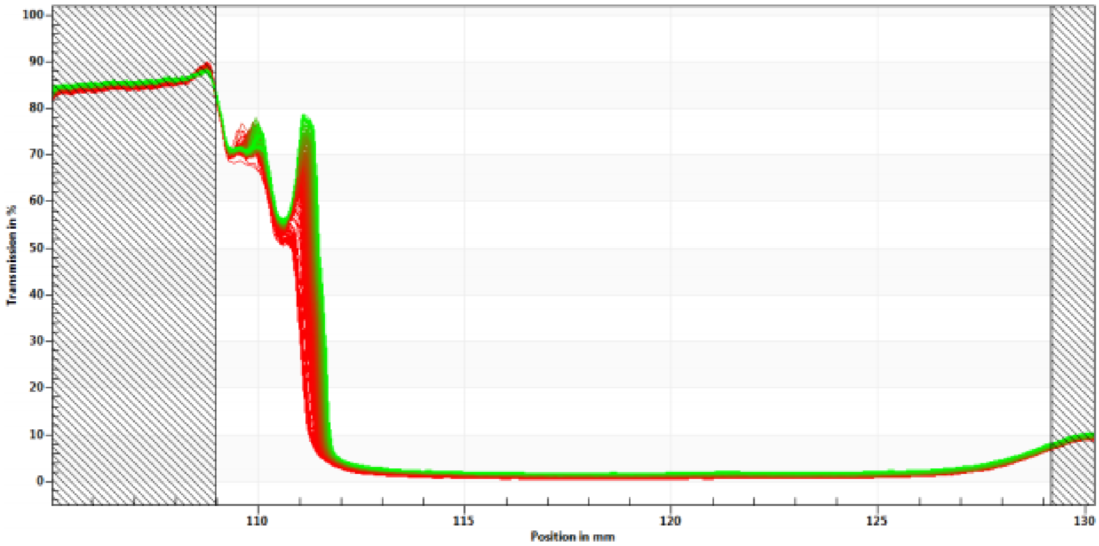

Figure 17. Lumiziser curve of the B Foundation manufactured by doubling homogenization times

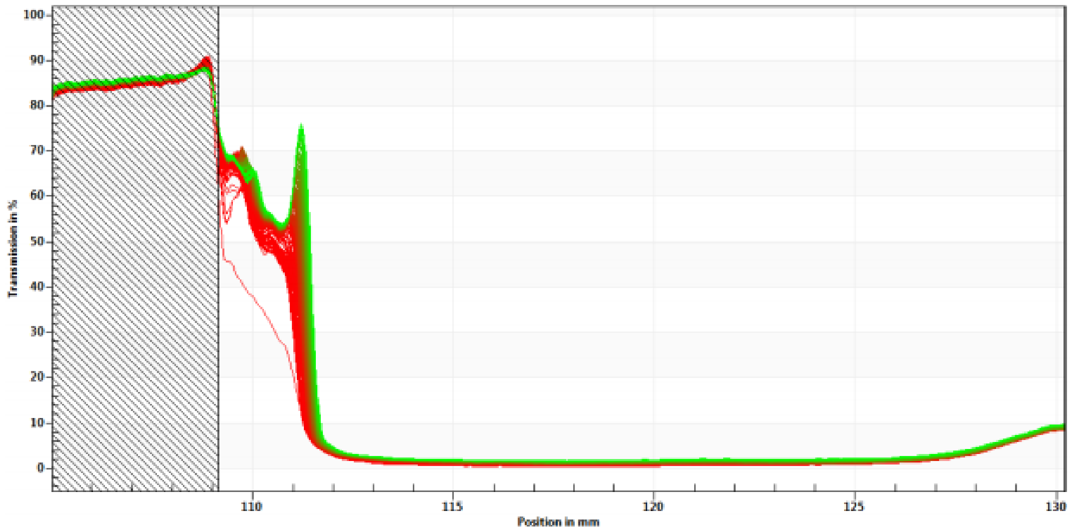

Figure 18. Lumiziser curve of the B Foundation manufactured using fixed homogenization times

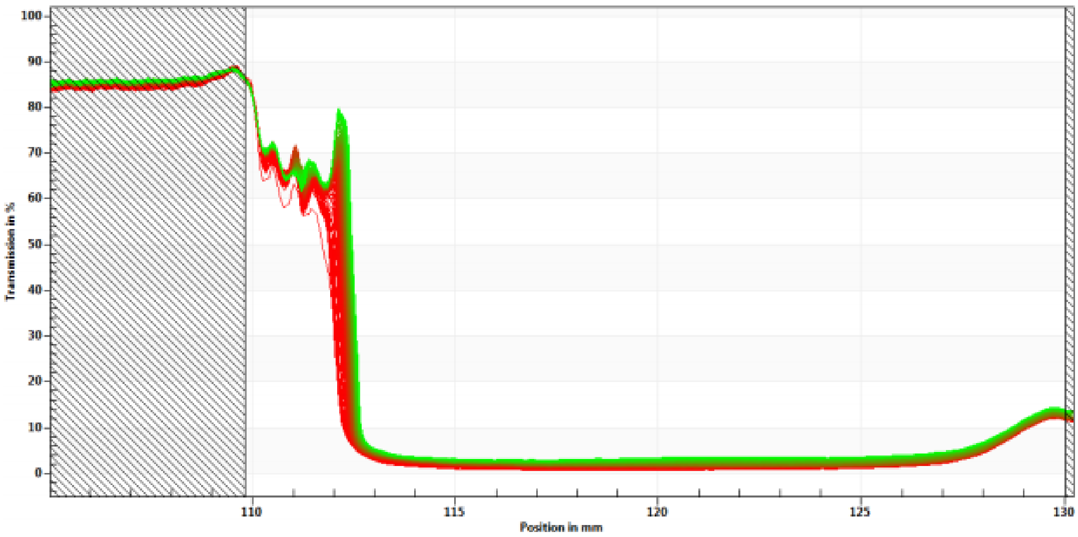

Figure 19. Lumiziser curve of the B Foundation manufactured by B600.

Also the results of the other stability tests (K-test, Shoukel, Freeze/melt, centrifuge) were comparable to those of the B600 bulk.

9 Summary and conclusions

Lumene skin care and make-up emulsions are core technologies which are manufactured in the Espoo factory. Device used in manufacturing emulsions are validated B-mixers with effective homogenizers. The main goal to this thesis and the investigations was to validate the scaling down from the bigger reactor to the smaller reactor. Also the theory of the colloidal chemistry and the viscosity analysis were investigated.

The cosmetic science and the technology is based on mainly in the emulsion and colloidal chemistry. The emulsions are mixtures of two phases that do not dissolve together. To get a stable emulsion for example with oil and water, the surfactant which reduces the surface tension is needed. Surfactants can be grouped into four main categories; anionic, cationic, nonionic and amphotenic surfactants.

The most important, convenient and simple way to analyse the stability of the emulsions is the viscosity. In the Lumene Research and Development laboratory there is Brookfield

DV 2 viscometer with different sizes of spindels. Also the stability tests and the Lumiziser analysis are performed.

All the make-up foundations were manufactured with B 600 before, but now it is dedicated to FDA products; hence all foundations must be manufactured with smaller B 250 kg. The homogenizer of this smaller reactor was doubted to be less effective than that of B600; therefore the test batches were manufactured and investigated in the laboratory. The test batches included three products. Two of those are silicone based water-in-silicone emulsion foundations (A Foundation and C Foundation) and the B Foundation is oil-in-water emulsion. The tests performed in the laboratory were viscosity and stability tests as well as Lumiziser analysis. Results were compared to the results for products manufactured with B 600 kg, which are already in the stores and conclusions were made according to that comparison.

B- reactors are designed to perform excellent scale-up from pilot to bigger batches. This test series shows that it is safe to change the manufacture from the bigger reactor to a smaller one using the same or almost the same instructions; thus the objective was achieved. The main concern of this particular scaling down was the new homogenizer of B250, but the results shows, that the product and the manufacturing are similar and equally good in both cases.

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