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RAZVOJ IN VREDNOTENJE EMULZIJ S PIGMENTI ZA PREKRIVANJE KOŽNIH NEPRAVILNOSTI

DEVELOPMENT AND EVALUATION EMULSIONS CONTAINING PIGMENTS FOR SKIN CARE IMPERFECTION

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Diplomsko nalogo in njen praktični del sem opravljala na Fakulteti za farmacijo v Padovi, Katedri za kemijo in farmacevstko tehnologijo pod somentorstvom doc. dr. Alessandre Semenzato, mag. farm., teoretični del pa na Fakulteti za farmacijo v Ljubljani, pod mentorstvom prof. dr. Mirjane Gašperlin, mag. farm.

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ABSTRACT

Skin imperfections caused by various external and internal factors are most commonly seen on the face, because it is the most exposed part of the body. Skin colour irregularities such as redness on the skin, pigmented skin, dark patches and yellow spots can occur on the face. In this thesis, we focused on development of emulsions containing pigments, which have a special effects on the skin. Special pigments create a shiny and healthy appearance of the skin, due to reflected daylight they also work as anti-redness on the face.

The formulations were prepared with the same composition of the hydrophilic phase, the different composition of the lipophilic phase and use of two different types of emulsifying agents which have effect on viscosity of emulsions. After production, emulsions were homogenized and we evaluated their organoleptic properties such as visual assessment and sensorial effect after application on the skin. Further, physico – chemical properties were evaluated where we measured pH, the distribution of droplets in the emulsions and their structure observed by optical light microscope. We determined stability of emulsions by stress test with centrifuge, where the first five formulations lead to phase seperations, other formulations remained unchanged. We continued with rheological properties measurements such viscosity as a function of share rate. The formulation that consists of emulsifying agent with more rich texture has a higher viscosity in stationary state than other formulation and due to the better consistency is more appropriate for dispersion of pigments. From selected emulsion we changed part of the lipophilic phase with emollient, which have a higher capabillity of wetting pigments and at the final stage of the manufacturing process we added pigments with special effects. Then we observed distribution of pigment in emulsions and its colour by the optical microscope. We have seen that the pigments in contact with the other ingredients in the emulsion stained purple and yellow, which is not visible to the eye. We evaluated and compared the colour difference between emulsions without pigments and emulsions with added pigments by using chromameter. Colour differences were interpreted in the colour scale CIE L* a* b*, which gives information such as brightness / darkness (L * value), red / green (a * value), blue / yellow (b * value) as a results of special pigments.

Formulations could be use as a base before applying creams and make-up. Special pigments reduce the appearance of yellow spots and redness of the skin, as well as provide more shiny and healthy skin tone.

POVZETEK

Kožne nepravilnosti nastanejo zaradi različnih zunanjih in notranjih dejavnikov. Bolj pogosto so vidne na obrazu, saj gre za najbolj izpostavljen del na telesu. Pojavi se lahko obarvanost kože kot so rdečica, pigmentirana koža, temni madeži in rumene lise. V diplomski nalogi smo se osredotočili na izdelavo emulzij z dodanimi pigmenti, ki imajo poseben učinek na koži, saj na obrazu ustvarijo sijoč in zdrav videz kože, zaradi reflektirane dnevne svetlobe pa delujejo tudi proti rdečici na obrazu.

Izdelali smo formualcije z enako sestavo hidrofilne faze, različno sestavo lipofilne faze in uporabo dveh različnih tipov emulgatorjev, ki vplivata na viskoznost emulzij. Po izdelavi smo sisteme homogenizirali in ovrednotili njihove organoleptične lastnosti kot so vizualna ocena in učinek po nanosu na kožo. Formulacijam smo nato ovrednotili fizikalno – kemijske lastnosti, kjer smo jim izmerili pH, z optičnim svetlobnim mikroskopom smo opazovali porazdelitev kapljic v emulzijah in njihovo strukturo, ter jih izpostavili obremenilnim testom s centrifugiranjem, kjer je pri prvih petih formulacijah prišlo do ločitve faz, pri ostalih formulacijah pa nismo opazili sprememb. Vrednotenje smo nadaljevali z reološkimi testi, kjer smo preučevali vpliv strižne obremenitve na viskoznost formulacije. Ugotovili smo, da je viskoznost v mirovanju višja pri tisti formulaciji, ki skupaj z emulgatorjem tvori bolj bogato teksturo. Zaradi trše konsistence je tako ta formulacija bolj primerna za nadaljno dispergiranost pigmentov. Izbrani emulziji smo nato zamenjali del lipofilne faze, z emolientom, ki ima večjo sposobnost močenja pigmentov, ter ji v zadnji fazi postopka izdelave dodali pigmente s posebnim učinkom. Z optičnim mikroskopom smo opazovali porazdelitev pigmentov ter njihovo barvo. Videli smo, da se pigmenti v stiku z drugimi sestavinami v emulziji obarvajo vijolično in rumeno, kar pa ni vidno s prostim očesom. Z uporabo kromametra smo ovrednotili in primerjali barvno razliko emulzij brez pigmentov in emulzije z dodanimi pigmenti. Bavne razlike v emulzijah smo interpretirali v barvni skali CIE L*a*b*, ki poda informacije kot so: svetlost / temnost (vrednost L*), rdeče / zeleno (vrednost a*), modro / rumeno (vrednost b*) kot posledica dodanih pigmentov s posebnim učinkom.

Formulacije, katerim smo dodali pigmente se lahko uporabljajo kot podlaga pred nanosom make-upa. Pigmenti s posebnim učinkom zmanjšajo videz rumenih lis, ter pojav rdečice na obrazu, pigmenti na koži pa ustvarijo tudi bolj sijoč in zdrav videz.

KEY WORDS

Skin colour imperfections, special effect pigments, CIE L*a*b*

LIST OF ABBREVIATION

CIE (L*a*b*) – colour space specified by the International Commission on Illumination which describes all the colours visible to the human eyes.

Illuminant D65 – it is a commonly used standard illuminant defined by the CIE, also called a daylight illuminant. It is part of the D series of illuminants and represent average daylight and has a correlated colour temperature of approximately 6500 K.

UV - ultraviolet light

Tristimulus system - a system for visually matching a colour under standardized conditions against the three primary colours - red, green and blue.

Freedonia group - a leading international business research company, that provide critical market research through the publication of research studies.

BB cream - Blemish Balm cream

CC cream - Color Correction cream

DD cream - Daily Defense cream

1. INTRODUCTION

1.1. SKIN IMPERFECTIONS

Skin is the largest organ of human body, exposed to every day´s internal and external factors which lead to a various skin colour imperfections most commonly seen on the face. Beauty consumers, especially women, have high expectations from cosmetic companies to come up with new formulations that hide surface imperfections, discolourations, blemishes, making complexion more shiny and silky. A preference for a fair skin is a common recent trend among women, especially in Asia, where whitening cosmetics is increasing and is expected to improve dullness as well as lightness (1). There are different dermatologic causes including eczema, rosacea affected skin (Figure 1), irritant contact dermatitis, teleangiectasias, and acnes where all of these conditions have redness effect on the skin in common, which results in dilation of blood vessels. External factors, such as stress, cold wind, sunburn, exposure to extreme temperature, moving from cold environment to hot or warm one, smoking, foods (rich with histamines), and drinks (coffee, hot tea, alcohols), cause flushing and blushing on the skin. Facial redness is minimized by cosmetic active ingredients; moisturizers and anti-inflammatory cosmeceutical agents, such as aloe vera, bisabolol, allantoin, panthenol and polyphenolos, used to prevent skin barrier damage (2). Skin pigmentation disorders can also occur on the face, as a result of producing too low or too high quantities of melanin. This results in depigmentations of skin such as vitiligo and albinism. In both case, due to the lack of melanin pigment, depigmentations affects the skin and (in the second case) also eyes and hairs. On the other hand, there is hyperpigmentation, such as chloasma where due to hormonal changes during pregnancy or estrogenic therapy, it causes skin discolouration and solar lentigo where darkened spots occur due to excessive sun exposure (3).

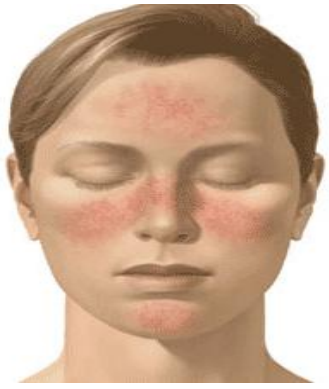


Figure 1: Rosacea affected skin

1.1.1. COLOUR THEORY

To develop emulsions with special pigments effect and reduce undesirable redness and colouration of the skin it is necessary to know some of the colour theory. Colour is a sensory impression and the result of interpretation of the human eye which can distinguish different colours by using the photoreceptors. Colours are defined as an electromagnetic wave in the range of visible light spectrum, which is a mixture of wavelengths between 400 nm to 700 nm. The sensory impression of colour can also depends on the perception ability of observers and energy distribution in the visible spectrum (4).

We can classify colours as **achromatic** (grey, white and black colour) or **chromatic** (colour with hue) where each colour is indicated by three coordinates (Figure 2):

a) **HUE / Colour tone** – indicates the colour quality, characteristic, where colours are separated by diversity and determined by wavelength. These colours are green, red, blue, violet and yellow**.**

b) **CHROMA / Saturation** – expresses the intensity of colour and deviation of colour tone from the neutral grey. Chroma with high value has an intensive and brilliant colour while a chroma with low value has no intensive and dull colour**.**

c) **VALUE / Brightness** – describes the degree of brightness level of a particular colour in comparison with the grey scale. The colour is bright when the reflection from an object surface is high or dark colour when the reflection is low (5).

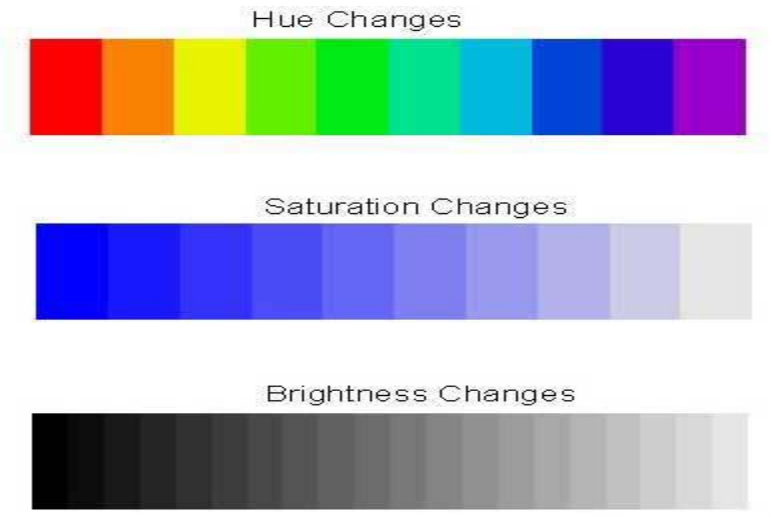


Figure 2: The color, composed of three elements

Primary Colours

These colours are green, red and blue. From these three hues we can make different combination of other colours.

Secondary Colours

These colours are cyan, yellow and magenta. They are made by combination of mixing two primary colors (6).

Tertiary Colours: These colours are yellow-orange, red-orange, red-purple, blue-purple, blue-green and yellow-green where hue is a two word name. They are made by mixing primary and secondary colours.

Complementary colours: They are known as opposite colours where two colours in the colour system are located on the opposite side form each other. These colours are yellow-purple, red-green, blue-orange (7).

In cosmetic industry, colours play an important role in decorative cosmetics. They have been used in make-up products such as eye-liners, mascara and lipsticks, where colour mixtures are significant. Colours are also important in the face products against skin colour imperfections and they have been used such as makeup neutralizers and undertoners for colour corrections on the skin. The colour wheel is a great tool for combining different colours (Figure 3). Most of colour used in cosmetics gained popularity of neutralizing the redness effect on the skin, because they offered green colour (8).

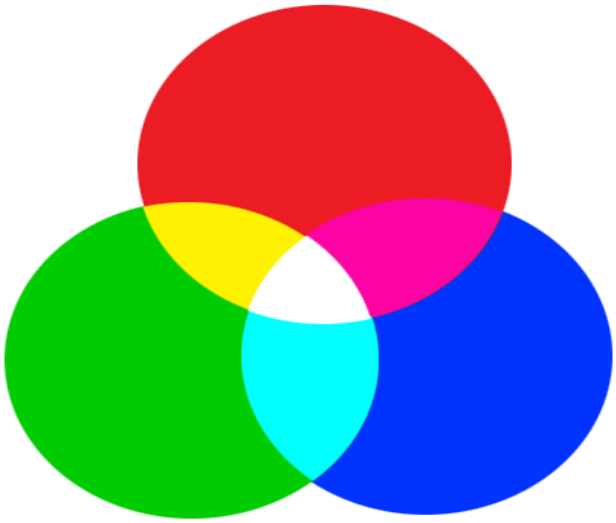


Figure 3: The colour wheel is the basic tool for combining colors

1.1.2. COLOUR OF SKIN

A primary characteristic we have observed on the human body is colour of skin, one of the attributes which help to classify people into geographic groups (9). Skin colour also varies with individuals, with age, season, and part of the body. People who live close to the equator have darkly pigmented skin which protect them from ultraviolet (UV) light, on the other hand, people from north of the equator have paler skin. The most used system to classify people within the skin is the skin human phototype scale which was launched by the dermatologist Fitzpatrick in 1975. Phototype scale classifies skin colour from type I (pale white skin) to type VI (deeply pigmented dark skin**)** (10).

The main chromophores which are located in our skin are described below:

- ***Melanin*** - it is located in the melanocytes, in the lower layers of the epidermis where its synthesis is carried out by the organelles melanosome. Influence of ultraviolet rays also accelerates the formation of melanin which may be brown, black or yellow-red.
- ***Carotene*** - is a carotenoid pigment with red-orange colour which is located in the horny layer of epidermis. It helps to prevent the skin from undesirable ultraviolet light with its absorption and protect the skin against the free radicals.
- ***Haemoglobin*** - it is a red pigment which is located in red blood cell. It has a function of transferring oxygen to the different parts of the body. Typical red colour of haemoglobin is often seen close to the thin skin surface (5).

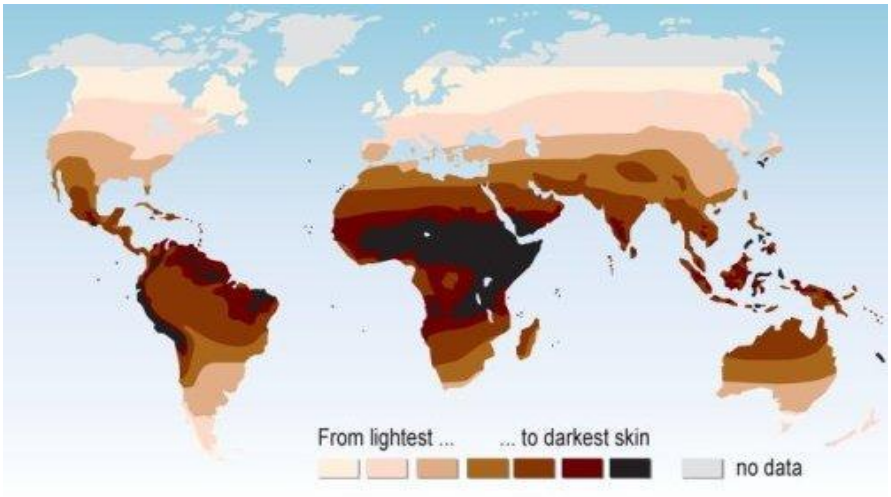


Figure 4: Skin colour map predicted form multiple environmental factors

1.2. NONINVASIVE TECHNIQUES TO THE EVALUATION OF SKIN COLOUR

Detection of colour is dependent on different factors such as nature of light, interaction of matter and light, and the physiology of human vision. The human eye is extremely sensitive in grading different colour intensities especially when there is a comparison available side by side. Even if the human eye is capable of differentiating between colours and is an expert eye, it works better with high contrast (11).

Nevertheless, the human eye plays an important role for visual assessment of colour. It is one of the methods besides the modern instruments and techniques which provide reproducible and objective results of skin pigmentation and colour (12).

The most common techniques and instruments to evaluating the pigmentation and skin colour are:

- *Rating scales and indexes (for example: Visual hyperpigmentation scale)* - the scale consists of plastic cards where each card has 10 different skin colours, presenting 10 graduation of hyperpigmentation. There are 100 possible ratings**.**
- *Melasma area and Severity index (MASI)* - it is used to assess the percentage of affected face area from melasma and determined homogeneity and darkness of its appearance.
- *Ultraviolet light* - it is used to observe changes in skin colour by using lamps which emit light at wavelengths of 300 nm to 400 nm. It is a useful diagnostic tool in dermatology.
- *Photography* - it is a method where the whole body is photographed and where the pictures are used to assess the pigment changes and disorders over time.
- *UV light photography* - it assesses epidermal changes with UV light, where the photographic film and blue light are used.
- *Polarized light photography* - it works on two components of reflected light from the skin – light-back-scattered and regular reflectance. It is useful in dermatology for erythema and other diagnosis.
- *Dermoscopy* - it is an important diagnostic method in dermatology for the assessment of pigmented skin lession. Alcohol solutions or mineral oil is applied on the skin and by dermatoscope we examine possible lessions.

- *Narrowband spectrophotometers* - they work on the basis of two pigments, melanin and haemogoblin, where results are obtained such as melanin (M) or erythema (E) indices. Spectrophotometers (commonly used Mexameter and Derma Spectrophotometer) recorded spectral curves which are different for each pigment and showing absorption of light.
- *Tristmilus colourimetry* - it is a technique where the instruments measure the intensity of reflected light from an object. It consists of photodiode array or wavelength filters with a pulsed xenon lamp. The results are expressed in the most widely used CIELAB colour system (12).

1.2.1 CIELAB COLOUR SYSTEM

CIE L*a*b* is the colour space specified by the organization CIE (Commission Internationale de l'Eclairage) determined standard values that are used worldwide to measure colour. It is one of two colour notation systems that have been applied in cosmetology and dermatology (13).

The CIE system was devised in 1976 to a tristimulus system where the **intensity vs. wavelength** are converted into three values described an object colour to the observers´ eyes. The system expressed a great correlation with the human eye and represent all possible perceivable colours in a three-dimensional space (Figure 4). The values of colour are described below**:**

a) **L*** describes light intensity and take values from 0 for black to 100 for white. Values which are > 50 indicate light while values < 50 indicate dark. L* value form a reading expresses the relative brightness; lightness or darkness.
b) **a*** is chromacity coordinate (hue of a colour), where axis going from –60 (negative number) for green to +60 (positive number) for red. Value a* best captures erythema or skin redness.
c) **b*** is also chromaticity coordinate where axis going from –60 (negative number) for blue to +60 (positive number) for yellow. Value b* is used to measure pigmentation.

Colours which are located at zero values for a* and b* are achromic, grey, white or black. Value Δ E* does not indicate colour difference directly but presents total differences between L, a, and b, in comparison with standard and sample (14).

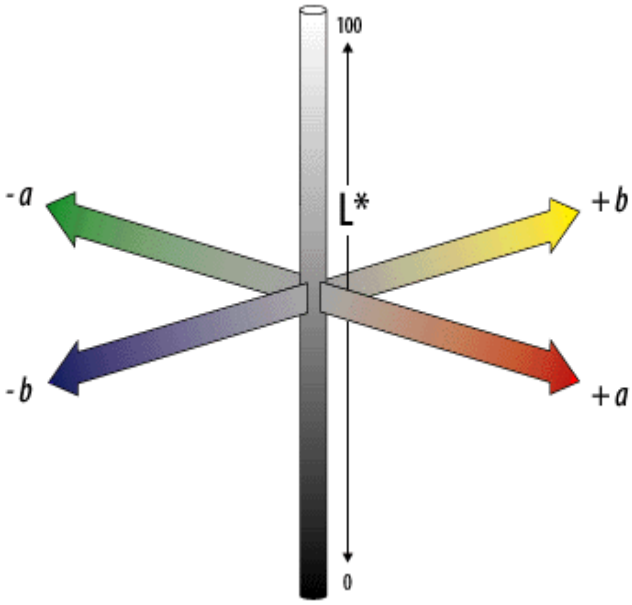


Figure 5: CIELAB coordinate system

Table I: Meaning of Δ E values

Δ E values	**Meaning**
0 - 1	A normally invisible difference
1 - 2	Very small difference, only obvious to a trained eye
2 - 3.5	Medium difference, also obvious to an untrained eye
3.5 - 5	An obvious difference
> 6	A very obvious difference

1.3 SPECIAL EFFECTS PIGMENTS

In July 2005, The Freedonia Group (an international business research company) made a report about pigments which are commonly used in the US cosmetics and toiletries industry. The company divided pigments into three main groups**:**

1. ***Organic pigments*****:** They are pigments composed of long complex chemical molecules which could be oil-soluble, water-soluble or insoluble – also known as a *lake.* Those pigments are azo pigments, indigo pigments etc.

2. ***Inorganic pigments***: They are pigments which consist of metallic compound, usually from oxides which are insoluble. Those pigments are titanium oxides, iron oxides and ultramarines. Inorganic pigments have also larger particle size of pigments comparing to organic.

3. ***Special effect pigments*****:** These types of pigments operate on the principle of complementary colours where they create visual effects on the skin. Special pigments help to achieve an attractive look with their pearlascence, glow and matt white aspects. The most common types of these pigments are synthetic fluorphlogopite, mica, guanine and bismuth oxychloride (15).

Formulating emulsions with special effects is one of the approaches where pigments reflect light from the skin and thereby create an attractive appearance. We can combine different particle size of pigments, dependent on the effects we want to achieve for skin care product (Figure 6). The most often pigments for facial products are used in proportion of 0.1 % to 2.0 % and it may also vary with different manufacturers (16).

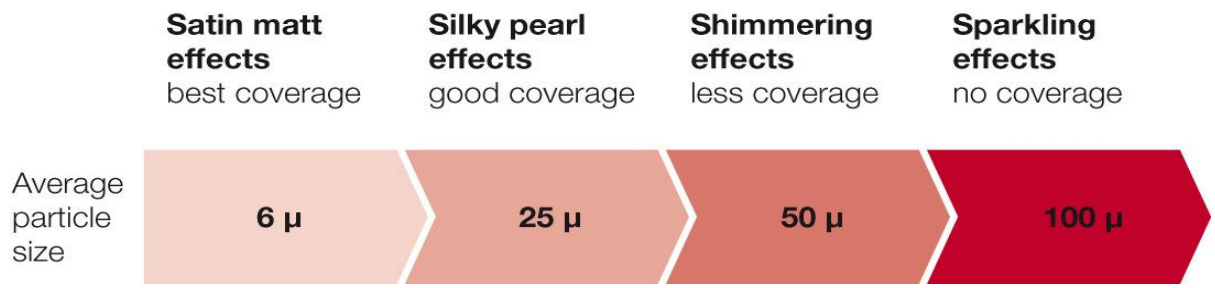


Figure 6: Particle size of pigments defines the effect

1.3.1. FACIAL COSMETIC TO COVERAGE IMPERFECTION

Nowadays, the beauty market offers variety of formulations which make skin silky, shiny, and with anti-redness effect over time. They guarantee textures with ingredients which benefit for concealment of skin irregularities, evenness of complexions and with good feeling on the skin all day long (17).

Commonly used cosmetic products with covering effect on the market are:

a) FLUID FOUNDATIONS – EMULSIONS

Fluid foundations include O/W and W/O emulsions. Their properties are poor coverage, rapid drying, and they are appropriate for mixed to oily skin. Throughout the years, fluid foundations have been changing their structure (silicone oils have been introduced which create a long – lasting foundations**)**. Today 90% of the foundations are water/silicone/oil emulsions (17).

b) COMPACT POWDER FOUNDATIONS

Compact powder foundations are made up of pigments and powders which are dispersed in the oil phase under heat. They often contain silicone oils and esters which improve foundations qualities such as application on skin with no heavy and greasy feel (17). Pigmented coloured foundation creams are used extensively and have tended to replace the often tinted. The formulation and preparation of pigmented products is technically far more difficult on two main counts. First, the pigments which have a high specific surface may preferentially adsorb emulsifying agents and sometimes tend to destabilize or even invert the resultant emulsion. Secondly, adequate dispersion of the pigments to give reproducible colours can be very difficult. Powder creams and make-up creams differ from pigmented foundation creams only that they normally contain 10-25 % powder, opposed to 3-10 % (18).

c) BLEMISH BALM (BB) and COLOUR CORRECTION (CC) CREAMS

BB creams are an Asian import that has become popular in the last two years first in the US and all around the Europe. BB creams provide good coverage with sun protection benefits and anti-aging effects. They are lighter than foundations but heavier than tinted moisturizers. CC creams are not so much different from the previous ones, but they are

lighter and make complexion fresher with natural look**.** The beauty market already has DD creams, known as daily defence creams (19).

1.3.2. OVERVIEW OF FORMULATIONS ON THE MARKET WITH COVERING AND SPECIAL EFFECT ON THE SKIN

- Eucerin® Redness relief concealer - contains green colour neutralizers.
- Rosaliac® Anti-redness moisturizer - it is based on vitamin C and pigments with green tint which help to act against the anti – redness on the face (20).
- Lierac® Luminiscence serum complexion corrector - diminishes the appearance of pigment spots and redness with reactivate light reflection by Illuminating pearly particles (21).
- Prime time™ Neutralizing Foundation Primer – it is based on pigments neutralizers with yellow base for reducing redness of the skin and visual correction of skin tone unevenness (22).
- Neutrogena® Healthy Skin primer- it is based on optical modifiers which reduce appearance of the skin imperfections during the day and make skin brighter (23).
- L'Oréal® Paris Lumi Magique Pure Light Primer – it is used before make-up or cream foundations is applying on the face. Its ingredients work against skin irregularities and to make complexion more even (24).
- L´Occitane Perfecting cream – it contains a peony extract with an optical correctors for visible perfecting look of the complexion.

2. AIM OF THE WORK

The aim of diploma thesis is to develop emulsions containing pigments with special effects for optical correction on the skin such as anti-redness, white, shiny and silky pearl effect for reducing skin colour imperfections. At the beginning we will make formulations without pigments with the same composition of hydrophilic basis, but with different type and concentration of oil phase and with specific O/V emulsifying agents. We´ll evaluate organoleptic and physico – chemical properties of basic emulsions by pH measured, stress test with centrifuge, microscopy observations of emulsion structure and rheological properties. On the basis of the results, we will select formulations and optimize them with addition of pigments, dispersed in oil phase. We will determine the colour difference where the reflected light from optimized formulations will be evaluated by using chromameter. Results will be expressed in CIE L*a*b* (CIELAB) colour space, which describes all the colours visible to the human eye. We´ll evaluate brightness / darkness, redness / greenness, blueness / yellowness of system comparing to standard formulations.

3. EXPERIMENTAL PART

3.1. MATERIALS

3.1.1. INGREDIENTS OF FORMULATIONS

- **INCI**: **Candelilla/Jojoba/Rice bran polyglyceryl-3 esters, Glyceryl Stearate, Cetearyl Alchol, Sodium Stearoyl Lactylate**

  Trade name: Emulium® Kappa 2, Gateffossé, France

It is a natural, PEG-free emulsifier bringing extreme, luxurious and softness to the formula. Emulium® Kappa 2 is based on a patented technology of hydrophilized vegetable waxes that can absorb up to 6 times their weight in water (25).

- **INCI: Isostearyl alcohol/Butylene glycol Cocoate/Ethylcellulose**

  Trade name: Emulfree® CBG, Gateffossé, France

It is a lipid based stabiliser consisting of a synergistic association of ethylcellulose polymer with emollients. Offers excellent emulsion-like sensory benefits and provides natural non-transfer and water-resistance properties (26).

- **INCI: Disodium EDTA**

It is a chelating agent, used to decrease the reactivity of metal ions that may be present in a product (27).

- **INCI: Glycerine**

Glycerine is used primarily for its humectant and emollient properties in topical pharmaceutical formulations. Glycerine is used as a solvent or cosolvent in creams and emulsions. It is a clear, colorless, odourless, voscous, hygroscopic liquids and mainly obtained form oil and fats as a by-product in the manufacture of soaps and fatty acids (28).

- **INCI: Microcristalline cellulose/celullose gum**

  Trade name: Vivapur® Cos 5, Gattefossé, France

It is a fine, white, odorless powder with a wood origin that functions as a stabilizer for multiphase systems like emulsions, dispersions, and foams. Due to its neutral and inert character it can be used universally in practically any area of personal care and oral care without sensory interference (29).

- **INCI: Xantan Gum**
  Trade name: Keltrol TF, Unifarco, Italy

Xanthan gum is a polysaccharide secreted by the bacterium *Xanthomonas campestris*, used as a rheology modifier and stabilizer. It is also used in oil-in-water emulsions to help stabilize the oil droplets against coalescence and has some skin hydrating properties (30).

- **INCI: Cetearyl alcohol**
  Trade name: Lanette O, Eurotrading, Italy

It is used for viscosity modifying in cosmetic oil-in-water emulsions. It is a white to light yellowish hydrophilic wax that is supplied in pellets (31).

- **INCI: Caprylic/capric trigliceride**
  Trade name: DUB MCT (Myritol 318), Eurotrading, Italy

Caprylic, capric trigliceride is a triglyceride that is a traditional, medium spreading emollient for modern cosmetic applications. It is a clear, slightly yellowish, polar and odorless oil (32).

- **INCI: Isohexadecane (97,5%), PPG-15 stearyl ether (2,5%)**
  Trade name: Dermoil HDE, Unifarco, Italy

It has emollient properties in cosmetic products (33).

- **INCI: Hydrogenated Vegetable Oil Candelilla Cera**
  Trade name: CEGE SOFT VP, Eurotrading, Italy

It is an oil and wax blend that is used as a basic mass for the preparation of sticks, especially for decorative cosmetics and waxy components for cosmetic emulsions. It is a yellowish waxy solid, with a bland odour (34).

- **INCI: Acacia Decurrens/Jojoba/Sunflower Seed Wax/Polyglyceryl-3 Esters**
  Trade name: HYDRACIRE S, Unifarco, Italy

It is a vegetal active texture agent based on an hydrophilized complex of jojoba, mimosa and sunflower waxes. It improves sensorial properties and stability of O/W or W/O emulsions (35).

- **INCI: Coco-Caprylate**
  Trade name: CETIOL C5, Eurotrading, Italy

It is a clear, colourless to slightly yellowish, medium polar oil with a slight fatty odor. It is a fast spreading emollient for personal care applications, particularly designed to offer a good alternative to volatile silicones like cyclomethicones (36).

- **INCI: Olus**
  Trade name: CEGESOFT® PS 17, Eurotrading, Italy

Olus is a clear yellow, odourless oil and slow spreading emollient that gives a luxurious, long lasting feel on the skin (37).

- **INCI: Macadamia Oil, Eurotrading, Italy**

It is oil from the nut meat of the macadamia tree, which is rich oil and with high oxidative stability . It is an excellent emollient in cosmetic products (38).

- **INCI: Dicaprilyl ether**
  Trade name: CETIOL® OE, Eurotrading, Italy

It is a fast-spreading emollient which gives the skin a light, silky feel and is ideal for innovative green formulations without silicone (39).

- **INCI: Propylene glycol dicaprylate/dicaprate**
  Trade name: LABRAFAC® PG, Gattefossé, France

Propylene glycol dicaprylate is oily vehicle for use in self-emulsifying lipid formulations to obtain a coarse dispersion with excelent emollient properties (40).

- **INCI: Butylene Glycol Cocoate**
  Trade name: COCOATE® BG, Gateffossé, France

Butylene glycol cocoate is recommended for cosmetic formulations. It is used as an ester for make-up, make-up removal and suncare applications. This product is also used as emollient, disperser for organic and mineral sun filters and excellent pigment wetting agent (41).

- **INCI: Gliceryl monooleate**

  Trade name: PECEOL®, Gateffossé, France

Gliceryl monooleate is oily vehicle for use in self-emulsifying lipid formulations to obtain a coarse dispersion and good solvent for lipophilic active pharmaceutical ingredients (42).

- **INCI: Gliceryl linoleate**

  Trade name: MAISINE 35-1, Gateffossé, France

Gliceryl linoleate is oily vehicle for use in self-emulsifying lipid formulations to obtain a coarse dispersion and good solvent for lipophilic active pharmaceutical ingredients (43).

- **INCI: Dimethicone**

  Trade name: Dow Corning® 200 fluid, Dow corning, England

Dimethicone-also called polymethylsiloxane is a silicon-based polymer used as a lubricant and conditioning agent (44).

- **INCI: Caprylyl methicone**

  Trade name: Dow corning® FZ 3196, Dow corning, England

It is a volatile alkyl methyl siloxane fluid that combines compatibility with a wide range of ingredients. It can be used with vegetable oils or other naturals for enhanced sensory benefits, as a carrier for other ingredients, or as a dispersing medium for hydrophobic powders and pigments (45).

- **INCI: O-Cymen-5-ol**

  Trade name: Biosol, Changsa Sunfull bio, China

It is a white crystal powder and being used as preservative in various kinds of cosmetic products (46).

- **INCI: PEG-8, Tocopherol, Ascorbyl palmitate, Ascorbic acid, Citric acid**

  Trade name: Oxynex® K liquid

Oxynex® K liquid is especially suitable for the preservation of high-grade fats and oils with a low to medium tocopherol content. Oxynex® K Liquid is a clear, yellow to orange, viscous liquid (47).

- **Destillated water**

Ingridients of hydrophilic phase.

- **PIGMENTS**

INCI	Trade name	Manufacturer	Particle size	Aspect	Effect
Synthetic Fluorphlogopite and Lauroyl Lysine/Synthetic mica	**Chione M-SVA**	Eurotrading BASF	8 μm	White	"Soft focus", white velvet and satin matt effect
Synthetic Fluorphlogopite and Titanium dioxide	**Chione HD infinite white S130V**	Eurotrading BASF	10 μm	Pearly white satin	Light and silky effect
Synthetic Fluorphlogopite and Titanium dioxide	**Chione HD Crystal mint S830V**	Eurotrading BASF	14 μm	White with green reflection	Anti-redness
Synthetic Fluorphlogopite and Titanium dioxide	**Chione snowfall white S130D**	Eurotrading BASF	20 μm	Pearly white light	Silky pearl effect and brilliant white

Use of pigments in skin care products:

Chione M-SVA: **≥ 2 %**

Chione HD infinite white: **1-2%**

Chione HD Crystal mint : **1-2%**

Chione snowfall white: no data (48)

** certain amount of pigment was taken into account in our formulations*

3.1.2. DEVICES AND EQUIPMENTS

* Water bath (GFL, Germany)
* Analitical Scale (Mettler Toledo, Switzerland)
* Homogenizator (L4RT Silverson,United Kingdom)
* Centrifuge (LW Scientific M24, United States)
* pH meter (HI 2212 Flexible Calibration, United States)
* Rheometer (Anton Paar MCR 101, Austria)
* Microscope (Zeiss Axiovert 40CFL, AXIO VISION, Germany)
* Chroma meter (Konica Minolta CR-400, United Kingdom)
* Tubes
* Beakers
* Pipettes
* Plastic cards, pots and spoons

3.2 METHODS

3.2.1. COMPOSITION AND MANUFACTURING PROCEDURE OF BASIC FORMULATIONS

At the begining we made 20 basic formulations or empty bases without pigments. All emulsions were prepared by the same procedure. We used two different types of emulsifying agents which were added to the lipophilic phase and dispersed in the hydrophilic phase. All emulsions were prepared under the technological form of creams, type O / V.

Manufacturing procedure:

- We weighed the oil component, including emulsifying agents Emulium® Kappa 2 and Emulfree® CBG in the beaker, and heated in a water bath of temperature to 70°C.
- In the second beaker, EDTA was solubilised in water then we added microcrystalline cellulose (hydrophilic phase). Xantan gum was dispersed in glycerine, a mixture thereof we added to a hydrophilic phase, and heated to the temperature 70°C under mixing for 10 minutes.
- Under mixing (3000 rpm) with rotor-stator homogenizator (high shear mixer-model with a capacity from 1ml up to 12 litres) we added lipophilic phase to hydrophilic phase and mixed for about 5 minutes.
- After homogenization we cooled formulations under mixing.
- We controlled the initial pH and eventually adjusted to final pH 5,4 – 5,9

Composition of basic formulations is shown on tables II and III.

Table II: Composition of basic formulations containing emulsifying agent Emulfree®CBG

	1a %	2a %	3a %	4a %	5a %
Water	83,05	82,05	81,05	71,85	79,85
Disodium EDTA	0,1	0,1	0,1	0,1	0,1
Glycerine	3	3	3	3	3
Xaantan gum	0,2	0,2	0,2	0,4	0,4
Microcristalline celullose	1,5	1,5	1,5	2,5	2,5
Emulfree® CBG	4	5	6	6	6
Dicaprilyl ether	2	2	2	4	
Caprilyc triglyceride	2	2	2	4	
Dimethicone	2	2	2	4	4
Dermoil HDE	2	2	2	4	
Caprylyl methicone					4
O-Cymen-5-ol	0,1	0,1	0,1	0,1	0,1
Oxynex® K liquid	0,05	0,05	0,05	0,05	0,05

Hidrophilic phase

pH adjuster

Humectant

Rheology modifiers

Emulsifying agent

Emollients; lipophilic phase

Preservative

Antioxidant

Table III: Composition of basic formulations containing emulsifying agent Emulliim® Kappa 2

	1 %	2 %	3 %	4 %	5 %	6 %	7 %	8 %	9 %	10 %
Water	83,35	81,85	81,85	79,85	81,35	79,35	75,35	77,35	77,35	77,35
Disodium EDTA	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1
Glycerine	3	3	3	3	3	3	3	3	3	3
Xaantan gum	0,4	0,4	0,4	0,4	0,4	0,4	0,4	0,4	0,4	0,4
Microcristalline celullose	2,5	2,5	2,5	2,5	2,5	2,5	2,5	2,5	2,5	2,5
Emulium® Kappa 2	2,5	4	4	6	2,5	2,5	2,5	2,5	2,5	2,5
Cetearyl alcholol					2	2	2	2	2	2
Dicaprilyl ether	2	2	4	2						
Dermoil HDE	2	2		2						
Caprylyc triglyceride	2	2		2						
Dimethicone	2	2	4	2						
Cege soft VP						2	2			
Coco-caprylate					2	2	4	4	4	4
Olus					2	2	5			
Macadamia oil					4	4	3			
Propylene dicaprylate								8		
Glycerol linoleate									8	
Glycerol monooleate										8
O-Cymen-5-ol	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1
Oxynex® K liquid	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05

3.2.2. ORGANOLEPTIC AND PHYSICO – CHEMICAL EVALUATION OF THE STABILITY OF EMULSIONS

For each formulation we carried out an evaluation of the organoleptic properties such as visual assessment and sensory feeling on the skin after application of the emulsions. We measured pH, we observed the structure of emulsions under optical light microscope, performed stress test with a centrifuge to determine the stability of the emulsion and evaluated viscosity as a function of shear - rate on selected emulsion.

3.2.2.1. MEASUREMENT OF pH

The initial pH of basic formulations was controlled and eventually adjusted to final pH in the range from 5.4 to 5.9 with pH meter. Electrode, calibrated in a buffer solution having a pH value of 7, was immersed in the sample and after a certain time, pH value of the sample was scanned at room temperature. To the samples which had a value of pH > 5.9 citric acid was added for lower pH and the samples which had value of pH < 5.4 sodium hydroxide was added for higher pH. Each measurement was repeated twice and after each measurement, the electrode was washed with destillated water.

3.2.2.2. ORGANOLEPTIC EVALUATION OF EMULSIONS

We visually assessed the colour, odour, aspect of basic emulsions and the consistency, spreadability and film on the skin after applications of emulsions. We wanted to formulate emulsions with no sticky effect, good spreadability and with rich consistence. Samples must be free of unwanted lumps, bubbles and must remain homogeneous, with no visible oil droplets on the surface. The colour of samples was compared in terms of a white background. All samples were evaluated after manufacture procedure and after the measurement of pH.

3.2.2.3. MICROSCOPY FOR THE OBSERVATION OF EMULSION STRUCTURE

We used optical light microscope at 200x magnification connected to the PC to observe the cosmetic formulations and their structure. It is able to assess the presence and possible of aggregation in sample as well as check the homogenization of emulsion in micrometer size range. Microscopic structure was observed on freshly prepared basic formulations after 24 hours. Small amount of samples was placed on an object slide, covered and analyzed immediately. The observation of emulsion structure is one of the tools to predict the emulsion stability in early stage.

3.2.2.4. STRESS TEST BY CENTRIFUGATION TO EVALUATE PHYSICAL STABILITY OF EMULSIONS

Physical stability was evaluated by a stress test, which predicts the formulations stability under stress conditions where the emulsion has to be unchanged before is subjected to further study of stability. Stress test was performed after one week from the homogenization process where 5 grams of each basic formulation were put in the test tube and centrifugated for 30 minutes at 3000 rpm. After that we visually assessed the stability of emulsions and separation or non-separation of phases.

3.2.2.5. RHEOLOGICAL MEASUREMENT

Rheology is the study of flow and deformation of materials from fluids to semi - solids under applied forces**.** Systems are divided into Newtonian – ideal and non-Newtoninan – real. Newtonian systems present the ideal liquids where the viscosity is independent on shear rate, but depending on the pressure and temperature. Non–Newtonian systems present the real liquids and semi-solid systems where the viscosity at a given pressure and temperature is not constant but depends on the operation of shear stress (49). Rheological analysis was implemented by rheometer Rheoplus Anton Paar MCR 101, termostated at 23 ± 0.05°C. For the evaluation of the sample the sensor system PP50-2 was used, plate-plate with fixed gap 1mm. This sensor system allows the measurement of small quantities of sample. We recorded viscosity curve as a function of controlled shear rate. The viscosity was measured in the range of shear rates from 0,0001 s^{-1} to 100 s^{-1} where we measured 30 measuring points. Rheological analysis was performed on two basic formulations which were selected on the basis of good sensory properties on the skin and stability test.

Figure 7: Rheometer Anton Paar

3.2.3. OPTIMIZATION OF FORMULATIONS

On the basis of the organoleptic and physical - chemical properties of emulsions, the formulation which proved good consistency and spreadability on the skin was selected. Part of the lipophilic phase was replaced with emollient, which has a great ability to wetting pigments. Three new basic formulations were made, where pigments were added to the lipophilic phase and dispersed. The distribution of pigments in the emulsion was observed under a microscope and evaluated the colour difference of formulations containing pigments comparing to the basics optimized formulations.

3.2.3.1 MICROSCOPIC ANALYSIS OF PIGMENTS DISTRIBUTION

Distribution of pigments was observed by the same method and microscope as for the observation of emulsion structure, where we used 200x magnification connected to the PC. Under microscope we can see morphological properties of the phase and particle distribution of the emulsion droplets and pigments, which should be evenly distributed throughout the emulsion. Microscopic structure was observed on freshly prepared optimized formulations with pigments after 24 hours.

3.2.4. EVALUATION AND MEASUREMENT OF COLOUR DIFFERENCIES OF FORMULATIONS

Colourimetry is the science used to quantify and describe physically the human colour perception and one of method for measuring surfaces colour (50).

We used Konica Minolta CR-400, a transmission tristimulus chroma meter, to measure transparent colours of liquids (Figure 8). The lighting was provided by a pulsed xenon arc lamp using illuminant D65 with 8 mm measuring area suitable for measuring reflected colour and colour difference. The probe of chromameter was immersed into a 5 mm deep plastic pot where samples were filled. Measurement were made on the basic optimized formulations without pigments and formulations containing pigments, where the brightness / darkness, redness / greenness, blueness / yellowness of system comparing to the standards or basic formulations were determined.

Table IV: Principal specifications of chromameter

Detector	Light source	Measurment time	Minimum measurement interval
Silicon photocells (6)	Pulsed xenon light	1 sec.	3 sec.

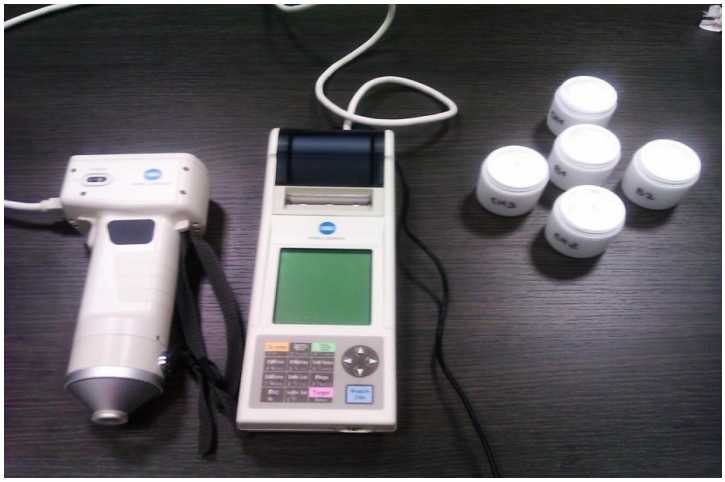


Figure 8: Konica minolta chromameter

4. RESULTS and DISCUSSION

4.1. DETERMINATION OF PHYSICAL STABILITY AND ORGANOLEPTIC PROPERTIES OF FORMULATIONS

All of our formulations were prepared with the same procedure, where we added the oil component, containing the emulsifying agents, to the hydrophilic phase. This resulted into the technological form of a cream - type O / W. We produced 200 g of each emulsions by the following percentage of each phase:

- hydrophilic phase: up to 90%
- emulsifying agent: 2.5% - 6%
- lipophilic phase: up to 25%

We selected individual components on the basis of literature review of the most commonly used composition in cosmetic products including pigments for skin care. Those products are various of correctors, primers, bb-creams, anti-imperfection concealers, fluid foundations and also empty bases of emulsion. We wanted to create a viscous emulsion with a rich consistency and good spreadability on the skin. For the first five formulations, liquid emulsifying agent Emulfree® CBG was used which is a surfactant-free stabilizer, based on lipid - based stabilizing base (26). In other formulations, emulsifying agent Emulium® Kappa 2 in solid capsules was used, based on a rich texture and powdery touch (25).

Organoleptic and physical – chemical properties of emulsions are shown in tables (V - IX) and figures (9 - 11).

Table V: pH value of basic formulations with Emulfree®CBG

	1a	2a	3a	4a	5a
Initial pH	5.55	6.20	6.14	6.19	5.57
Additive of citric acid/sodium hydorxide	/	+ 0.01 % of citric acid (*)	+ 0.01% of citric acid (*)	+ 0.01 % of citric acid (*)	/
Final pH	5.55	5.48	5.22	5.73	5,57

(*) % of citric acid relative to the whole % of formulation

Table VI: pH value of basic formulations with Emullium®Kappa2

	1	2	3	4	5	6	7	8	9	10
Initial pH	6.02	5.81	5.73	5.83	4.89	4.85	5.20	5.65	5.47	5.76
Additive of citric acid/sodium hydorxide	+ 0,01 % of citric acid (*)	/	/	/	+ 3 of gtts NaOH	+ 3 of gtts NaOH	+ 3 of gtts NaOH	/	/	/
Fianl pH	5.70	5.81	5.73	5.83	5.19	5.13	5.45	5.65	5.47	5.76

pH measurements were performed at room temperature (25°C) after the homogenization process, when the emulsions were cooled. We wanted to get a final pH of formulations which is in accordance to the healthy skin (ie. pH 5.4 - 5.9), and would be suitable for application to the skin. We found out that formulation, which contained the emulsifying agent Emulfree® CBG, have a more basic pH, so we added citric acid, which was previously dissolved in small droplet of water, to adjust the acidity and a decrease in pH. Other formulation that contained the emulsifying agent Emulium® Kappa 2 was more acidic, therefore, we added 3 gtts of NaOH to increase the pH. Most formulations suited to the natural pH of the skin, which is particularly important especially for the maintenance of natural acidic protective fatty layer. Their acidity also prevents the development of pathogenic micro-organisms and protects the skin against external harmful compounds (16).

Table VII: Organoleptic properties of emulsions 1a - 5a

ORGANOLEPTIC PROPERTIES		1a	2a	3a	4a	5a
Visual assessement	**Aspect**	Opaque, slight phase separation	Opaque, slight phase separation	Opaque, slight phase separation	Opaque	Opaque
	Colour	Matt white	Matt white	Matt white	Matt white	Matt white
	Odour	Without	Without	Without	Without	Without
After application on the skin	**Consistency**	Very light	Very light	Very light, unsatisfying	Unsatis-fying	Unsatis-fying
	Spreadability	Good, rapidly absorbed	Good, rapidly absorbed	Good, rapidly absorbed	Good	Good
	Film on the skin	Unsuitable, sticky	Unsuitable, sticky	Unsuitable, sticky	Un-suitable	Un-suitable

Table VIII: Organoleptic properties of formulations 1-5

ORGANOLEPTIC PROPERTIES		1	2	3	4	5
Visual assessement	**Aspect**	Viscous	Viscous	Viscous, creamy	Viscous, creamy	Viscous
	Colour	White	White	White	White	White
	Odour	Without	Without	Without	Without	Slight odor of macadamia
After application on the skin	**Consistency**	Satisfying	Satisfying	Satisfying	Satisfying	Satisfying
	Spreadability	Satisfying	Satisfying	Satisfying	Satisfying	Satisfying
	Film on the skin	Visible, greasy	Visible, greasy	Visible, greasy	Visible, greasy	Visible, greasy

Table IX: Organoleptic properties of formulations 6 - 10

ORGANOLEPTIC PROPERTIES		6	7	8	9	10
Visual assessement	**Aspect**	Viscous	Viscous	Viscous, creamy	Viscous	Viscous
	Colour	White	White	White	White	White
	Odour	Slight odor of macadamia	Slight odor of macadamia	Slight odor of coconut	Slight odor of coconut	Slight odor of coconut
After application on the skin	**Consistency**	Satisfying	Satisfying	Satisfying	Satisfying	Satisfying
	Spreadability	Satisfying	Satisfying	Good	Good	Good
	Film on the skin	Visible, satisfying	Visible, satisfying	Visible, satisfying	Visible, satisfying	Visible, satisfying

We assessed that formulations containing emulsifying agent Emulfree (1a - 5a) have lighter texture in comparison to the formulations containing emulsifying agent Emulium® Kappa 2. They are also all opaque and matt white. In some formulations with Emulfree® CBG we can see a slight separation of the phases, as a result of the weakness of system. This could be due to inappropriate emulsifying agent. Formulations with Emulium® Kappa 2 added richness to the structure and they look more compact, homogenous, and creamy. They leave more satin and silky effect with good spreadability while the formulations containing Emulfree®CBG are stickier with greasy feel on the skin, the film on the skin is unsatisfying. Formulations with Emulium® Kappa 2 predict a more stable structure and suitability for further analysis.

MICROSOPIC OBSERVATION OF EMULSION STRUCTURE

The microscopic structures of emulsions were observed on the freshly prepared formulation containing emulsifying agent Emulfree® CBG and on the formulation containing emulsifying agent Emulium® Kappa 2. On the basis of microscopic images of emulsions at 10 μm (Figure 9) we can predict the physical stability of two different system.

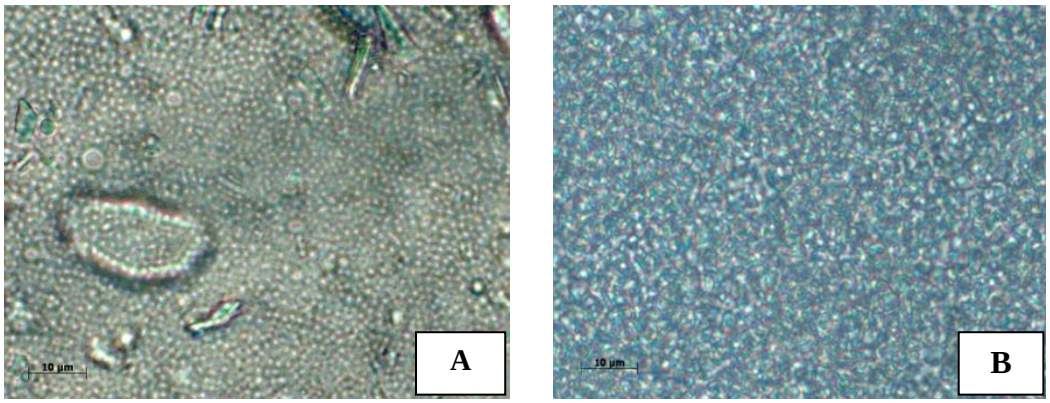


Figure 9: Microscopic images of basic formulations; A-emulsion with Emulfree® CBG, B-emulsion with Emullium® Kappa 2

Formulation A: The system with emulsifying agent Emulfree® CBG is non-homogeneous, because drops are unevenly distributed. They are seen as larger than smaller droplets with visible instability of emulsion where big drop absorbed the smallest ones (coalescence). The formulation consists in lighter structure of emulsifying agent where drops are not closely link to each other important for the emulsion stability. The system is inappropriate for further analysis because it predicts physical instability.

Formulation B: The system with emulsifying agent Emulium® Kappa 2 is homogeneous, drops are evenly distributed. It is a completely different system from the previous one, where emulsifying agent add richness to the structure and drops are closely link. The system predicts physical stability and it is appropriate for further analysis.

PHYSICAL STABILITY OF EMULSIONS BY STRESS TEST

Determination of physical stability of emulsions is particularly important in the early stages of product development. In this way with a centrifugal test, we can eliminate those samples where their unstable structure is not suitable for further analysis. Physical stability of the emulsions may be expressed in various forms (Figure 10). The most common is the ″creaming″ where oily droplets from inside of emulsions rise to the top of emulsion in the shape of aggregates. The oil and aqueous phases are separated (51).

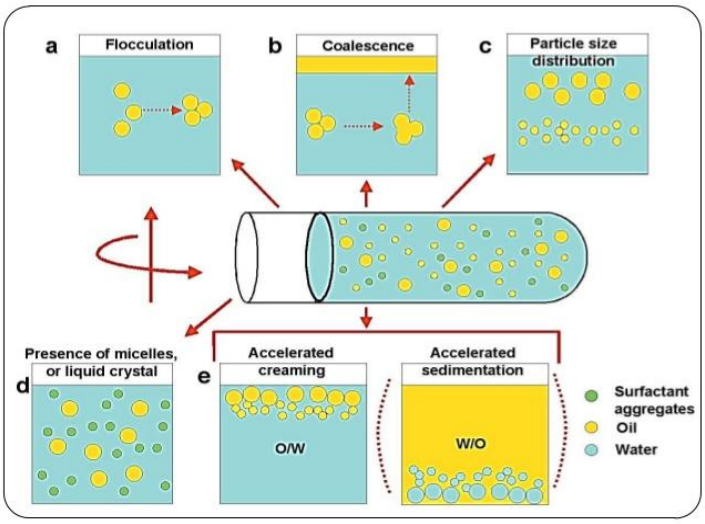


Figure 10: Overview of the possible effects during emulsion centrifugation for O/V and V/O emulsions

To determine the physical stability of our formulations, we performed a stress test with centrifuge for 30 minutes at 3000 rpm after homogenization process.

The basic formulations from 1a to 5a with emulsifying agent Emulfree® CBG were changed due to the separation of lipophilic and hydrophilic phase. The system was unstable because of the lightness structure; this could be due to inappropriate choice of emulsifying agent. Formulations with Emulfree® CBG were rejected because of inappropriate systems for further analysis.

The formulations with other emulsifying agent (Emulium® Kappa ²) were remained unchanged. Emulium® Kappa ² is emulsifying agent which formula is based on combination of consistency agent which helps to stabilize the viscosity of formulations and ingredients with more richness structure. The formulations with this emulsifying agent are suitable for further analysis because they were no visible phase separation.

RHEOLOGICAL PROPERTIES OF EMULSIONS

The rheological analysis was implemented on the formulations 4 and 8 with Emulium® Kappa 2 because they proved good sensorial properties on the skin, was proved as stable (centrifuge test) and expressed stable emulsion structure. The analysis was also made on the formulation 5a with Emulfree® CBG where we compare viscosity between two different systems. Viscosity is an important rheological characteristic which reflects the structure of the system and also helps to evaluate the stability of the system. The formulations were classified as non-Newtonian fluids because the viscosity of systems is not constant and is dependent on shear rate.

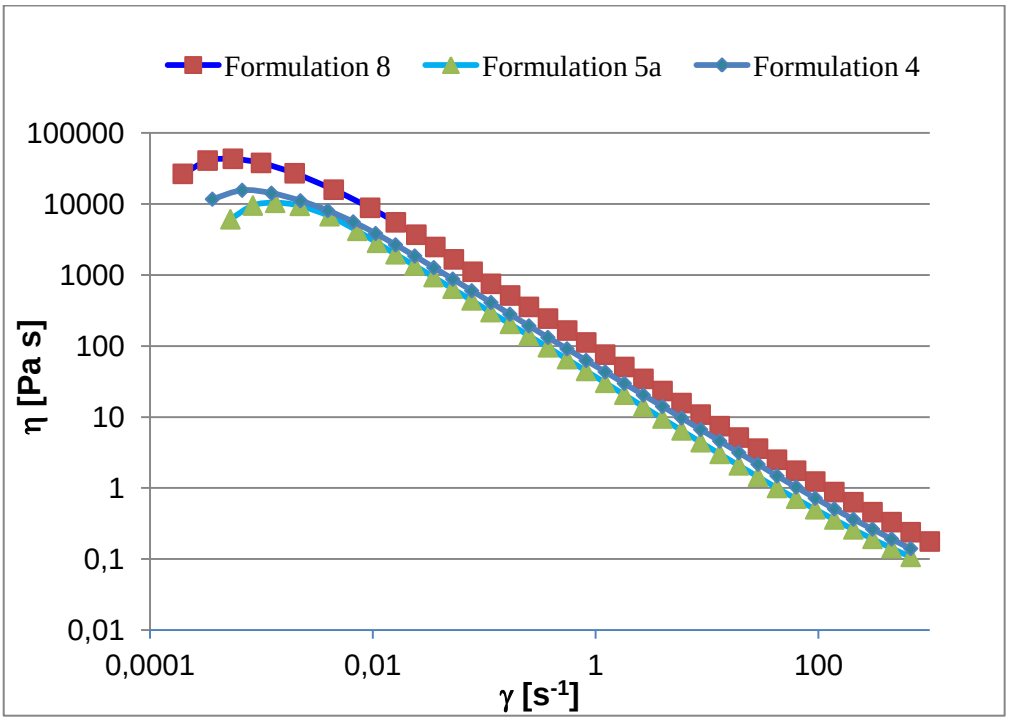


Figure 11: Viscosity curve of selected formulations 4, 8 and 5a as a function of shear rate

The figure 11 shows the viscosity measurement of selected formulations, which is dependent on shear rate. We can see that viscosity of formulations containing emulsifying agent Emulium® Kappa 2 is higher from formulation with Emulfree® CBG. This confirms properties of the samples we collected in the sensorial effect on the skin. It can be seen that all the samples show the same behaviour where none of the curves does not stand out from other. Viscosity curve show us also the pseudoplastic system of samples, where viscosity decreases with increasing shear rate.

4. 2. OPTIMIZATION OF FORMULATIONS

On the basis of the physical - chemical and organoleptic properties, the formulation 8 was selected, which proved appropriate consistency and a high viscosity. From the basic formulation, two additional optimized formulations (8a and 8b) were made, where we added alternative replacement for propylene glycol dicaprylate/dicaprate. We added emollient butylene glycol cocoate which has a greater capability of wetting pigments. This was assessed by different tests from manufacturer Gattefosse where emollient was tested versus 6 emollients, presents superior wetting power for a variety of pigments (speed and quality), pigment dispersions with much lower viscosities compared to other emollients (good dispersion, no particle agglomeration) and highly homogenous and bright colour development (52). Then we dispersed pigments into oil phase of optimized formulations in a proportion of 3% to 4%.

Composition of formulations containing pigments is shown in table X.

Under the optical light microscope, distribution of pigments was observed on freshly prepared emulsions, as showed in Figure 12.

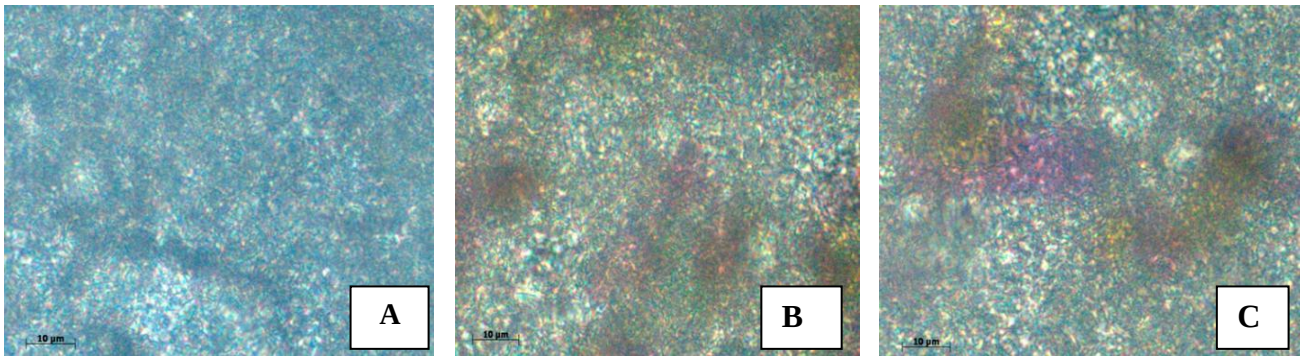


Figure 12: Microscopic images of distribution of pigments; A-emulsion 8a with 3% chione M-SVA, B-emulsion 8b with 3% chione M-SVA and 1% crystal mint, C-emulsion 8b with 1,5% chione M-SVA, 0,75% of crystal mint and snowfall white, 1% of infinite

Formulation A: the system consists of the 3% of white pigment, visible as white islets evenly distributed within the emulsion. This was expected, due to the synthetic mica inside with white aspect.

Formulation B and C: the system consists of the white and green reflection pigments. Under the microscope we can see yellow and violet islets within the emulsion system. This

could be due to the effects of pigments colour and contact with other ingredients. Pigments are unevenly distributed throughout the emulsion; the reason may be that the pigments were not well dispersed in the oil phase during the process of homogenization.

Table X: : Composition of optimized formulation 8 with substituted part of oil phase (EK 8a, EK 8b) and with pigments (EK8a+chione, EK8b+chione, EK8b+chione1)

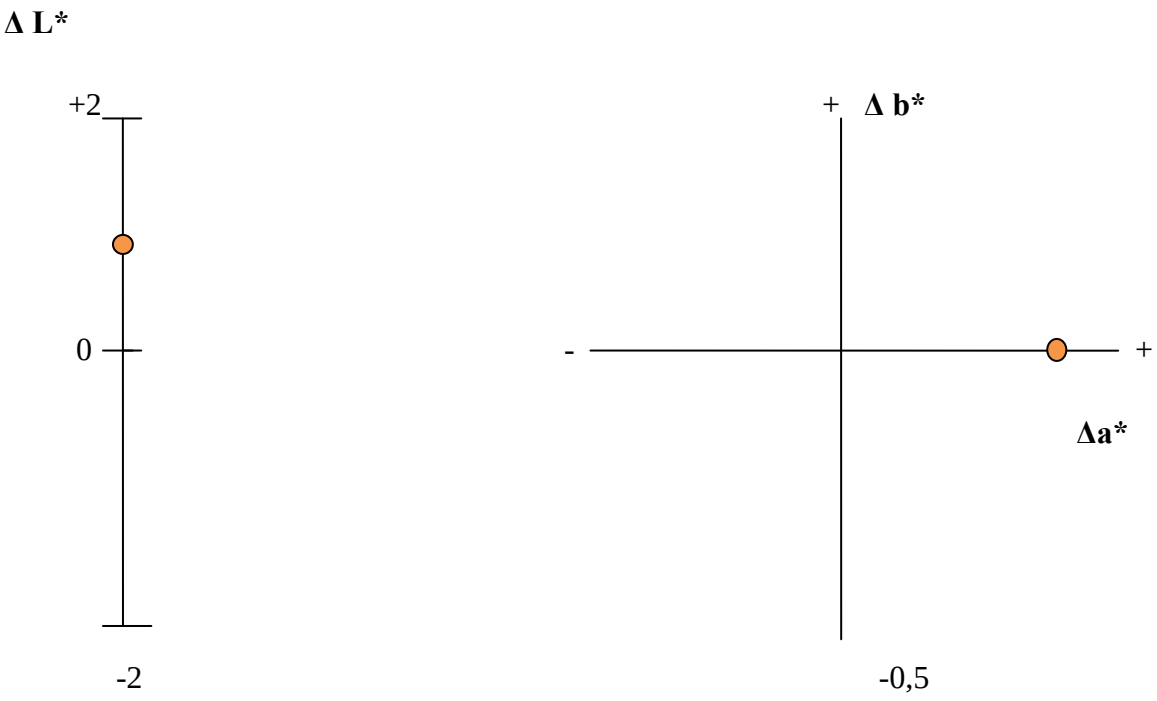
	EK 8 a (%)	EK 8 a+chione (%)	EK 8 b (%)	EK 8 b+ chione (%)	EK 8 b+ chione 1 (%)
Water	75,35	72,35	75,35	71,35	71,35
Disodium EDTA	0,1	0,1	0,1	0,1	0,1
Glycerine	3	3	3	3	3
Xaantan gum	0,4	0,4	0,4	0,4	0,4
Microcristalline celullose	2,5	2,5	2,5	2,5	2,5
Emulium® Kappa 2	2,5	2,5	2,5	2,5	2,5
Cetearyl alcholol	2	2	2	2	2
Cege soft VP	2	2	2	2	2
Propylene glycol dicaprylate	4	4			
Butilen glycol cocoate	4	4	8	8	8
Coco caprilate	4	4	4	4	4
Chione M-SVA		3		3	1,5
Chione HD infinite white S					1
Chione HD Crystal mint				1	0,75
Chione snowfall white					0,75
O-Cymen-5-ol	0,1	0,1	0,1	0,1	0,1
Oxynex® K liquid	0,05	0,05	0,05	0,05	0,05

4.3. EVALUATION AND MEASUREMENT OF COLOUR DIFFERENCIES OF FORMULATIONS

The measurements were performed at the optimized formulations 8a and 8b without the pigments and on formulations where the pigments were dispersed. Among them, we compared the colour difference. The results we obtained are written in the tables (XI – XIII), the brightness / darkness (Δ L *) is displayed on the line, redness / greenness, blueness / yellowness (Δ a * and b * Δ) are shown in a coordinate system.

Table XI: Colorimetric measurment for formulation 8a with chione compare with the formulation 8a

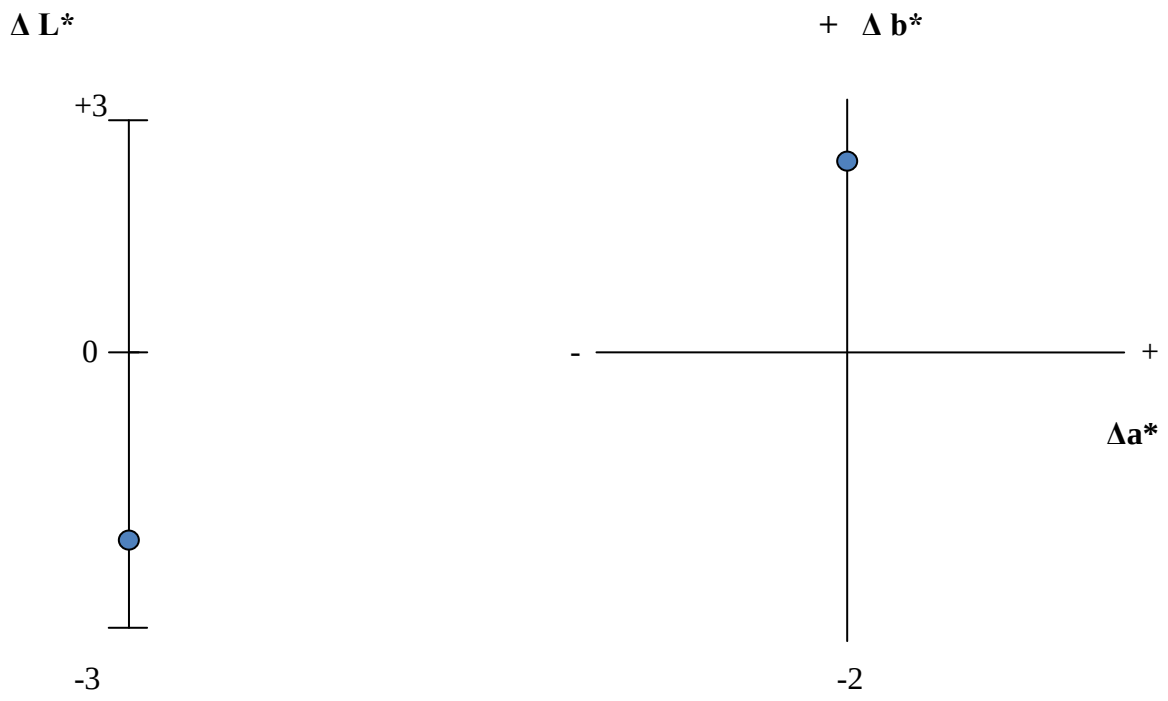
	Formulation 8a	**Formulation 8a +chione**	**Δ total difference**
L*	93,14	93,91	+0,78
a*	-0,60	-0,14	+0,46
b*	+4,32	+4,33	+0,01
Δ E*	/	/	0,66



Findings for formulation 8a / 8a+chione: The L* value of formulation 8a is a little highest from formulation 8a+chione and increased by the pigment Chione M-SVA. This was expected because the pigment inside has the white aspect and due to its particle size (8 µm) could offer a good coverage to the skin and make skin more shiny with ″soft focus″ effect. The a* value is more close to zero than from formulation 8a, this equates the greenness of system, and results in neutral of system, greater impact was not expected. The b* value is the same as from formulation 8a, which indicate the yellowness. Yellow colour could reduce purple tone of skin such as bruises and broken capillaries. The formulation has the minimal total difference comparison with standard formulation 8a, because the ΔE* is less than 1 which is a normally invisible difference. Due to the minimum value of a* and b*, the effect of pigments on the skin will be invisible.

Table XII: Colorimetric measurment for formulation 8b + chione compare with formulation 8b

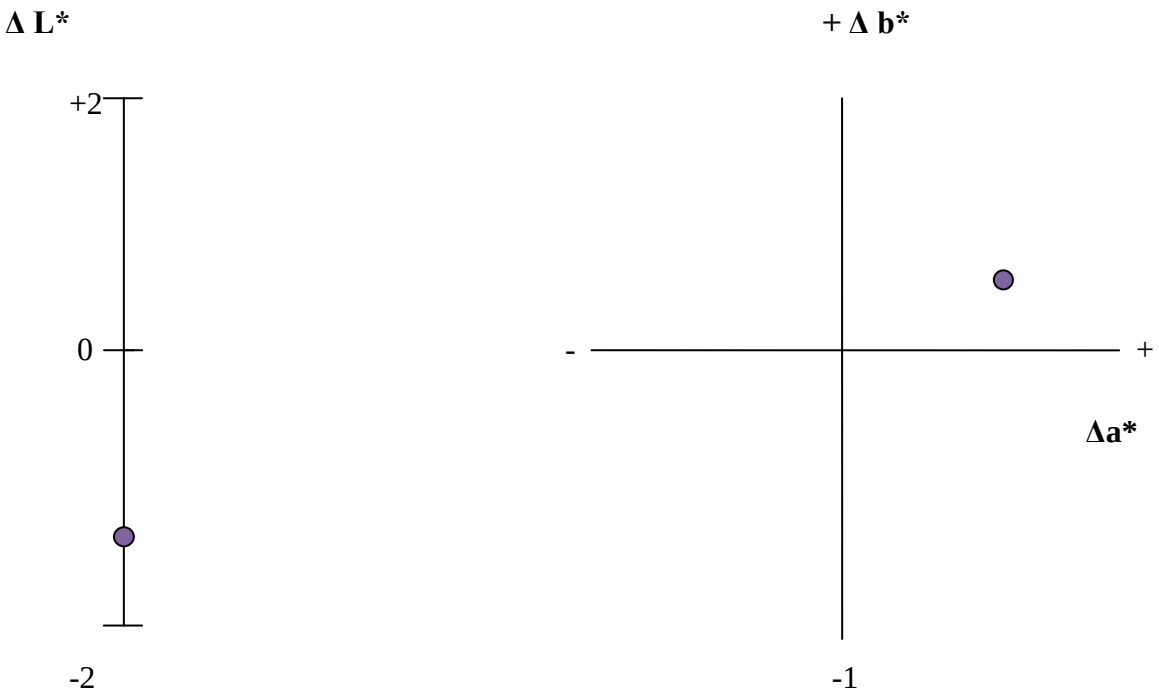
	Formulation 8b	**Formulation 8b+chione**	**Δ total difference**
L*	93,71	91,37	-2,33
a*	-0,96	-0,96	+0,01
b*	+4,38	+5,89	+1,56
Δ E*	/	/	2,78



Findings for formulation 8b / 8b+chione: The formulation 8b indicates L* value darker comparison to the formulation 8b+chione, which is more light. Value a* is the same as in target, where in both cases indicates to the greenness of system. This value has an important role against to the redness effect on the skin, because the green colour neutralizes red colour by the system of contrasting colours, the redness of skin can be camouflaged. The value b* indicates more yellowness effect from the standard formulation and this is a great use against to the blue colour of the skin such as bruises and dark circles, to neutralize the blue tone of skin. Due to the pigments particle sizes 8 μm and 14 μm, formulations could offer a good coverage to the skin. The total difference in value Δ E* indicate medium difference between standard and sample also obvious to an untrained eye.

Table XIII: Colorimetric measurment for formulation 8b + chione 1 compare with formulation 8b

	Formulation 8b	Formulation 8b+chione 1	Δ total difference
L*	93,71	92,08	-1,63
a*	-0,96	-0,39	+0,57
b*	+4,38	+4,83	+0,45
Δ E*	/	/	1,79



Findings for formulation 8b / 8b+chione 1: The formulation 8b + chione 1 includes all special effect pigments we used for formulations. The pigments inside reduce brightness of emulsion, which is darker comparing to the formulation without pigments but still indicate light system. They have a particle size up to 20 μm, indicated satin matt effect with the best coverage. Value a* is close to zero, sample is neutral, with a slightly greenish. Value b* is little more higher compare to formulation 8b which indicate the yellowish tint important to reduce the blue tone of the skin. The value Δ E* indicates very small difference, only obvious to a trained eye.

GENERAL OBSERVATIONS OF RESULTS IN COLOUR DIFFERENCIES

- In all samples, the value of redness / greenness (a*) and blueness / yellowness (b*) is low, which is not enough for a complete overlap of skin colour imperfections, while the brightness / darkness (value L*) is high in all emulsions.
- All of three formulations have a value b* higher than value a*, which add yellowness to the system. They are more appropriate to reduce blue tone on the face such as bruises, dark spots, broken capillaries and also dark circles around the eye. Value L* offers a white and shiny effect in all samples.
- We can classify our formulations as fluid foundations - emulsion, the most commonly used cosmetic products with covering effect. Pigments inside would work for optical corrections complexion.
- The real value of the results could be realised by tests on the skin before and after applications to assess and evaluate effect of special pigments.
- The formulations could be use as primer foundation of complementary colour before application of the cream or make up and a basis for further development of cream and anti-redness moisturizers.
- For more concrete results of special pigments effect, further study would be required. The effect could be seen with a higher proportion of pigments in emulsions or the use with combination of other pigments (organic or inorganic)

5. CONCLUSION

- We have developed a stable emulsions with emulsifying agent Emulium® Kappa ² which add richness to the structure, important for dispersion of pigments with good consistency and spreadability on the skin.
- pH of formulations is in the range of natural pH of skin (ie. pH 5.4 – 5.9), suitable for application on the skin and also for the maintenance of natural acidic protective fatty layer.
- Under the optical light microscope, the emulsion structure of two different systems was observed, where the emulsions containing emulsifying agent Emulfree® CBG predict the instability of system, while the emulsions containing emulsifying agent Emulium® Kappa 2 predict the stable structure with evenly distributed droplets throughout the emulsion.
- With stress test by centrifuge, we confirmed our assumptions regarding the stability of emulsions, where the lipophilic and hydrophilic phase of emulsion with Emulfree® CBG separated, while other emulsions containing Emulium® Kappa 2 remained unchanged.
- The viscosity of systems was observed by rheological analysis, which reflects the structure of the substance and also helps to evaluate the stability of the system. Emulsions with Emulium® Kappa 2 hive a higher viscosity than emulsion with Emulfree® CBG. Emulsions are pseudoplastic systems, where viscosity decreases with increasing shear rate.
- Under the optical light microscope we saw that the pigment containing synthetic mica with white aspect is evenly distributed throughout the emulsion, while other pigments are unevenly distributed, combined the yellow and purple beads or ″islets″.
- We measured colour differences in the emulsions and defined a low value of a * and b* present the redness / greenness and blueness / yellowness of the system. Real value of the results could be realised by tests on the skin before and after applications to assess and evaluate effect of special pigments. For this reason, further study would be required.
- We can conclude that emulsions could be used as primer foundation of complementary colour before application of the cream or make up. They can be

also a good base for further development of creams used for anti-redness treatments and other skin colour imperfections.

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