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Methodological approach for the sustainable design of structured chemical products during early design stages

Doctoral Dissertation

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PhD in Engineering – Industrial Systems Engineering

by

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To expert and non-expert chemical product designers, with the hope they will find this contribution useful.

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Approche méthodologique pour la conception durable de produits chimiques structurés dans les premières phases de la conception

RÉSUMÉ

En raison de la compétitivité dans le marché des produits chimiques et la demande croissante pour les produits de qualité, l'industrie et l'académie sont à la recherche de nouvelles méthodes pour la conception des produits chimiques. Par conséquent, cette étude propose une approche méthodologique pour faciliter la prise de décisions dans la conception de produits de type émulsion. Les caractéristiques de la méthodologie proposée sont les suivantes: elle propose des méthodes pour l'analyse des besoins de consommateurs, la génération d'idées pour la conception du produit et la sélection du meilleur produit.

INTRODUCTION

L'industrie chimique évolue rapidement en réponse à de nouveaux défis tels que la forte compétitivité du marché de la chimie, les préoccupations du public concernant les impacts environnementaux et les exigences en constante évolution des clients (Charpentier, 2009). Dans ce scénario, de nombreuses entreprises trouvent de nouvelles opportunités de croissance dans le développement de produits à forte valeur ajoutée tels que les produits chimiques de consommation. Pour saisir ces opportunités, les entreprises ont besoin d'une méthodologie systématique de conception de produits différente de la méthode d'essai et d'erreur habituellement mise en œuvre pour cette tâche. Une telle méthodologie peut leur permettre de générer efficacement des produits innovants et de répondre à un marché diversifié.

Problème de recherche

Pour contribuer au développement d'une telle méthodologie, cette étude se concentre sur trois aspects principaux qui constituent sa problématique de recherche: l'intégration des besoins des clients dans le processus de conception, le processus de prise de décision adaptable à la complexité des produits d'émulsion et l'intégration des principes de durabilité. Ils sont expliqués ci-dessous :

1. Intégration des besoins des clients dans la conception des produits chimiques: La valeur du produit du client n'est pas directement liée à son coût, mais à sa capacité

à répondre aux besoins du client. Ces besoins sont difficiles à analyser parce qu'ils sont décrits en termes non techniques, certains d'entre eux peuvent être subjectifs ou même liés aux émotions du client (Cussler et al., 2010).

Cette étude prend en compte les besoins du client au début du processus de conception en appliquant deux méthodes : le modèle Kano pour l'analyse des besoins et la matrice QFD (Quality Function Deployment) pour la traduction des besoins. Ces méthodes fournissent aux concepteurs une procédure pour transformer les besoins en spécifications de produits.

2. La complexité inhérente aux produits chimiques microstructurés : Les produits chimiques microstructurés (sous forme d'émulsions) sont des systèmes complexes formés par de multiples éléments en interaction (Charpentier, 2009). Leurs propriétés finales dépendent de leurs composants, de leur composition et de leur structure, ces dernières étant en partie définies par les procédés de production (Ng et al., 2007).C'est la raison pour laquelle plusieurs chercheurs ont proposé une tâche simultanée de conception du produit et du procédé.

   Pour contribuer à l'élaboration d'une méthodologie systémique, cette étude propose une méthode de conception multivariable applicable à la conception d'émulsion, dans laquelle les variables de conception et les caractéristiques du produit sont considérées simultanément.

3. l'intégration des critères de durabilité dans le processus décisionnel : aujourd'hui la durabilité est une préoccupation générale, reflétée dans les réglementations légales, les pratiques industrielles, les domaines scientifiques, et elle est devenue de plus en plus un facteur dans le comportement d'achat des clients. Par conséquent, une méthodologie de conception incluant l'application de principes durables pour la génération de nouveaux produits et procédés est considérée dans cette étude. Il existe de nombreuses approches méthodologiques qui incluent des critères de durabilité (Srinivasan and Nhan, 2008)(Banimostafa et al., 2012)(Serna et al., 2016), mais il existe des possibilités d'amélioration en 1) incluant des indicateurs de durabilité liés à l'utilisation des produits et à la santé des clients 2)

appliquant des méthodes d'analyse multicritères pour intégrer des évaluations individuelles à un indicateur global avec l'aide de spécialistes.

Les objectifs

Les objectifs de cette recherche sont :

Objectif principal

Proposer une approche méthodologique pour guider le processus de prise de décision pendant les premières étapes de conception des produits chimiques de type émulsion en tenant compte des besoins des clients et des critères de durabilité

Objectifs spécifiques

1. Choisir une méthode d'analyse des besoins afin de classifier et de traduire les besoins des clients en spécifications de produits chimiques de type émulsion.

2. Identifier les limites générales et les stratégies de solution pour la conception de produits chimiques structurés en mettant l'accent sur les produits de type émulsion.

3. Proposer un outil pour identifier les composés chimiques qui peuvent être utilisés dans la conception de produits chimiques en émulsion.

4. Choisir et appliquer une méthode d'évaluation de la durabilité pour la conception des produits et des procédés applicables aux produits de type émulsion.

5. Proposer un cadre décisionnel pour la sélection d'alternatives de produits en fonction des besoins des clients et des exigences durables.

Méthodologie de recherche

L'élaboration de la présente étude s'articule autour de trois grandes étapes : 1) Recherche documentaire, 2) sélection, adaptation et proposition de méthodes pour la méthodologie de conception et 3) expérimentation. L'objectif est d'élaborer une approche méthodologique fonctionnelle (les produits réels sont développés grâce à la méthodologie), globale (des besoins au produit) et transférable (les concepteurs de produits peuvent comprendre la méthodologie et la réutiliser de façon autonome) pour la conception de produits chimiques.

RÉSULTATS

Méthodologie de conception

Sur la base de la proposition de Cussler et Moggridge (2011), mais en considérant la conception du produit et du procédé simultanément (comme le suggèrent plusieurs auteurs) (Eden et al., 2003)(Bernardo and Saraiva, 2005)(Cheng et al., 2009), un flux de travail pour la conception des émulsions cosmétiques est présenté sur la Figure H-1.

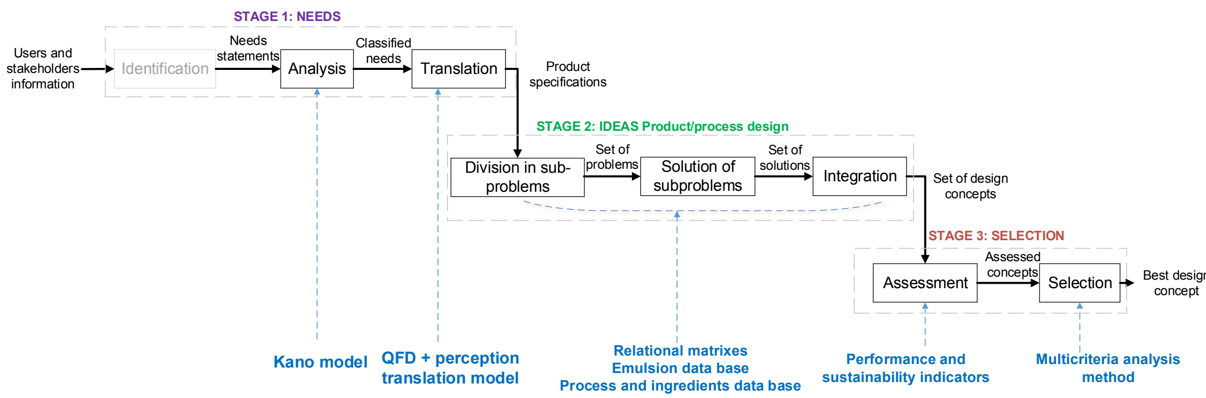

Figure 1: Flux de travail de la méthodologie

Les étapes de la méthodologie sont les suivantes :

Étape 1 - besoins - énoncé du problème : Au cours de cette étape, les besoins des utilisateurs sont analysés en fonction de leur importance relative et traduits en des spécifications du produit. il commence par l'information sur les clients et les parties prenantes, le plus souvent exprimées dans un langage commun, et le résultat correspond aux spécifications du produit, exprimées en termes d'ingénierie. Pour développer cette étape, deux méthodes sont mises en œuvre : le modèle Kano pour l'analyse des besoins et la matrice QFD (Quality Functional Deployment) pour la traduction des besoins. Ces méthodes nécessitent la collecte d'informations auprès d'experts et de clients.

Étape 2 - idées - conception du produit et du processus : C'est à cette étape que les concepts de produits répondant aux spécifications sont générés. En raison de la complexité des systèmes d'émulsion, il est suggéré d'effectuer cette étape en suivant trois sous-étapes: 1) Les spécifications des produits sont classées en sous-problèmes de conception à l'aide d'une liste de sous-problèmes généraux prédéfinis. 2) Les sous-problèmes sont reliés à une liste prédéfinie de stratégies de solution en utilisant une première matrice relationnelle proposée dans ce travail. Les stratégies de solution sont des voies de solution générales liées à la structure et aux fonctions de l'émulsion. 3) Les stratégies de solution sont liées aux ingrédients et aux conditions de transformation, en utilisant une deuxième matrice relationnelle. Le résultat de ce processus consiste en des concepts de produits, c'est-à-dire, des ensembles d'ingrédients et des conditions de processus qui répondent aux spécifications de conception. Pour développer cette étape, une liste de sous-problèmes généraux, une liste de stratégies de solutions, une base de données d'ingrédients et deux matrices relationnelles reliant les éléments mentionnés sont proposées.

Étape 3 - sélection : Au cours de cette étape, les concepts de conception générés sont évalués et classés en fonction des spécifications du produit définies à l'étape 1 et d'un ensemble d'indicateurs de durabilité. Pour réaliser cette étape, un cadre de sélection est proposé. Il comprend une liste d'indicateurs de durabilité et une méthode de décision multicritères pour intégrer l'évaluation.

L'étude de cas

L'étude de cas est la conception d'une crème hydratante pour le visage contenant de l'huile de calendula comme antioxydant naturel. Cet exemple est né de la nécessité du projet entrepreneurial "Xiu Aguee - Aceites esenciales" de donner une valeur ajoutée à ses produits. Xiu Aguee est une entreprise colombienne qui produit des huiles essentielles et des hydrosols (eau d'huiles essentielles) par distillation à la vapeur pour usage cosmétique et aromathérapie depuis 2015.

Dans le but de produire des produits cosmétiques plus élaborés et de bénéficier de l'excédent de production d'huile de calendula, la conception d'une crème hydratante visage à base d'huile de calendula est proposée.

Le secteur de clientèle cible comprend les femmes de 20 à 29 ans

Résultats de l'Etape 1 - besoins

L'étape des besoins commence par l'identification des besoins du client, qui sont décrits en termes non techniques, et se termine par les spécifications du produit. Pour cette transformation, trois sous-étapes et deux méthodes sont utilisées : Tout d'abord, les besoins des clients sont analysés à l'aide du modèle Kano, une méthode basée sur les réponses des clients à un questionnaire, qui classe les besoins en quatre catégories : besoins unidimensionnels (objectifs d'optimisation du problème de conception), besoins essentiels (contraintes du problème de conception), besoins attractifs (besoins facultatifs à inclure dans le problème de conception) et besoins indifférents (besoin à exclure du problème de conception). Deuxièmement, sur la base de la structure d'information de QFD, les besoins sont transformés en spécifications de produits en demandant aux experts d'évaluer la relation entre les besoins analysés et les spécifications de produits. Troisièmement, des valeurs cibles sont attribuées aux spécifications des produits sur la base d'une consultation des clients. La figure H-2 montre la connexion des informations.

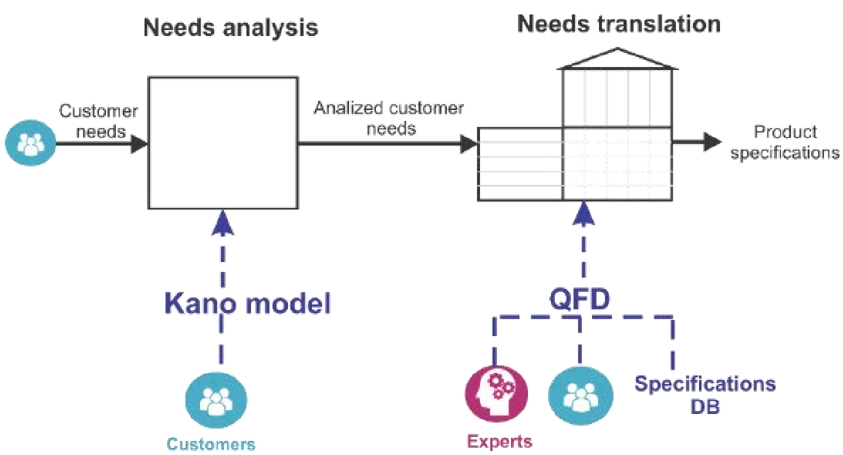

Figure 2: Connexion de l'information - Étape des besoins

L'étude de cas met en évidence le rôle important joué par les experts et les clients pour analyser et traduire les besoins des clients. La communication avec les clients est facilitée par l'utilisation d'échantillons de produits, un outil flexible qui permet leur participation active au processus de conception et une meilleure compréhension de leurs besoins. Grâce à ces échantillons, il a été établi que les clients cibles veulent une crème légère. De plus, les experts ont une grande connaissance non seulement des procédures techniques, mais aussi des clients et de leurs besoins. La formalisation de ces connaissances est un impératif qui peut être atteint par la consultation d'experts et l'analyse des données.

Résultats de l'Etape 2 - Conception du produit

Dans l'etape de conception du produit, le travail des concepteurs consiste à concevoir des prototypes de produits répondant aux spécifications définies lors de l'étape précédente. Ce n'est pas une tâche simple, car les émulsions sont des systèmes complexes dont les composants, les structures, les phénomènes et les processus sont étroitement liés. Par conséquent, toute décision de conception doit être prise en tenant compte de ses effets multiples sur les propriétés du produit final.

Pour surmonter cette difficulté, cette étude propose une méthodologie qui prend en compte la nature multivariable du problème, permettant aux concepteurs de produits d'explorer systématiquement l'espace de solution et de créer des options de conception possibles. Le flux de travail méthodologique comprend les trois sous-étapes suivantes et utilise deux bases de données matricielles, comme le montre la figure H-3 :

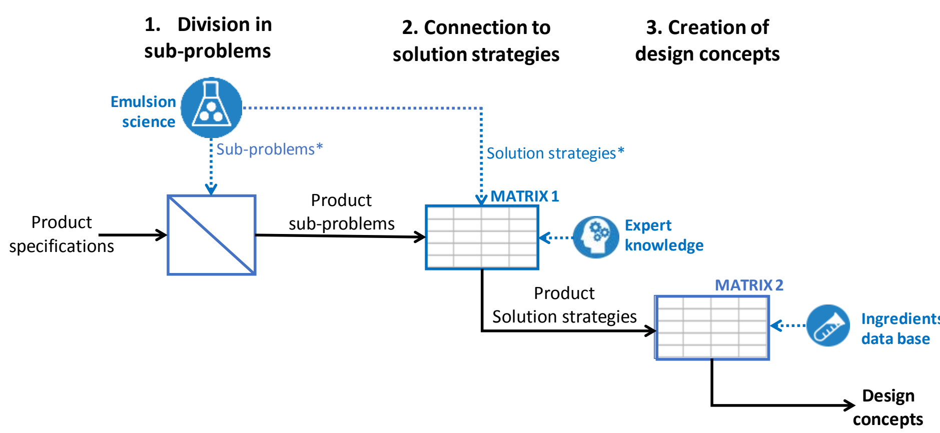

Figure 3. Flux de travail à l'étape de la conception du produit

- Dans un premier temps, les spécifications des produits sont classées en fonction d'une liste de 21 sous-problèmes généraux, qui ont été prédéfinis en fonction des principes de la science des émulsions. Les sous-problèmes sont des phénomènes ou des interactions. Il s'agit par exemple de la viscosité de l'émulsion, du comportement de viscoélasticité de l'émulsion et de la stabilité de l'émulsion, entre autres.

- Dans la deuxième sous-étape, les sous-problèmes sont reliés à une liste de 34 stratégies générales de solution. Les stratégies de solution sont des chemins de solution généraux prédéfinis basés sur les principes de la science de l'émulsion et liés à la structure et à la nature de l'émulsion, mais non directement liés à un composé ou à une technologie de traitement spécifique. Exemples : l'utilisation d'un type de système émulsifiant, l'augmentation/diminution de la taille des gouttelettes ou des particules, la modification du pH de l'émulsion, etc. La connexion entre les sous-problèmes et les stratégies de solution est possible grâce à une première matrice relationnelle qui a été préremplie avec l'aide d'experts en science de l'émulsion. Chaque stratégie de solution est un élément constitutif du concept de produit. De cette façon, le concepteur peut définir des ensembles de stratégies de solutions compatibles pour un problème de conception de produit spécifique, en identifiant leurs interrelations, leurs compromis et leurs synergies.

- Dans la troisième sous-étape, les stratégies de solutions sont liées aux ingrédients et aux conditions de transformation grâce à une deuxième matrice relationnelle. Cette matrice relie les stratégies de solution à une base de données de composés et de conditions de traitement afin de créer des concepts de conception possibles.

Résultats de l'Etape 3 - Analyse de durabilité

La présente étude propose un cadre fondé sur une analyse multicritères pour évaluer différentes alternatives de produits selon des critères de durabilité. Le cadre comporte trois sous-étapes : (1) l'identification et la caractérisation des solutions, (2) l'évaluation des solutions au moyen d'indicateurs de durabilité et (3) l'intégration des évaluations avec un index global par une méthode d'analyse décisionnelle multicritères (MCDA) (figure H-4).

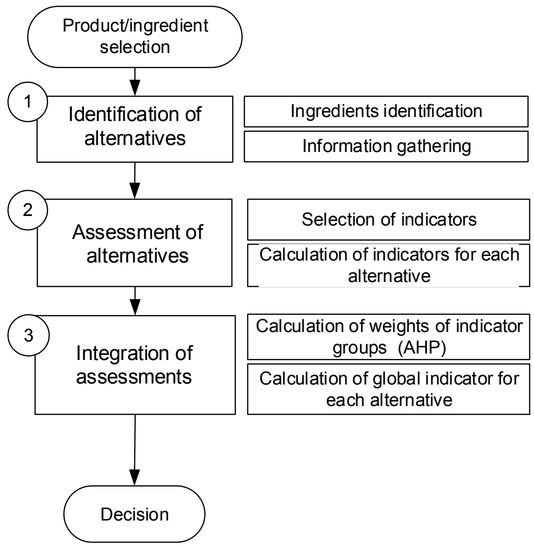

Figure 4 : Cadre de sélection des ingrédients/produits tenant compte des critères de durabilité

Pour la étape de sélection, il est proposé d'utiliser des indicateurs de durabilité pour évaluer les alternatives de produits et des méthodes d'analyse multicritères pour les intégrer. Les indicateurs ont été calculés sur la base des énoncés H du Système général harmonisé de classification et d'étiquetage des produits chimiques (SGH), car leur signification est acceptée dans le monde entier et les énoncés H sont disponibles pour presque tous les produits chimiques commerciaux. La méthode d'analyse multicritères AHP a été utilisée pour intégrer l'évaluation en raison de sa grande flexibilité dans l'analyse de problèmes complexes.

En ce qui concerne l'étude de cas, l'approche a été appliquée à 6 prototypes. Il a été constaté que l'option la plus durable est celle qui contient des esters de saccharose comme émulsifiant, car elle est biobased, suivie de près par l'option préparée avec l'ester de sorbitane et le polysorbate. La pire solution était celle qui utilisait de l'acide stéarique.

De plus, les ingrédients utilisés dans les différentes formulations sont relativement sûrs. Ceux qui ont plus d'avertissements sont les conservateurs.

Conclusions

Par rapport à l'hypothèse de cette étude, il a été possible d'aborder systématiquement la conception de produits chimiques de type émulsion par la mise en œuvre d'une approche multivariée. Une telle approche comprend trois étapes de conception : les besoins, la conception du produit, la sélection. Elle a été appliquée avec succès à un cas d'étude de conception.

De plus, cette étude a exploré certains aspects de l'innovation en donnant aux concepteurs des outils qui leur permettent d'introduire de la nouveauté.

Bien que le flux de travail ait été présenté dans un certain ordre, les concepteurs peuvent réorganiser les étapes de conception en fonction de leur problème spécifique.

De plus, la première matrice relationnelle et la base de données présentées ici peuvent être enrichies avec plus d'ingrédients et de phénomènes, chaque fois qu'un concepteur introduit un nouveau scénario de conception qui a besoin d'aborder de nouvelles informations.

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Introduction

This research proposes a methodological approach to guide the decision making process for the design of emulsion based chemical products by considering elements from innovation engineering and emulsion science. It is presented within the field of Chemical Product Design, which is looking for a systematic methodology for the design and development of chemical products. This research focuses on emulsion based chemical products, which belong to the category of micro-structured chemical products and it is applicable for the design of cosmetic products. However, the concepts developed here can be extended to a broad range of commercial applications.

The key factor for the design of micro-structured chemical products is not to produce large quantities of certain chemical compounds with a certain purity, but to develop products with properties that meet customers and other stakeholders needs (Costa et al. 2006). Despite the importance of these products, the trial and error method and random experimentation continue to be the main forms of addressing their design (Mattei et al. 2014). Companies with large experience in the market have developed their own methods for product design based on their know-how and staff experience. However, this type of knowledge, is difficult to develop, transmit and maintain over time (Chandrasegaran et al. 2013).

The lack of a systematic methodology is a major problem, because nowadays product designers are facing several challenges such as the market pressure for the development of new products in less time and spending less resources, and the social concern on safety and sustainable products. Considering this situation, a systematic methodology for chemical product design based not only on experience but also on scientific knowledge is needed. It can potentially reduce the time required for product development and foster the design of reliable products based on customer needs and sustainable principles.

Although Chemical Product Design is a relative new research field, there are many advances regarding this subject. For example, Bernardo and Saraiva (2004, 2005,) presented a product/process integrated design methodology, which was applied to a cosmetic design problem. Cussler and Moggridge (2011), and separately, Hill (2009), proposed a workflow for chemical product design. Gani et al. developed methods based on Computer Aided Molecular Design (CAMD) and property prediction by group contribution (GC) for product-process design applicable to liquid homogeneous mixtures (Conte et al., 2011a) (Conte et al., 2011b), and recently extended to emulsions (Mattei et al., 2013)(Mattei et al., 2014). Additionally, researches are also integrating methods and tools from fields out of the chemical engineering background such as management, experimental design and statistics into a chemical product design methodology.

Despite the multiple proposals, there is still not a robust methodology for chemical product design. Different approaches define similar design stages, but these stages cannot be applied sequentially in all cases. Specifically in the case of micro-structured products (such as emulsions and colloidal products), it is difficult to establish a workflow because of the intrinsic complexity of the system to be designed. Micro-structured chemical products are formed by multiple components interacting in different scales (Cisternas 2006); (Charpentier 2009). They have to be designed in a manner that guarantees its technical feasibility, the satisfaction of customer needs and the fulfillment of sustainability requirements (Charpentier 2009). The achievement of such a design is not straightforward, because components, structures, phenomena and processes that constitute the product are highly interrelated. Therefore, design decisions have to be taken considering this complex scenario.

This thesis aims to contribute to the field of Chemical Product Design by proposing a methodology for emulsion based chemical products with emphasis on cosmetic emulsions. Emulsion is a good example of a micro-structured chemical product because it involves the same challenges presented by the general case. It is a complex system in which ingredients, phases, structures and processes are highly interrelated. Its design requires a methodology that enable to make decisions that affect the entire system. An advantage of emulsion over other colloidal systems or solids is that there is a very well-developed theory of emulsion science and they are relatively ease to manage experimentally in comparison to solids or aerosols. The cosmetic application has been selected due to its high potential of giving added value to natural resources and because, as consumer sector, products on this field have to be designed based on customer needs, which constitute an extra challenge and an opportunity for innovation.

The methodology considers the following aspects:

1) The implementation of methods for the analysis and translation of needs into specifications in order to integrate customer needs from the beginning of the design process.
2) The implementation of a method that supports the decision making process during the design of emulsion systems and overcomes its intrinsic complexity.
3) The integration of sustainability principles for the design of emulsion products based on assessment by indicators and multi-criteria analysis methods.

This document is divided in six chapters:

Chapter 1 presents the context, objectives, investigation problem and methodology for the doctoral research. Chapter 2 introduces a theoretical framework, containing general concepts about the topic Chemical Product Design and a short review of the approaches developed until now. At the end of this chapter, an overview of our methodology is presented. The methodology comprises three design stages: needs, ideas generation and product selection, which are presented in chapters 3, 4, 5, respectively.

Chapter 3 explains the needs analysis stage and two methods selected and implemented for need description and interpretation: Kano model and Quality Functional Deployment (QFD). The first classifies needs and identifies those that are more important for customer satisfaction. It is implemented as suggested by Rejeb et al. (2008). QFD enables the translation of needs into product specifications. For its implementation experts and users are consulted.

Chapter 4 explains the ideas generation stage and a decision making method to propose emulsion based chemical products. The method enables the division of the design problem according to general sub-problems which are subsequently connected to solution strategies to generate feasible design concepts. General sub-problems and solution strategies are proposed based on emulsion science principles from the literature. The connection between them is done with the aid of experts. Solution strategies are then connected to components and processing conditions with the aid of a data base. This stage is inspired from a methodology for choice intensified equipment presented by Commenge and Falk (2014).

Chapter 5 shows a decision making method to select the most sustainable design concepts. The method uses indicators of the environmental, economic and social dimensions in order to assess alternatives and Multi Criteria Analysis Methods (MCAM) to rank them according to their sustainability.

Chapter 6 contents conclusions and recommendations for further research.

This doctoral thesis is inter-disciplinary because it combines concepts of chemical and industrial engineering to face integrally the problem of chemical product design. It is done under joint supervision by the Superior National School of Systems Engineering and Innovation (Université de Lorraine, in France) and the Department of Chemical and Environmental Engineering (Universidad Nacional de Colombia). It was financed by Colciencias and la Universidad Nacional de Colombia, through the calls “Beca de Doctorado - Doctorados Nacionales – Convocatoria 617” and “Convocatoria del Programa Nacional de Proyectos para el Fortalecimiento de la Investigación, la Creación y la Innovación en Posgrados de la Universidad Nacional de Colombia 2013-2015" respectively.

Results of this study have been presented in four congress:

Poster: Esneider Díaz, Juliana Serna, Paulo César Narváez Rincón, Vincent Boly, Veronique Falk. Evaluación de sostenibilidad en las etapas tempranas del diseño de procesos incorporando métodos de análisis multi-criterio. Congreso Colombiano de Ingeniería Química, Bogotá. 2 – 30 October 2015.

Oral presentation: Juliana Serna, Paulo César Narváez Rincón, Vincent Boly, Veronique Falk. Decision making process for the design of emulsion products during early design stages considering appearance, rheology and stability. SFGP - Société Française de Génie des Procédés. Nancy. 11 – 13 July 2017

Oral presentation: Juliana Serna, Paulo César Narváez Rincón, Vincent Boly, Veronique Falk. Decision making methodology for the design of emulsion-type chemical products during early design stages. 10th World Congress of Chemical Engineering. Barcelona. 1 – 5 October 2017

Oral presentation: Juliana Serna, Vincent Boly, Paulo César Narváez Rincón, Véronique Falk. Improving knowledge capitalization in product formulation: a cosmetic industry study case. IAMOT – International Association for management of technology. Birmingham 22 – 26 April 2018

And an article was published:

Serna, J., Díaz, E., Narváez, P., Camargo, M., Gálvez, D., Orjuela, Á., 2016. Multi-criteria Decision Analysis for the Selection of Sustainable Chemical Process Routes During Early Design Stages. Chem. Eng. Res. Des. doi:10.1016/j.cherd.2016.07.001

1. Context and research problem statement

Chemical industry is changing rapidly in response to new challenges such as the high competitiveness in the chemical market, the public concern about environmental impacts and the ever changing customer requirements (Charpentier, 2009). In this scenario, many companies are finding new growth opportunities in the development of high added value products as specialty chemicals and consumer chemical products. To seize those opportunities, companies require a systematic product design methodology, enabling them to efficiently generate innovative products and respond to a diversified market.

To contribute to the development of such methodology, this study focuses on three main aspects which constitute its research problem: integration of customer needs within the design process, decision making process adaptable to the complexity of emulsion products and integration of sustainability principles.

This chapter begins showing the context of this study. Then it explains the research problem and finally, it presents the hypothesis, objectives and the general methodology followed during this research.

1.1. Some chemical market trends

From 2006 to 2016, the global chemical market has changed significantly. In just a decade, the European Union lost the leadership of the market and China became the dominant country with higher global sales than the combined sales of USA, Germany and Japan (CEFIC, 2017). The best opportunities of growth are no longer in commodities but in the generation of high added value products (Saraiva and Costa, 2004)(Cussler and Moggridge, 2011). As example, Figure 1-1 shows that from 2006 to 2016 the Europe chemical trade balance (which corresponds to the chemical exports minus the imports) presented an upward trend based on consumer and specialty chemicals rather than on commodities.

Under this very competitive scenario, research, development and innovation are key factors to conquer new markets.

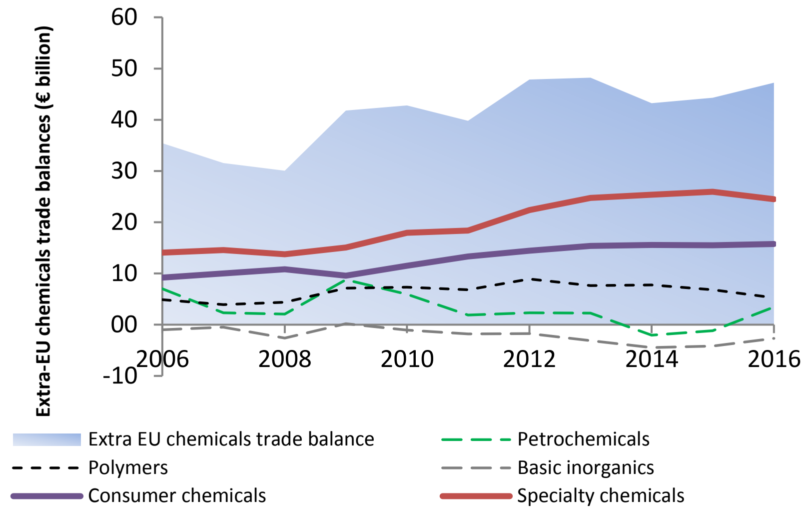

Figure 1-1: European Union Chemical Trade Balance from 2006 to 2016 (CEFIC, 2017)

For its part, the Colombian chemical sector is also facing important changes. Although petroleum derivatives, specially fuels, continue to be the main chemical products with a gross production equivalent to 16.7 % of total Colombian production during 2016 (DANE, 2017), other chemicals, foods and beverages also stand out with a gross production of 7.1%, 5.6% and 5.2%, respectively. Additionally, with the aim to reduce the economic dependence on oil and carbon, there are some perspectives towards a more diversified production as the Productive Transformation Program (Programa de Transformación Productiva, Ministerio de Comercio Industria y Turismo). This program promotes a productive diversification by the enhancement of business lines able to give value to regional and local raw materials under sustainable conditions (Ministerio de Industria y Turismo - Colombia, 2016).

Within this program, a business segment with a high potential growth is the cosmetic and house hold products line. Colombia has an ambitious business plan for this line with the goal to become the leader in the continent with sales of USD 2200 million and exports of USD 783 million by 2032 (Ministerio de Industria y Turismo - Colombia, 2016). This market has presented a growth from 2009 to 2015 of around 40% (Gómez, 2017) and despite a decline in the years 2014, 2015 and 2016, the sector ended 2017 with a growth of 8.4% in relation to 2016 (Portafolio, 2018). Additionally, the cosmetic global market is huge with a value of

205 billion euros in 2016 and presented an average annual growth of 4.1 % from 2009 to 2016 (Loreal, 2016).

Additionally, the cosmetic sector has a high potential in the generation of high added value products based on natural resources, in which Colombia is rich. Colombia is the second country in the world in terms of biodiversity (Ministerio de Comercio Industria Y Turismo - Colombia, 2013), which means it has extensive resources that can be used to create added value products in sustainable ways.

The previous facts show that there are several opportunities in the chemical market, especially in chemical specialties and consumer products, as cosmetics, rather than in commodities. Regarding consumer products and focusing on emulsion type products, which have many applications in the cosmetic sector, there are some challenges that have to be faced to profit from the market opportunities: 1) they are based on customer needs and not on technical well defined industrial requirements. 2) In the case of emulsion products, their design becomes more complex because they depend highly on their micro-structure, defined partly by their composition and partly by the production process. 3) As for any product, they have to be designed under sustainability principles.

Concerning these challenges, the investigation problem is described below.

1.2. Research problem

In recent years, opportunities and challenges for the chemical industry have increased continuously. Opportunities comprise the emerging of new information, methods, technologies and ingredients that can be used for chemical product design (Commenge and Falk, 2014). Challenges include new customer demands and stronger sustainability requirements (Charpentier, 2010) that require a systematic consideration. Thus, on one hand, there are a wide range of resources for chemical product design, and on the other hand, design problems contain diverse requirements and possibilities that must be taken into account. Under this scenario, product designers require methodologies that enable them to assemble previous information flows and aid them to make the best possible design decisions in a systematic and efficient form. This study aims at providing a decision methodology that helps chemical engineers to relate identified needs with a solution space of possible design alternatives. The methodology is applicable for the design of emulsion-type chemical products and it addresses specifically the following problems:

1. Integration of customer needs into a methodology for chemical product design: Customer product value is not directly related to its cost but to its capacity to respond and satisfy customer needs. Moreover, it is even more valuable when it is capable of introducing a novelty appreciated by customers, i.e., when it is innovative.

   Considering this, a main stage for chemical product design in the case of customer products is the analysis of needs and its transformation into product specifications (Kind, 1999)(Bernardo and Saraiva, 2005). This task is not straightforward because customer needs are described in nontechnical terms, they are subjective and, sometimes, they are related to human perceptions or even to feelings and opinions (Cussler et al., 2010).

   This study aims to consider customer needs from the beginning of the design process, by applying the method Kano model for needs analysis and the method Quality Function Deployment for needs translation. In this process, both customers and experts are involved. These methods provide to the designers a procedure to analyze and to transform needs into product specifications.
2. Inherent complexity of structured chemical products: Micro-structured chemical products as emulsions are complex systems formed by multiple elements interacting in multiple scales (Charpentier, 2009). Their final properties depend on their components, composition and structure, with the latter being defined partly by the production processes (Ng et al., 2007). This is the reason why a simultaneous product and process design task was proposed by several researchers (Bernardo and Saraiva, 2005)(Gani et al., 2007), which in turn complicate the design process (Eden et al., 2003)(Cheng et al., 2009). This can be even more difficult during early design stages, because variables and interrelations are ill defined, and it is unclear how one decision can affect the entire design. So, although there are proposed workflows for product design, it does not happened straightforwardly, and many times it is necessary to review early decisions in late design stages (Cisternas, 2006). Moreover, traditionally, micro-structured chemical products have been designed based on experience, in the best case, and by trial and error in many cases (Mattei et al. 2014). The trial and error method requires time and many experiments and the use of significant resources to finally find a good, but not necessarily the best, solution. A design of micro-structured chemical products based on a systematic methodology may bring many advantages: the design process can be faster, reliable,

reproducible, easier to follow and control. In consequence, the resulting products can be positioned in the market in shorter time and they can be developed under sustainable principles.

To address this problem, this study proposes a multi-variate design method applicable to emulsion design, in which, several design variables are considered simultaneously. In this method, first product specifications are divided according to general sub-problems defined based on emulsion science principles. Second, sub-problems are connected to sets of general solution strategies thanks to a relational matrix. Third, components and processes that enable the application of solution strategies are selected. The advantage of this approach is that it enables the identification of possible synergies and the prevention of adverse effects since design variables and resulting product characteristics are considered simultaneously. Similar approaches have been used in the field of Process Intensification (PI) (Commenge and Falk, 2014)(Lakerveld et al., 2010), but they have not been yet implemented in chemical product design.

3. Integration of sustainability criteria in the decision process: "Sustainable development is an approach that strives to satisfy human needs in an economically viable, environmentally benign, and socially beneficial way" (Azapagic, 2014). It is currently a general concern, reflected in legal regulations, industrial practices, scientific fields, and it has increasingly become a factor in customer purchasing behavior. For example in Europe since 2007, the REACH regulation (Registration, Evaluation, Authorization and Restriction of Chemicals) places the responsibility over industries to manage risks from chemicals and to provide safety information on such substances (EC Environment, 2015). Similarly, the United States Environmental Protection Agency (EPA) is working to examine the scope of the chemicals included in the Toxics Release Inventory (TRI) program, providing communities more information on the issue (EPA, 2015). Non-governmental institutions, as the International Organization for Standardization (ISO), have supported this trend, by establishing requirements for environmental management in the ISO14000 standard and for social responsibility in the ISO 26000. In the same direction, an increasing number of high education institutions have incorporated the principles of sustainable development into their curricula, as analyzed by Lozano (2010). Moreover, recently there have been emerging mobile applications influencing consumers for buying

sustainable cosmetics. Examples are Inci Beauty, PharmaPocket, CosmEthics, among others.

Even if the awareness on developing sustainable chemical products and processes has been a hot topic for some years, the industrial sector is still in search for practical tools to conduct systematic sustainability assessments, overall for new products at early design stages, when there is not enough information for a complete sustainable analysis, but decisions have to be made. Consequently, a design methodology including the application of sustainable principles for the generation of new products and processes is considered in this study. There are many methodological approaches that included sustainability criteria (Srinivasan and Nhan, 2008)(Banimostafa et al., 2012)(Serna et al., 2016), but there are possibilities of improvement by 1) including sustainability indicators related to product use and customer health 2) applying multi- criteria analysis methods to integrate individual assessments into a global indicator with the aid of experts.

1.3 Hypothesis

This study proposes the development of a methodological approach for chemical product design based on the next hypothesis:

Emulsion-type products can be designed more systematically and under sustainable principles implementing a methodological approach for decision-making that enables designers to analyze the problem, explore and screen alternatives and focus fast in effective solution strategies. For emulsion-type products this approach includes methods and tools for the analysis of needs, the definition of product specifications and their relationship with general solution strategies proposed according to scientific and expert knowledge. Subsequently, the proposed approach enables the designers to explore and to screen components and processing technologies for the generation of product alternatives. Decision making methods are implemented to consistently select the most promissory (sustainable) alternatives, which can be evaluated experimentally in a further detailed design stage.

1.4 Objectives

Main objective: To propose a methodological approach to guide the decision-making process during early design stages of emulsion-type chemical products considering customer needs and sustainability criteria.

Specific objectives

1. To select a method for need analysis in order to classify and translate customer needs into product specifications for emulsion-type chemical products.
2. To identify general limitations and solution strategies for the design of micro-structured chemical products with focus on emulsions-type products.
3. To propose a screening tool to identify chemical compounds that can be used in the design of emulsion-type chemical products.
4. To select and apply a sustainability assessment method for product and process design applicable to emulsion-type chemical products during early design stages.
5. To propose a decision framework for the selection of product alternatives based on customer needs and sustainable requirements.

1.5 General methodology

The development of this study considers three main steps: 1) Literature research, 2) selection, adaptation and proposal of methods for the design methodology, and 3) experimentation. The aim is to elaborate a functional (real products are developed thanks to the methodology), global (from needs to product) and transferable (product designers may understand the methodology and re-use it autonomously) methodological approach for chemical product design.

1. Literature research: a literature research with the objective of reviewing methods for the design of chemical products is conducted. Based on the workflow proposed by Cussler and Moggridge (2011), but integrating the stages of ideas generation and process design, as suggested by several authors (Eden et al., 2003)(Bernardo and Saraiva, 2005)(Cheng et al., 2009), a product design methodology comprising three design stages is proposed: needs stage, ideas generation stage and product selection stage. For each stage a literature review of methods is done.

- For the needs stage, a review focused on the work developed by the investigation group “Equipe de Recherche des Processus Innovatifs” – ERPI is done. This, because the researches at ERPI have an extensive experience in needs analysis and innovative projects and products.
- For ideas generation, current methods for components screening and selection are reviewed. Emphasis is done for existing design methods for emulsions and mixtures. Additionally, methods used in other disciplines for multivariate systems analysis are also considered.
- For the selection stage, multi-criteria analysis methods and sustainability indicators are reviewed.

2. Selection, adaptation and proposal of methods to develop design stage: Based on the literature research, tools and methods that enable the proposition of a design methodology are defined.
    - For the needs stage, methods that facilitate the analysis of needs and their translation are selected. With this purposed Kano model is used for needs analysis and an adaptation of Quality Functional Deployment for cosmetic products is implemented.
    - For the ideas generation stage, a matrix decision method that enables the simultaneous consideration of multiple design factors affecting multiple emulsion characteristics is proposed. It is developed based on emulsion science principles and expert knowledge.
    - For the selection stage, methods and indicators that enable the assessment of ingredients and product alternatives are selected. Indicators that are possible and easy to calculate at early design stages, i.e., when product ingredients have not been completely defined, are preferred.

3. Experimentation: The methodology is shown through a case study, where the design of a moisturizing cream using the proposed methodology is developed. The case study includes all the design stage from needs analysis until the creation and evaluation of prototypes.

2. Workflow of the design methodology

Nowadays, for the topic chemical product design, researchers are expanding their knowledge regarding the relation between micro-structure, chemical nature and product performance. Special emphasis has been placed in the development of methods based on Computer Aided Molecular Design (CAMD) and property prediction by group contribution (GC), which enable to find molecules that satisfy target properties. Additionally, researches are also integrating methods and tools from fields such as design management and numerical analysis to develop a robust methodology for chemical product design.

This chapter presents a theoretical framework explaining chemical product concepts to establish a common language. Then, some product design topics, including customer needs, product-process design and sustainability, among others, are presented, highlighting the way existing approaches have addressed them. Subsequently, available tools and methods for chemical product design are presented. Finally, the workflow and information connection between design stages of the methodology proposed in this work is explained.

2.1 Theoretical framework: Chemical product and related concepts

2.1.1 Chemical products

"A Chemical product is defined as a system made up by different chemical substances, which is manufactured for one or more purposes" (Cisternas, 2006). Its characteristics are determined through multiple scales, thus, it is necessary to use a multi-scale approach for its design (Charpentier, 2009). Product functional properties are determined at the nano- and micro- scales (Kind, 1999), the production process is defined at the meso- and macro-scales (Costa et al., 2006), and product interactions with the users and the environment occur at the mega- scale (Cisternas, 2006). The multi-scale nature of chemical products is schematically showed in Figure 2-1.

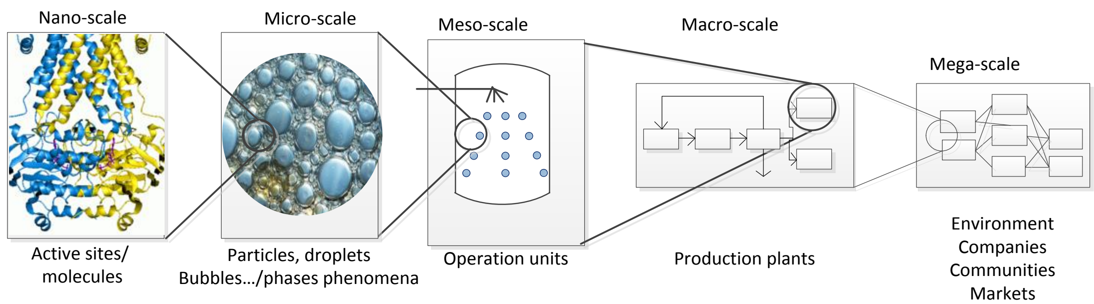

Figure 2-1: Scheme of chemical product in different scales - adapted from (Costa et al., 2006) and (Kind, 1999)

2.1.2 Chemical products classification systems

Cussler and Moggridge classified chemical products according to their key design aspect (2011). They found four categories: commodities, molecular products, micro-structured products and devices. Commodities are traded in the global chemical market at relative low prices and large quantities (both in comparison to specialties). The key aspect in their design is the production process. Examples of commodities are petrochemicals. Molecular products are chemicals with a special function that determines their value. The key aspect in their design is the identification of their activity or function. Examples of them are surfactants and pharmaceutical molecules. Micro-structured chemical products are those whose specific micro-structure performs a desired function. The key aspect in their design is the relation of its micro-structure with their functions. For example, a cosmetic emulsion with a determinant droplet size and droplet size distribution, has a consistency that may be pleasant to touch. Devices are hand size products that perform a desired physicochemical process. The key design aspect is the process scale-down. An example is a water purification system. As it is shown in Figure 2-2, different chemical products have different critical sizes.

Costa et al. (2006) added three more categories to the first classification: bio-based concepts regarding bioengineering technologies as biomaterials and tissues; virtual chemical products as for example chemical engineering software; and technology based consumer goods referring to devices with a chemical function as for example post-it notes.

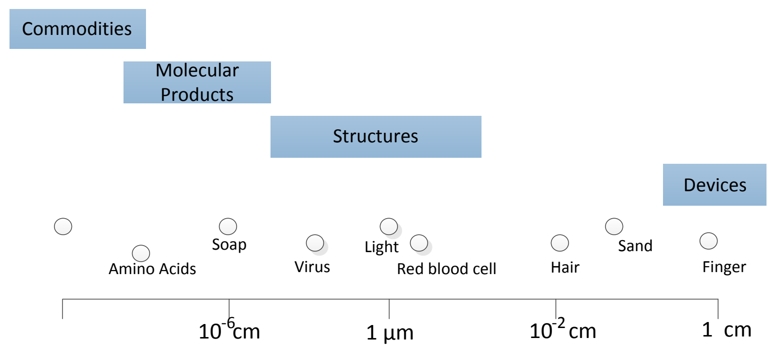

Figure 2-2: Classification of products according to key scale for their design, from (Cussler and Moggridge, 2011)

Chemical products are also classified according to raw materials and type of customer (Seider et al., 2009). In this approach chemical products can be basic chemicals, which are produced from natural resources and sold to industries; industrial products, which are generated from basic chemicals and are also sold to industries; and consumer chemical products, which are produced from the previous two and are normally sold directly to the final consumer. Product specifications for the first two types are technically well defined, while for the last type, they are not easy to define and depend on the final consumer needs.

Another approach is provided by Wibowo and Ng (2002), who defined chemical-based customer product as “a mixture of one or more key ingredients responsible for its functionality (active ingredients), and some supporting ingredients for enhancing its performance”. In this approach, a chemical product is classified according to its physical form, also called delivery system, as shown in Table 2-1. The advantage of this classification is that it enables the comparison of products from different sectors and the transfer of knowledge from one sector to another. For example, the properties and production processes of two solid products, such as powder detergent and eye shadow are described by similar variables, even if product applications are different (Falk, 2009).

All the classification systems previously presented are complementary. The classification of Cussler and Moggridge (2011) connects the product with the key design stage(s) and the key design variable(s). The classification of Seider et al. (2009) relates the product with resources and type of market, while Wibowo and Ng (2002) classification relates the product with its form, usage properties and process variables. Similarly, other classifications are possible.

Classification can be used to facilitate the design process. It can give a form to the solution space, working as a guide for the design process and enabling the retrieval of a solution. This process may be more difficult when there is not a structure for the comprehension solution space.

Table 2-1: Classification of chemical product according with physical form, taken from (Wibowo and Ng, 2002)

Physical Form		**Product form/ Delivery system**	**Examples**		
			Cosmetics and personal care	**Health care and pharmaceuticals**	**Household and office supplies**
Solid	Shaped	Composites	Bar soap, lipstick	Inhalant stick	Compact disk, glue stick
		Capsules	-	Whale oil capsule	Microencapsulated carbonless paper
		Tablets	-	Aspirin tablet	Moth balls
		Solid foams	-	-	Styrofoam
	Bulk	Powders and granules	Facial powder, baby powder, diaper absorbent	Powdered herbal medicine	Powdered detergent, dry toner
Semi- solid		Pastes	Toothpaste	Pain relief ointment	Silicone sealant metal adhesive
		Creams	Cleansing cream, hair cream	Pharmaceutical cream	Multipurpose adhesive
Liquid		Liquid foams	Shaving foam	-	-
		Macromolecular solutions	Mouth wash, shampoo	-	Dish washing cleaning
		Micro- emulsion	Skin cleanser, Hair conditioner	Hydrocortisone, cyclosporine	-
		Dilute emulsions and suspensions	Suntan lotion, nail polish	Penicillin	Correction fluid, Writing ink
		Solutions	Perfume	Eye drop, ginseng extract	Drain cleaning solution
Gas		Aerosols	Hair spray	Sore throat spray	Aerosol paint, antifreeze spray

2.1.3 Micro-structured chemical products

This study is focused on a specific type of micro-structured chemical product: emulsions, giving special emphasis to their application in the cosmetic sector. This sector was selected because of its high potential for the creation of high added value products using natural resources and because it enables a complete exploration of the research problem of this doctoral thesis:

1) Cosmetic emulsions are consumer products and they must be designed based on customer needs. These needs can be implicit, explicit, technical and subjective (Cussler et

al., 2010). A special characteristic of cosmetics design is that needs related to aspects as appearance and sensations are fundamental for product success and they are difficult to identify and translate due to their subjective nature (Pensé-Lhéritier, 2016). Such characteristic constitutes a challenging research subject.

2) Cosmetic emulsions, as any emulsion, are examples of micro-structured chemical products, whose design addresses the typical difficulties of the general case. Emulsion design comprises the selection of ingredients and the design of the production process, which together define emulsion structure, interactions, characteristics and functions (Charpentier, 2009)(Cisternas, 2006). Consequently, decisions made for their design are interrelated, affect more than one emulsion characteristic and have to be made simultaneously (Bernardo and Saraiva, 2005). A method to deal with the intrinsic complexity of emulsions is needed. The advantage of selecting emulsions as a study subject is that there is a very well-developed theory of emulsion science and they are relatively ease to manage experimentally in comparison to solids or aerosols.

3) Cosmetic emulsion based chemical products, as all chemical products, must be designed based on sustainability principles. As consequence, during product design it is necessary to apply a practical method to assess alternatives. The challenge is to select an assessment system that enable the consideration of both product and process for the selection of the most sustainable design concept.

2.2 Methodologies for chemical product design

Chemical product design is a "methodical procedure which integrates methods and tools in order to define the characteristics of the product that best meet customer needs" (Costa et al., 2006). It is systematic, because it is based on scientific knowledge and engineering practices (Costa et al., 2006). It is interdisciplinary, because it integrates concepts from engineering, biology, marketing, industrial design, psychology, among others knowledge areas (Bröckel et al., 2013). It is multi-scale (Charpentier, 2009) and it is not sequential but iterative (Cisternas, 2006).

Cussler and Moggridge proposed a generic methodology for chemical product design (2001, 2011), based on the procedure for mechanical product design proposed by Ulrich and Eppinger (2004). They divided chemical product design process in four stages as presented in Figure 2-3: (1) needs identification, (2) generation of product ideas, (3) selection of the more promising idea, (4) process design. Some aspects of stages are summarized in Table 2-2.

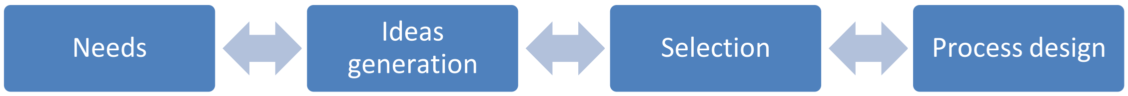

Figure 2-3: Product design workflow (Cussler and Moggridge, 2011)

Table 2-2: Aspects of the design stages proposed by Cussler and Moggridge (Cussler and Moggridge, 2011)

Design stage	Tools and methods	Contributions	Opportunities to improve
Needs: The objective is to identify and translate customer needs into product specifications	- Market research techniques are used for customer and needs identification. - Once identified, needs are analyzed and ranked with the participation of the design team. - Chemical engineering principles are used to understand needs and principles of design solutions. - Statistical methods are suggested to relate consumer attributes and instrumental measurements - Benchmarking to define target values.	This approach aims to be holistic by considering all design stages. It gives methods for customer needs identification, ideas generation, product selection and process design. The description of all design steps is done with examples and case studies. It is remarkable the depth discussion about needs and their importance in the whole product design process.	Translation of needs in to properties is not completely explained. In a later article Cussler outlined that more knowledge of perception is required to be able to translate customer needs properly (Cussler et al., 2010).
Ideas generation: In this stage product ideas are generated and screened	- Human ideas (from researches, designers, experts, leading users) as a source for possible product ideas. - Chemical ideas: Natural-product screening and combinatorial chemistry. - Screening is done using the concept of screening matrix, which considers selection criteria and weights given by designers or experts	Two methods to find chemical products ideas are presented. Additionally, methods for ideas screening are presented.	Described methods are applicable mainly for the discovery phase. Screening methods such as reverse design and selection methods are not completely developed here.
Selection Best product ideas are chosen according to design criteria.	- Technical and subjective criteria are considered. - Selection matrix is used for the selection	Criteria and methods for product selection are implemented and presented through examples	For the selection step general guidelines are given. This topic can be complemented by including multi-criteria decision analysis methods (MCDA). Criteria for product selection in sustainability terms are not defined.
Process design: Final specifications are set, and economic aspects are analyzed before process is designed.	- Experiments and prototyping are used to set final specifications. - For the economic analysis the life cycle of the product is analyzed.	Information about patents and procedures to elaborate a business plan is presented. The importance of a financial study is highlighted	The relation between product structure and processes is described with examples but not systematically. Mixture and micro-structured product properties are not completely addressed.

Similar workflows with equivalent stages, were proposed by other authors (Conte et al., 2011)(Gani, 2004)(Hill, 2009)(Martín and Martínez, 2013)(Mattei et al., 2013)(Wibowo and Ng, 2001). The various approaches differ in their specific focuses and applications. Following, some topics that were highlighted in different approaches and the form they were addressed are presented.

2.2.1 Customer needs

In their methodology, Cussler and Moggridge proposed three steps for customer needs analysis and translation: In the first step, needs from customer and other stakeholders are gathered and identified through interviews and other market investigation techniques. In the second step, needs are interpreted, analyzed and organized. The third step comprises the translation of each need to product properties in order to generate product specification (2011).

The translation step is specially challenging, because customer needs are expressed in common language which is difficult to convert into technical terms (Cussler et al., 2010). To overcome this difficulty, there are approaches that ask customer preferences using product prototypes and, with a suitable experimental design, correlate those preferences with product composition (Smith and Ierapepritou, 2009)(Bagajewicz et al., 2011) or with measurable product properties (Cussler and Moggridge, 2011)(Gilbert et al., 2013). Additionally, some methodologies use the Quality Functional Deployment (QFD) method, translating needs with information from heuristics (Wibowo and Ng, 2001)(Cheng et al., 2009), data bases, literature research (Conte et al., 2011b)(Mattei et al., 2013)(Fung et al., 2016), and expert consultation.

Despite the existing contributions, the number of researches done in the topic customer needs within the field of Chemical Product Design is limited, overall considering the growth potential of the chemical industry in the consumer products market (Cussler et al., 2010). The exploration of customer needs beyond technical aspects has not been deeply studied yet. Most publications focus on other design stages, and do not address the problem of how to generate product specifications. Physical sensations have been translated in some cases by evaluation panelsand instrumental measurements, but feelings and psychological effects of the product on customers have been practically ignored. Much more investigation is needed in this topic, in order to generate a theory of perception enabling a systematic interpretation and translation of needs (Cussler et al., 2010).

2.2.2 Simultaneous chemical product-process design

Bernardo and Saraiva presented an approach for simultaneous chemical product and process design (2005, 2014). In their proposal, the design problem is expressed mathematically using three design functions: a process function, a product function and a quality function. The functions help to write an optimization problem, which includes cost as a criterion. This approach was exemplified with the case of a cosmetic cream, where the process function comprises a relation for droplet size according to homogenization conditions, the property function describes the product viscosity based on ingredients concentration and the quality function defines the sensation of the cream based on its resulting viscosity (Bernardo and Saraiva, 2005). A similar approach for simultaneous product-process design is presented by Fung et al. (2016). In that approach, an optimization problem is written, in which the net present value is maximized subject to constraints represented by six models: process, property, quality, costs, pricing and economic models (Fung et al., 2016). The approach is illustrated with two cases: a die attach adhesive and a hand lotion. In this latter case, the process, property (product) and quality models are similar to those proposed by Bernardo and Saraiva (2005). The economic model calculates net present value based on product costs and price. Product costs comprises capital and operation costs, while product price is defined based on competitors' prices and market size.

Martín and Martínez presented a methodology in which process and product constrains are combined to perform a cost and environmental optimization for a product – process design (2013). The approach was exemplified with the case a powder detergent (Martín and Martínez, 2013). Other examples of publications that highlight the importance of a simultaneous design are: Gani (2004), Hill, (2009), Ng et al. (2006) and Sapuan, (2017). From all these examples, it is possible to infer the advantage of a simultaneous design and the applicability of modelling and computer optimization to face its difficulties. The main disadvantage in this approach is the need of realistic models, properties and data to simulate factual product design problems, which are not always available.

2.2.3 Sustainability

In general, the different methodologies for chemical product design have considered to a greater or lesser extend the inclusion of sustainability principles. As examples, in Conte et al. (2011b) and in Mattei et al. (2013), the criteria of flammability and toxicity in addition to cost, were taken into account to select safe and economic product components. Heintz et al. (2014b) proposed a framework for the substitution of possible toxic ingredients for more sustainable options (Heintz, 2012). In this approach, a computer-aided molecular design technique was implemented, in which molecular patterns that correlate with toxicity are avoided during the construction of molecule candidates. The criteria of lethal dose LC50 and bio- concentration factor (BCF) were considered to assess toxicity and eco-toxicity. In the same direction, a framework integrating computer-aided molecular design and a complete evaluation of occupational health and safety criteria was presented by Ten et al. (2017a). In that proposal, seven indices related to the safety and health characteristics of chemical molecules are selected and implemented for the generation of molecular products. The indices are flammability and explosiveness for safety; viscosity, material phase, volatility and exposure limit for occupational health. They are calculated with group contribution techniques and empirical correlations.

There is an opportunity of improvement of existing assessments by 1) including sustainability indicators related to product use and customer health 2) applying multi- criteria analysis methods to integrate individual assessments, considering indicators importance and interrelations.

2.2.4 Other design aspects

Cosmetic products

Many publications about chemical product design have presented examples in the cosmetic and personal care sectors. The review of these publications is interesting because the application case in this work is also cosmetic. Examples of them are: a cosmetic lotion (Bernardo and Saraiva, 2005)(Wibowo and Ng, 2002)(Bagajewicz et al., 2011), a personal detergent (Mattei et al., 2013), a spray insect repellent lotion (Conte et al., 2011b) (Bagajewicz, 2007), a sunscreen lotion (Conte et al., 2012), a hand lotion, the reformulation of a massage cream, the manufacture of a tooth paste and manufacture of an ophthalmic ointment (Wibowo and Ng, 2001) a laundry detergent, a shampoo (Wibowo and Ng, 2002), a skin care cream (Cheng et al., 2009), and an under eye cream (Smith and Ierapepritou, 2009).

Economic aspects

Cussler and Moggridge pointed out the importance of performing an economic analysis for product design, before the process is conceived (2011). Similarly, Hill presented a workflow of eight stages, in which risk and financial analysis are considered at the end of the product design process (Hill, 2009). In the same line, Bagajewicz presented a business model considering product costs and price (2007). In that approach, product costs are calculated based on raw materials, manufacturing and supply chain costs, and product price is calculated considering customer preferences and market conditions. This model was applied to the design of an insect repellent and later to a moisturizing lotion (Bagajewicz et al., 2011). The framework proposed by Fung et al. (2016), consists of a join of six interconnected models, three of them corresponding to a cost model, a pricing model and an economic model. Cheng et al. (2009) presented an integrative approach for product development, in which the importance of a market study and the role of the engineer in this activity is highlighted.

All these frameworks highlight the importance of the economical sustainability of the product and they provided tools to analyze it during product design. But all of them consider cost as the main economic variable instead of product value, which is a multi-criteria parameter that integrates financial, marketing, reputational, sustainable and strategic criteria (Marche et al., 2017). This concept can explain better why some products are more preferred by customers than others apparently similar and why the inclusion of an innovative characteristic, even if it increases product costs, may be a good idea as far as it is highly appreciated by customers. For example, in cosmetics there is an increasing trend for more sustainable products, reason why the inclusion of this characteristic, even though it generates more costs, generates a product with more value.

Decision making process and information management

Various authors stand out the aspects of project management and decision-making process within their methodology for chemical product design. Heintz et al. presented a framework for decision making for the design of sustainable chemical products within an enterprise structure (2014a). Their model comprises three stages: the intelligent phase, the design phase and the choice phase. In the intelligent phase, the enterprise organization is modeled in four layers where different stakeholders are located according to their decision level. The information and knowledge are managed using standard semantics and standard documentation, which enables information sharing between the different actors. The result of this phase are the product requirements based on stakeholders needs. By their part, Smith and Ierapepritou presented a decision approach to guide decision making for chemical product design considering product portfolio management considerations (2011). The relation between both domains (product design and management portfolio) are simulated with a relational matrix.

Seider et al. (2009) and similarly Cussler and Moggridge (2011), proposed the use of the State-Gate process to guide the design and development of chemical products. In this process, at the end of each stage, stakeholders evaluate the product in order to reduce project risk (Seider et al., 2009). By their part, Cheng et al. proposed the application of two methods for project and information management (2009). The methods are the Objective-Time Chart that helps to decompose the project into objectives and sub-objectives in a timeline, and the RAT2IO that helps to specify activities, resources, outputs and inputs to achieve each project objective. With this information it is possible to perform an optimization in which both activities and trade-offs can be decided with a global vision (Smith and Ierapepritou, 2011).

2.3 Tools and solution approaches for chemical product design

Methods and tools applicable to the stage of ideas generation are presented below, while methods for needs analysis and product selection are treated in chapters 3 and 5, respectively. Ideas or product concepts are defined in this work as the set of ingredients that combined in certain proportions and certain process conditions generate a product that responds to customer needs. In this section, ideas generation methods of the type computer-aided product design (CAPD) are highlighted, because they have probed their effectiveness in reverse engineering frameworks (to go from properties to molecules) and there is much data and information represented in the form of molecular patterns or group contribution models, typically used in CAPD approaches.

Ideas generation by people

For product ideas generation it is recommended to cover as many alternatives as possible by a broad exploration of the solution space. With this purpose, Cussler and Moggridge highlighted the role of the members of the design team, the customer and the consultants in proposing possible product alternatives (2011). To foster ideas sharing between individuals, it is possible to use techniques as brainstorming.

This approach makes a broad exploration for ensuring that good ideas are not left aside. It considers the interdisciplinary nature of chemical product design and makes possible the contribution of individuals with different backgrounds. It generates creative and innovative product ideas, which are fundamental for the creation of added value. Its main disadvantage is that it depends heavily on the expertise and experience of the design team.

Some heuristics have been proposed to drive ideation. TRIZ (Theory of The Resolution of Invention-Related Tasks), among others, propose the application of the so-called "laws of product evolution" in order to guide the reasoning modes of designers. As an example, this method have been used to solve green supply chain problems (Moussa et al., 2017).

Natural inspiration products and combinatory chemistry

Regarding to the chemical source of ideas, Cussler and Moggridge (2011) suggested two methods: natural-product screening and combinatorial chemistry. The first, also called bio-mimetics, draws inspiration in the active chemical ingredients present in nature (Chen and Hung, 2017). The second combines ingredients or fragments of molecules robotically in all possible combinations and tests their activity. These methods are useful to investigate and discover new active molecules, but they are difficult to implement, demand high resources and are not always effective.

Ideas generation and screening by CAPD

To perform a systematic exploration of possible chemical products, methods based on computer- aided product design (CAPD) can be applied. These methods, also called reverse design techniques, create thousands of alternatives computationally and screen them systematically in order to find those that match the desired product properties (Conte et al., 2011b). The origin of these techniques can be found in computer aided molecular design

(CAMD), approach in which “problems are defined as, given a set of building blocks and a specified set of target properties; determine the molecule or molecular structure that matches these properties” (Gani, 2007). Their main steps are (Gani, 2007):

1) Target properties and values are defined according to the design problem requirements.

2) Molecule candidates are generated. Alternatives can be formed by a combinatory of functional groups or they can be identified from data bases. The creation of alternatives with functional groups as building blocks has been done efficiently in the case of relative simple molecules with specific functions such as solvents and polymers (Brignole et al., 1986) (Joback and Stephanopoulos, 1995). The construction of complex molecules is difficult because the number of combinations increases exponentially. In those cases data bases can be used to delimitate alternatives as done in a study about surfactants (Mattei et al., 2014) and the design of a paint and an insects repellent lotion (Conte et al., 2011b).

3) Properties of generated molecules are calculated using estimation techniques and they are compared with target properties. The candidates with properties closer to target values are selected for further analysis. For properties estimation, there are various possible methods:

- Group contribution, which relates fragments of molecules to a certain amount of the value of a property (Joback and Stephanopoulos, 1995). It is used frequently due to its relative simplicity and its applicability has been expanded to cover a large group of product properties, including some that are specific for surfactant such as cloud point and critical micelle concentration (Mattei et al., 2013).
- Quantitative structure activity relationship (QSAR) and Quantitative structure property relationship (QSPR), which are regression models that relates molecular structure to an specific biologic activity or property as for example toxicity or krafft temperature (Joback and Stephanopoulos, 1995), (Mattei et al., 2013).
- Data bases, empirical and semi-empirical equations.

4) Properties of selected molecules are verified with accurate methods or experiments.

Techniques of CAMD have been extended to cover mixture properties by considering also the composition as an optimizing variable. This approach is relatively easy to implement in the case of properties with linear mixing rules, but they require a lot of computational capacity in other cases (Heintz et al., 2014b). To simplify the search some approaches divide the screening step in sub-steps. At first, an initial screening is done adopting a linear mixing for all mixture properties and in a subsequent step properties of candidates are verified with accurate mixing models (Yunus et al., 2014)(Fung et al., 2016).

In the case of emulsion properties, most approaches check them at the end of the design process. For example, in the workflow proposed by Mattei et al. (2013) emulsion stability is checked at the end of the conceptual design, before the experimental stage is performed.

In general, CAPD methods are systematic and enable a very exhaustive search. However, it depends on the existence of prediction models. Moreover, with this approach it is difficult to conduct an exploration of micro-structured products as emulsions, because many of their properties are generated by the product as a whole. Although there are modeling frameworks for product/process design (Bernardo and Saraiva, 2005)(Morales-Rodríguez and Gani, 2007, 2009), the high complexity of the models and the amount of required information makes difficult their implementation in real cases.

Ideas generation and screening by data base search

When target properties are more sophisticated, it is difficult to relate them to a molecular structure. It happens for example with sweetness. There is not a known relation between sugar structure and its ability to sweeten (Wei, 2007). However, sugar is used to sweeten because it is known that this molecule can produce the desired function. In these cases molecules are not created with CAMD techniques, but are searched in specialized data bases. This is reflected in the works done by Conte et al. (2011b) and Mattei et al. (2014), where a knowledge base is used for the selection of active ingredients.

Other approaches for ideas generation and screening

Instead of evaluating the properties of all possible compounds when reviewing if they match product specifications, Heintz (2012) suggested the use of meta-heuristic methods, like Tabu search or genetic algorithm to look faster for a group of good solutions. In this approach it is not necessary to calculate properties of all possible components. Based on the performance of a population, new possibilities are proposed and evaluated until a good group of possibilities within a tolerance of performance is found. This method uses some of previous presented methods for estimation of properties. It was applied in a methodology for chemical product substitution (Heintz et al., 2014a).

In the field of material science, there are also suitable approaches for ideas generation and ideas screening. In Ashby and Johnson (2010) an information structure to organize a knowledge base of materials and products is proposed. The structure is composed of multiple interconnected data bases, each containing information and data attributes of materials, processes, products, functions and perceptions. The novelty of this proposal is that the information structure is interlinked. It allows a flexible search of materials, products ideas and properties. Additionally, Ashby and Johnson (2010) also proposed the use of charts for visualizing materials selection. These charts enable not only screening and selection, but also information visualization, and material clustering.

An additional methodological approach was given by Johnson and Farr (2008) in their procedure for prediction of reactive chemical hazards. In their work, they classified chemical compounds in 43 functional groups categories, and each category was characterized based on a small group of representative compounds for which the information was available. Representative compounds were selected to cover some variations within the functional group that affects their reactivity such as varying hydrocarbon chain lengths and degrees of branching among others. Compounds with high probed reactivity where preferred for the characterization of the functional group considering that the aim to prevent hazards is the prediction of the worst case. Using representative compounds, they were able to draw general conclusions about the reactivity of functional groups of more than 6000 compounds. This methodology could be extended to cover other behaviors of chemical compounds beyond the reactivity.

These approaches stand out the structure of ideas generation process, which consist in a search for valid product candidates within a huge solution space. The more the designers know the structure of the solution space, the more rapid and effective is their search, which happens when they gain experience. Similarly, as computational tools have more information and use proper methods to search among it, the designers can take better informed decisions.

2.4 Workflow and information structure of the proposed methodology

In the previous section, approaches and methods for chemical product design were presented. Despite the important amount of publications, there are still some limitations that should be overcome to have a robust methodology for chemical product design. This work proposes a methodology that aims to address some of the exposed limitations. It gives tools to the designers to understand and translate customer needs (both technical and subjective) into product specifications and establish the design problem. It enables chemical product designers to explore broadly and systematically the solution space of emulsions to identify possible design options since the beginning of the design process. Finally, it enables the evaluation of possible candidates and the identification of the best alternative implementing a novel sustainability assessment.

The methodology is effective in solving real problems (as it can be seen in the case study elaborated in this work) and it can be transferred to engineers, who can understand the methods and reuse them autonomously.

2.4.1 Workflow of product design methodology

Based on the proposal of Cussler and Moggridge (2011), but considering the design of product and process simultaneously (as suggested by several authors) (Eden et al., 2003)(Bernardo and Saraiva, 2005)(Cheng et al., 2009), a workflow for the design of cosmetic emulsions is presented in Figure 2-4.

The stages of the methodology are:

Stage 1 – needs – problem statement: In this stage user needs are analyzed according to their relative importance and translated into product specifications. The input is information about customers and stakeholders, mostly expressed in common language and the output corresponds to product specifications, expressed in engineering terms. To develop this stage, two methods are implemented: Kano model for need analysis and Quality Functional Deployment (QFD) for needs translations. These methods require information gathered from experts and customers.

Stage 2 – ideas – product and process design: In this stage, concepts of products accomplishing product specifications are generated. Due to the complexity of emulsion systems it is suggested to perform this stage by following three steps: 1) Product specifications are classified into design sub-problems using a list of predefined general sub-problems. 2) Sub-problems are connected to a predefined list of solution strategies using a first relational matrix proposed in this work. Solution strategies are general solution paths related to emulsion structure and functions. 3) Solution strategies are connected with ingredients and processing conditions, using a second relational matrix. The result of this process are design concepts, i.e., sets of compatible ingredients and process conditions that respond to design specifications. To develop this stage a list of general sub-problems, a list of solution strategies, a data base of ingredients and two relational matrixes connecting the previous mentioned elements are proposed in this study.

Stage 3 - selection: In this stage generated design concepts are assessed and ranked according to product specifications defined in stage 1 and a set of sustainability indicators. To perform this stage, a selection framework is proposed. It comprises a list of sustainability indicators that can be used to assess product alternatives at early design stages and a multi-criteria decision method to integrate the assessment.

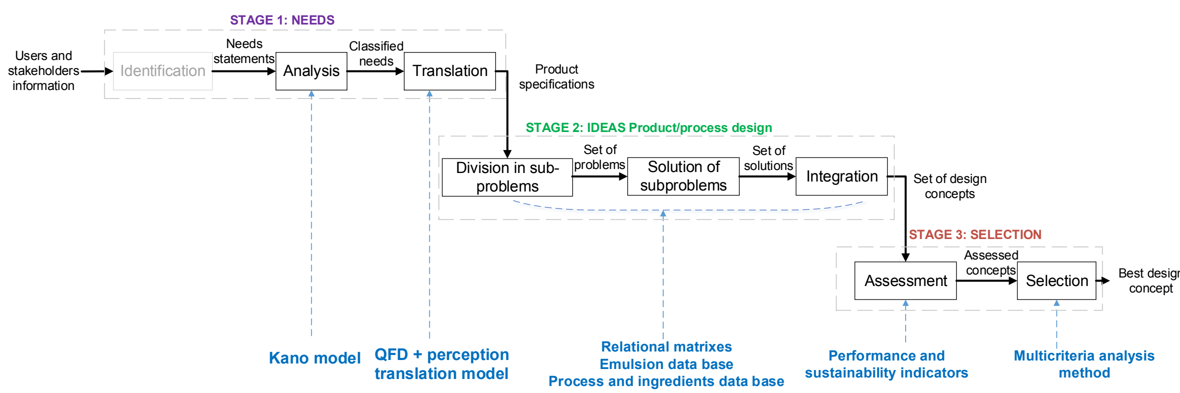

Figure 2-4: Methodology workflow

2.4.2 Information structure of the design methodology

The methodology proposes the following information structure, as shown in Figure.2-5:

For the needs stage, the methods Kano model and QFD are used:

Kano model classifies customer needs according to their importance and effect on customer satisfaction. Input information consists of the needs and the responds of customer to a questionnaire. The questionnaire contains a functional and a dysfunctional question related to each need and it enables the classification of them into four categories: must-be needs, one-dimensional needs, attractive needs and indifferent needs. Output information consists of the needs classified in categories. These categories enable to give relevance to those needs with high priority (must-be needs and one-dimensional needs) in the case that it is necessary to do trade-offs.

QFD is an information structure used to translate needs into product specifications. Input information consists of needs already analyzed with Kano model and information from customer and experts to perform the translation. Experts are asked to relate needs with a set of possible product specifications proposed based on a literature search. Simultaneously, customers are asked about the relation of some of the needs (those related to customer feelings and perceptions) with selected product samples. Based on answers of experts and customers, it is possible to define product specifications and target values. Output information consists of product specifications with their respectively target value and level of importance defined based on Kano categories. This output corresponds to the definition of the design problem that will be fed to the design stage.

For the design stage, two matrices containing interrelated information about the product structure and product ingredients were proposed in this study. The first enables the classification of product specifications into general sub-problems and the connection of the latter with a set of predefined solutions strategies. The second enables the connection of solution strategies with ingredients and process conditions. Input information consists of the product specifications defined in previous stage. Output information corresponds to sets of product concepts, i.e., sets of ingredients and process conditions, each of them being an alternative of solution. For the application of this method four elements were proposed:

1) A list of sub-problems and 2) a list of solution strategies, defined based on a literature review of emulsion science publications.

3) The first relational matrix connecting previous mentioned elements, which is formed by a relational score between each sub-problem and each solution strategy. Scores can be strong, weak, zero and can be positive or negative, to indicate when a solution strategy has a positive or negative effect into a sub-problem.

4) The second matrix is formed by a data base of cosmetic ingredients. Ingredients are classified into functional cosmetic groups as emollients, surfactants and rheological modifiers, among others, and they can be searched by their physical, chemical and performance properties.

For the selection stage, a selection framework comprising a set of sustainability indicators and a multi-criteria decision method is proposed. The input consist of product alternatives and the output corresponds to assessed alternatives, based on which product designers can take an informed decision on the product to be developed. The indicators are defined based on the H-statements of the Globally Harmonized System of Classification (United Nations, 2011a). This is done because the information is worldwide valid, and it is very accessible to compare ingredients at early design stages. For the integration of indicators, the multi-criteria method AHP is proposed, because of its high flexibility for the treatment of complex decision problems.

Need stage is fully developed in chapter 3, design stage in chapter 4 and selection stage in chapter 5.

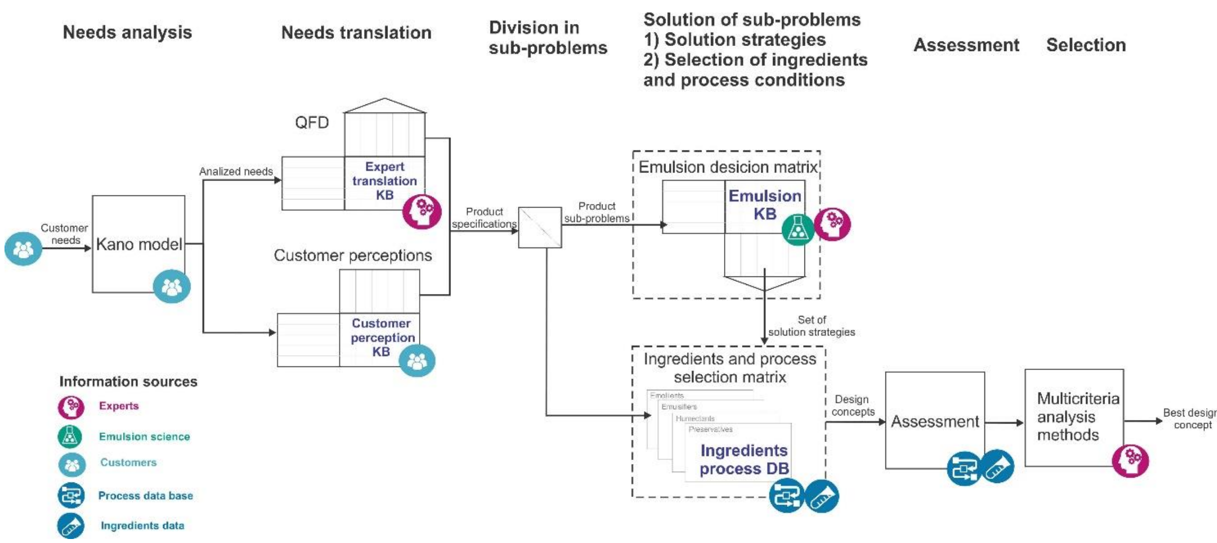

Figure 2-5: Information structure

3. Needs analysis and translation

Needs stage comprises needs identification, analysis and translations. It is the first part of this methodology. Needs are not only the beginning but also the *reason d'être* of the design. They can be defined as any characteristic of an individual or a group of people, who feels a lack that generates a dependency, affecting he/she/their experiences or activities (Boly et al., 2016). If the element on which there is dependency is present, the person can benefit of it: if not, the person suffers pain and dissatisfaction (Boly et al., 2016).

Designers' first tasks are to identify customer needs, to define their importance and to devise product characteristics able to respond to them. Those steps are called in this work needs identification, needs analysis and needs translation, respectively. From these three tasks, the last two are treated in more detail in this chapter.

The first section of this chapter begins with the explanation of the three steps of the needs stage and two methods for the development of the last two: Kano model for needs analysis and Quality Functional Deployment (QFD) for needs translation into product specifications. The second section introduces the study case: a facial moisturizing cream with calendula oil. The third section shows the application of the methods into the study case.

3.1 Framework for needs identification, analysis and translation

3.1.1 Needs identification

Needs can be identified by interviewing users, groups of users and/or user leaders (Cussler and Moggridge, 2011). They can also be found by market studies, data mining or they can be suggested by experienced designers or experts from different professions (for example, dermatologists may play an important role in cosmetics development). After raw needs are collected, they are organized and interpreted by designers, who express them in terms of what the product has to do. Interpretation of raw data to define needs requires a very good understanding of users, their words and meanings. The study of methods for needs identification are beyond the scope of this research.

In this work, needs for the study case were collected through customer survey, literature search and ideas of the design team.

In addition, information about the following topics was collected:

- Conditions of use of the potential product
- Characteristics of existing products related to identified needs which are potential competitive products (benchmarking)
- Regulations

3.1.2 Kano model for need analysis

Once needs are identified, it is necessary to analyze them to define which of them require more attention during the design process. The list of needs related to a product design project has many items: some of them can be interrelated and even, some of them can be contradictory. Thus, it is necessary to identify those needs that have a great effect on customer satisfaction and those that bring a competitive advantage in order to focus in their inclusion within the product (Gérson Tontini, 2007).

With this purpose, implementation of Kano model is suggested. This method classifies needs according to their effect in customer satisfaction into the following groups (Rejeb et al., 2008):

- One-dimensional: For this type of need, user satisfaction is directly proportional to the functional performance of the product. From a mathematical point of view, one-dimensional needs can be interpreted as objective variables to be optimized in a design problem. An example is the price in non-luxurious products, where satisfaction increases as product gets cheaper.
- Must-be: For this type of need, user is very dissatisfied when a minimum required performance is not achieved. Once this minimum is reached, user satisfaction does not increases and remains unchanged with an extra improvement in performance.

From a mathematical point of view, must-be needs can be interpreted as constrains in an optimization problem. An example is the stability of a cosmetic cream. If the product becomes unstable and separates into phases before the expiration date, the user will be very displeased. However, a product with an average use time of one year will not bring further satisfaction if it can remain stable for much more time.

- Attractive: For this type of need, the customer satisfaction increases with product performance, but it does not decreases when the performance is reduced or it is absent. These attributes are not necessary requirements, but they may become a competitive advantage to attract customers. They are key aspects in innovative products, because they may become differentiation factors. An example is a sunscreen with foundation, which may surprise the users for the additional function. Attractive needs tend to become must-be needs with time, once the customer has used them for long time (Gérson Tontini, 2007).
- Indifferent: For this type of need, customer satisfaction is neutral in relation to the improvement in performance of the product. They are normally not especially important for customer, thus resources should not be invested on them. An example is a moisturizing cream with an additional insect repellent function that may not be interesting for people living in climates where insects are not especially present.

Considering previous definitions, must-be needs have to be achieved but not optimized, one-dimensional needs can be optimized to increase customer satisfaction, attractive needs can bring a competitive advantage and time should not be expended with indifferent needs (Gerson Tontini, 2007). Figure 3-1 shows a representation of Kano categories, where the x axis shows product performance and the y axis represents customer satisfaction.

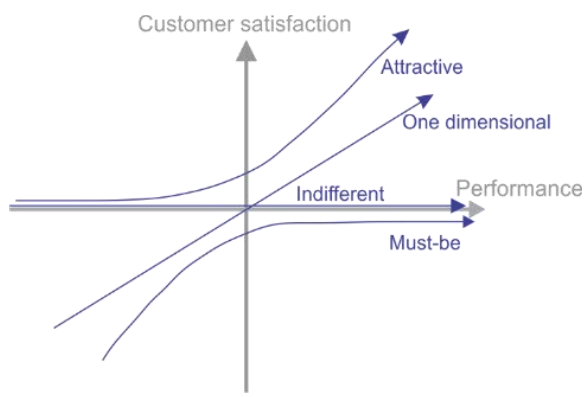

Figure 3-1: Categories of Kano model: need categories are presented according to the relation of product performance and customer satisfaction . Adapted from (Rejeb et al., 2008)

Kano classification is done based on a questionnaire applied to customers and on the analysis of their answers. The questionnaire has two questions related to each need: The first question identifies the reaction of a customer if the need under investigation is fulfilled, while the second identifies the reaction if it is not (Rejeb et al., 2008). Answers are rated and used to calculate scores for each need. An example of the questionnaire applied to the design of a sunscreen and adapted from Rejeb et al. (2008) is shown in Table 3-1.

Table 3-1: Example of a functional and dysfunctional question in relation to the need U.V. protection in the design of a sunscreen. Adapted from Rejeb et al. (2008)

Functional question: If you use a product that gives you a strong protection against U.V. radiation, how do you feel?	1. This would be very helpful to me (+2)
	2. This is a basic requirement for me (+1)
	3. This would not affect me (0)
	4. This would be a minor inconvenience, I can live with it that way (-1)
	5. This would be a major problem for me and I can't accept it (-2)
Dysfunctional question: If you use a product that does not give you a strong protection against U.V. radiation, how do you feel?	1. This would be very helpful to me (+2)
	2. This is a basic requirement for me (+1)
	3. This would not affect me (0)
	4. This would be a minor inconvenience, I can live with it that way (-1) 5. This would be a major problem for me and I can't accept it (-2)

Based on customer answers, three normalized coefficients are calculated with equations 3-1, 3-2 and 3-3: Functional score (FI), which considers positive answers at the functional question, Dysfunctional score (DI), which considers negative answers at the dysfunctional question and Reverse score (RI), which considers negative answers to the functional question (Rejeb et al., 2008). Equations to calculate coefficients are (Rejeb et al., 2011):

$$FI = \frac{\sum degree\ of\ satisfaction\ with\ existence}{Number\ of\ responses \times 2} \quad [3\text{-}1]$$

Summation of negative answers at the dysfunctional question

$$DI = -\frac{\sum degree\ of\ dissatisfaction\ with\ inexistence}{Number\ of\ responses \times 2} \quad [3\text{-}2]$$

Summation of negative answers at the functional question

$$RI = -\frac{\sum degree\ of\ dissatisfaction\ with\ existence}{Number\ of\ responses \times 2} \quad [3\text{-}3]$$

A need is classified into a kano categories according to its resulting FI and DI coefficients.

A need is Must-be if FI < 0.5 and DI > 0.5

A need is One-dimensional if FI > 0.5 and DI > 0.5

A need is Attractive if FI > 0.5 and DI < 0.5

A need is Indifferent if FI < 0.5 and DI < 0.5.

Figure 3-2 shows representative plot of FI - DI relationship and the classification of needs according to their location in the plot. The coefficient RI is used to compare the opinion of designers with customers. If RI is too high, it means that a need that is seen positively by the designers is seen negatively by customers and its inclusion should be analyzed by the design team (Rejeb et al., 2008). For example, it is possible that designers consider that a white cream is desirable, but some customers may prefer a cream with a “more natural color”, reason why they will rate the functional question about “white color” with negative values, increasing RI value. RI can be included in the FI - DI plot as the size of the point representing each need.

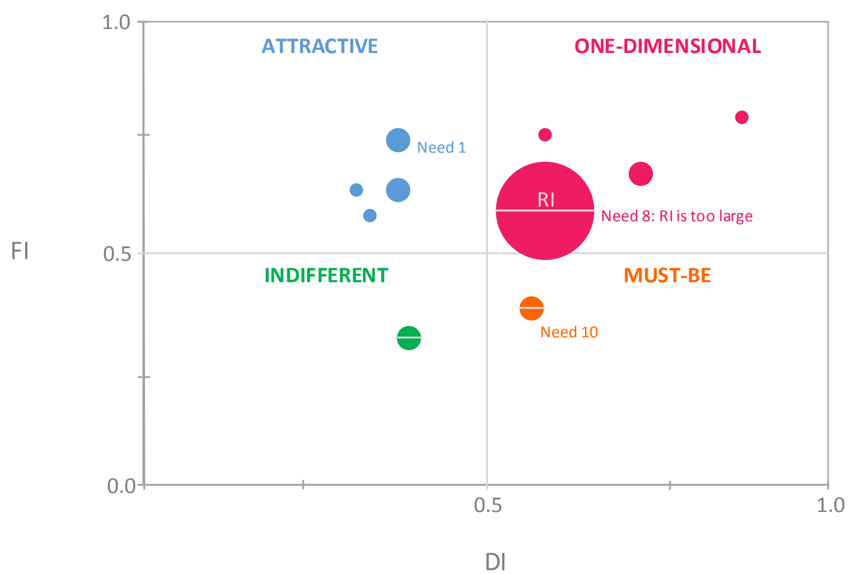

Figure 3-2: FI-DI plot to classify needs into Kano categories. Each circle represents a need, which is located in the plot according to its coefficients FI and DI. The diameter represents the coefficient RI. Adapted from (Rejeb et al., 2008)

3.1.3 Methods for needs translation

In this section two approaches to translate customer needs into product specifications are presented: one, to translate needs with the help of experts, and another, to translate needs with the help of customers. Both are implemented in a complementary way within the framework for need analysis and translation. In addition, Quality Function Deployment is used as an information structure to combine the results both approaches. They are explained below.

3.1.3.1. Translation with the aid of experts

Expert's knowledge about products, customer needs and their interrelation can be used to formalize needs translation. This study presents a method comprising three steps: First, a list of product specifications as wide as possible is built based on a literature review. Second, experts are consulted about the representativeness of those specifications in relation to customer needs. This relation can be measured in a four point scale: high (9), medium (3), low (1) and none (0), although other scales are also possible. Third, expert answers are analyzed to select the smallest possible number of specifications that best represent customer needs. For the third step, two multivariate analysis are proposed: Principal Component Analysis (PCA) and clustering, as explained below.

Principal component analysis:

It is a multivariate analysis tool that enables the reduction of high dimensional data while maintaining most of the original information (Lever et al., 2017). This analysis is frequently used in systems where many dependent and highly interrelated variables are measured for each sample, making difficult a direct analysis of data.

PCA projects data into a set of new non-correlated (orthogonal) dimensions, called principal components (PC), which are linear combinations of the original data that can explain most of the original variance with less dimensions (Lever et al., 2017). The first PC is calculated to explain most of the variance of the samples, the second explains as most of the remaining variance with the restriction it is orthogonal to the first PC and so on, until equal number of PC than original dimensions are calculated. Once all PC are calculated, a number of them explaining a desired percentage of variance is selected.

Steps for the application of PCA are explained below (Smith, 2002):

1) Organize data: Data are organized in a matrix, where the rows are observations (n) and the columns are the dependent variables or dimensions (m).

2) Standardize data: The mean of each dimension (m) is subtracted from each data within the column. This is done to center the mean of all data in cero. Additionally, in case data were measured in different scales, it is possible to normalize by divided them by the standard deviation. The resulting data are organized in a standardized matrix **X** of m×n dimensions.

3) Covariance matrix: The covariance matrix of **X** is calculated using equation 3-4. The covariance matrix is a symmetric matrix that contains the variance of the dimensions in the diagonal and the covariance of pairs of dimensions in the remaining matrix spaces.

$$\mathbf{C}_{\boldsymbol{x}} = \frac{1}{n-1}(\boldsymbol{X}-\overline{\boldsymbol{X}})(\boldsymbol{X}-\overline{\boldsymbol{X}})^{T} \quad [3\text{-}4]$$

Where **X** is the standardized matrix of data, $\overline{\boldsymbol{X}}$ is the mean of the set **X** and $\mathbf{C}_{\boldsymbol{x}}$ is the covariance matrix

4) Calculate the eigenvectors and eigenvalues of the covariance matrix: Given the fact that the covariance matrix is square, it is possible to calculate eigenvectors and eigenvalues, from equation 3-5

$$\mathbf{C}_{\boldsymbol{x}}\boldsymbol{v} = \boldsymbol{\lambda}\boldsymbol{v} \quad [3\text{-}5]$$

Where, $\boldsymbol{v}$ is the set eigenvectors and $\boldsymbol{\lambda}$ the set of eigenvalues of the covariance matrix.

5) Organize and select eigenvectors: Eigenvectors are organized according to their eigenvalues, from the highest to the lowest. The eigenvector with the highest eigenvalue is the first principal component. After eigenvectors are ranked. Then, to select a p number of them is required, where p is the number of dimensions selected to represent original data. A matrix contained the selected eigenvectors is defined in equation 3-6.

$$\mathbf{Feature\ Vector} = (\mathbf{eig_1},\ \mathbf{eig_2} \dots\ \mathbf{eig}_{\boldsymbol{p}}) \quad [3\text{-}6]$$

5) New data set: Data are transformed to the new coordinates established by the principal components as shown in equation 3-7. When two PC are selected, this transformation enable to plot data in a PC1 - PC2 diagram to further analyze data.

$$\mathbf{Transformed\ data} = [\mathbf{Feature\ Vector}]^{T}\boldsymbol{X}^{T} \quad [3\text{-}7]$$

Cluster analysis:

It is a method that enables the classification of a list of samples into groups (or clusters) according to their degree of similarity. Samples within a cluster have more similar properties between them than in comparison with samples of other clusters.

There are different algorithms for clustering and many methods to calculate degree of similarity between samples. Three examples of algorithm are presented: k-means, fuzzy c-means and hierarchical clustering.

- k-means: In this procedure, clustering is done with several k centroids (means) around which data are organized in defined groups. This algorithm has the following steps (Politecnico de Milano, 2018):

1) A number of k cluster are defined by the user
2) k initialization values are defined. These points are the initial cluster centroids.
3) Each sample to be classified is assigned to the group of the nearest centroid. Distance between points can be calculated with Euclidian distance
4) When all objects have been assigned to a group. The centroid of each group is recalculated by computing the mean of its elements.
5) Steps 3 and 4 are repeated until the centroids remain almost constant between iterations.

- Fuzzy C-means: This algorithm is very similar to the previous one, with the difference that an object can belong to more than one cluster. In this algorithm, the function in equation 3-8 is minimized in each iteration (Politecnico de Milano, 2018):

$$J_m = \sum_i^n \sum_j^C u_{ij}^m \left\| \boldsymbol{x}_i - \boldsymbol{c}_j \right\|^2 \quad [3\text{-}8]$$

Where m is a real number greater than 1 that controls how fuzzy the cluster will be, n is the number of samples $\boldsymbol{x_i}$, C is the number of clusters, u_{ij} is the degree of membership of $\boldsymbol{x_i}$ in the cluster j, $\boldsymbol{x_i}$ is a d-dimensional measured sample, c_j is the d-dimensional center of the cluster and $\|*\|$ is a measure of similarity between data.

The clustering process is iterative. In each iteration, the membership function and the cluster are updated according to equations 3-9 and 3-10 respectively (Politecnico de Milano, 2018).

$$u_{ij} = \frac{1}{\sum_k^C \left(\frac{x_i - c_j}{x_i - c_k}\right)^{\frac{2}{m-1}}} \quad [3\text{-}9]$$

$$c_j = \frac{\sum_i^n u_{ij}^m . \, x_i}{\sum_i^n u_{ij}^m} \quad [3\text{-}10]$$

The iteration process finishes when the difference between membership degrees u_{ij} between consecutive iterations is smaller than an established error.

- Hierarchical clustering: In this method, samples are pair compared and successively clustered according to their similarity, until a big cluster containing all samples is formed (Nagamachi, 2011). The result of this method is frequently shown in a tree diagram. The steps of this algorithm are (Nagamachi, 2011):

1) Similarities (or dissimilarities) between each pair of the n samples are calculated and a matrix (n-1)×(n-1) is built. Similarities can be calculated by diverse methods (Euclidean distance, cosine, Pearson correlation, hamming similarity, among others) (Nagamachi, 2011). Here, the minimal Euclidian distance between samples is used as the similarity criteria. Euclidean distance between two samples X_1 and X_2 represented by a vector of properties $\{x_{11}, x_{12}, x_{13} \ldots x_{1n}\}$ and $\{x_{21}, x_{22}, x_{23} \ldots x_{2n}\}$ can be calculated with equation 3-11 (Nagamachi, 2011):

$$d_{1-2} = \sqrt{\sum_{i=1}^n (x_{1i} - x_{2i})^2} \quad [3\text{-}11]$$

2) The pair of samples with the greatest similarity is merged into a cluster by calculating the mean of their properties.
3) The similarity matrix is rebuilt using the new cluster instead of the previous selected samples
4) This procedure is repeated until a unique cluster containing all samples is formed.

3.1.3.2. Translation with the aid of customers

Some needs can be translated to technical specifications with their respectively target values based on a literature review, knowing the standards of the industry or consulting experts. Some others are difficult to translate, because they cannot be directly measured through a standard test. This is the case of needs related to customer sensations, whose meaning has to be agreed with them, because it may change between groups of customers and in the same group within time.

To overcome this difficulty, it is proposed to involve the customers in the translation process. It can be done by using product samples to communicate clearly with the customers. Product samples are not necessarily perfect product prototypes but they are examples, product fragments, objects or images that represent well the concepts that will be evaluated by customers. For the design of products that are similar to already existing ones, it is possible to use samples taken from the market to explore some of their properties and their acceptability by customers. For innovative products which have non-equal in the market, product properties may be represented by pictures, videos or metaphors. For example, samples with colors can be used to represent not only product aspect but also its fragrance. Emulsions of other industrial sectors may be used to represent innovative product properties of new cosmetics. Videos of moving fluids may represent product desired rheology. Product fragments as for example, mixtures of water and rheological modifiers, mixtures of essences, among others, may be used to represent specific product characteristics.

The formalization of the translation process with the aid of customers is done with an approach based on Kansei Engineering, which is a methodology that enables the translation of customer feelings into concrete design parameters (Schütte et al., 2004). In a basic version, Kansei engineering describes the product to be designed from two domains: 1) from a semantic domain, i.e., with the customer words describing needs related to sensations and 2) from a product domain, i.e., with product samples representing product properties and attributes (Schütte et al., 2004).

For example, in order to describe the need “softness”, a wide set of pre-selected product samples is described in both domains: from the semantic domain, i.e., a group of customers are asked to assess product samples according to their level of softness, and from the product domain, i.e., the samples are measured with rheological and texture tests to characterize them. Subsequently, customer responses and product properties are statistically evaluated to define based on the answer of the first target values for the second. When possible, interrelation models between them are built. Table 3-2 summarizes the steps to apply this approach.

Table 3-2: Approach for translation of customer needs based on Kansei Engineering methodology. Adapted from (Nagamachi, 2011)

	Step	Explanation	Application in the case study
1	Design statement	The main idea of the product is defined based on customers and stakeholders expectations.	The design team decided to design a moisturizing cream as the case study
2	Collection of customer words	All possible words that describe customer needs related to sensations are collected. The idea is to get as many words as possible to make a complete description of the semantic domain. After the collection is done, words are reduced to obtain a manageable number. An affinity diagram can be used for this purpose. Customer words can be found in reviews, magazines, blogs, videos, by interviewing customers, by interviewing experts, etc. The search must not be reduced to words, but it can also include any expression or element used by customers to express their feelings such as pictures, emoticons, videos, etc.	For the case study words are collected through a survey applied to customers, where they are asked to describe their ideal moisturizing cream.
3	Scale for words assessment	The semantic differential method (SD) is used for measuring product sample according to customer needs related to sensations. In this method, needs are organized in pairs of positive and negative meaning. For example, the pair light and thick to describe product consistency. Scales of 5, 7, 9 or 11 points separating the word pair can be used.	For the case study, a 5-SD scale is used, because it is easy to understand by the customers (Nagamachi, 2011). An example of this scale for the pair light-thick is: very light, light, intermediate between light and thick, thick, very thick
4	Collection of product samples	Samples representing product desired properties are collected. When it is desired to build a model, it is recommended to collect at least 20 product samples (Nagamachi, 2011).	For the case study, a group of 12 product samples are collected. Six of them representing texture and rheological properties and other six representing product fragrance.
5	List of product properties and values	A list of properties to create product specifications is prepared. The selection of properties has to be done carefully because they have to represent completely the product performance and they have to be possible to measure. In this step an exhaustive literature review and/or the consultation of experts is advised.	For the case study a list of texture and rheological properties taken from (Gilbert et al., 2013) are selected to evaluate the first group of 6 samples. Levels of intensity and three fragrance families are used for the second group of 6 samples.
6	Evaluation of product samples properties	Product samples are measured in two domains: 1) Product samples are tested by a group of customers in relation to customer needs with the	For the case study, a group customers are asked to evaluate product sample according to needs related to sensations.

	Step	Explanation	Application in the case study
		semantic scale selected in step 3. 2) Product samples properties are measured in the properties selected in step 5.	In addition, rheological and texture test are used to measure them.
7	Statistical analysis	Data is statistically analyzed to known their structure and interrelations. There are mono-variable and multivariable analysis. Multivariable methods are very important because they enable to known the correlation between all variables. Examples of multivariate methods are Principal Component Analysis (PCA), Factor analysis, and cluster analysis, among others.	For the case study, PCA is used to get to know correlations between variables. Additionally, clustering is used to analyze similarities between samples.
8	Data interpretation – modelling and validations -	When there is enough information, it is possible to build correlations between measurements and needs. Possible methods to model customer needs based on product properties are: linear regression, partial least squares regression, clustering, neuronal network, genetic algorithm, rough set analysis, among others.	For the case study, a model is not built. Instead, data from customers and measurements are analyzed, and according to this analysis, values for product variables are defined.

3.1.3.3. A structure for needs translation: Quality Functional Deployment (QFD)

QFD is a customer based quality tool that enables the subsequently transformation of customer needs into product, component or process specifications and quality control parameters, using a series of matrices as shown schematically in Figure 3-3 (Franceschini, 2002a).

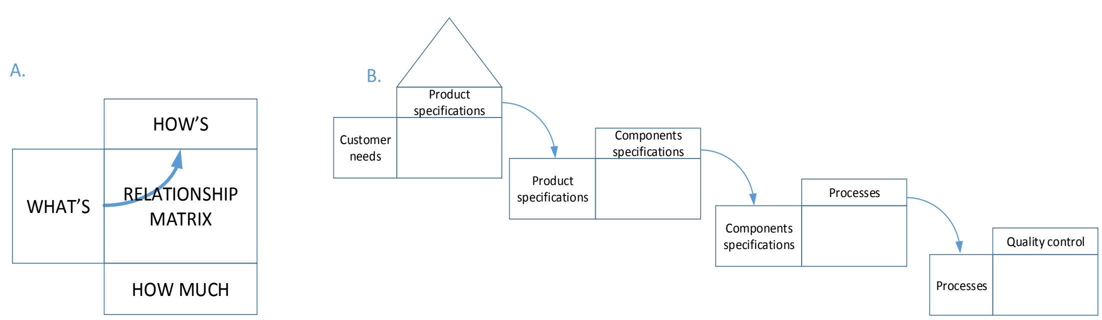

Figure 3-3: A) Basic structure of a QFD matrix B) Structure cascade of the four matrices of QFD. Adapted from (Govers, 1996) and (Franceschini, 2002a).

The first matrix, also known as the House of Quality (HoQ) is implemented in this study as an information structure for the translation of customer needs into product specifications. In that matrix, information obtained from the Kano model, expert consultation and customer consultation (sections 3.1.2, 3.1.3.1 and 3.1.3.2.) is organized and integrated to achieve the translation of customer needs to product specifications. Its construction comprises the stages shown in Figure 3-4 (Roberts, 2007)(Webducate.net, 2018), which are explained below.

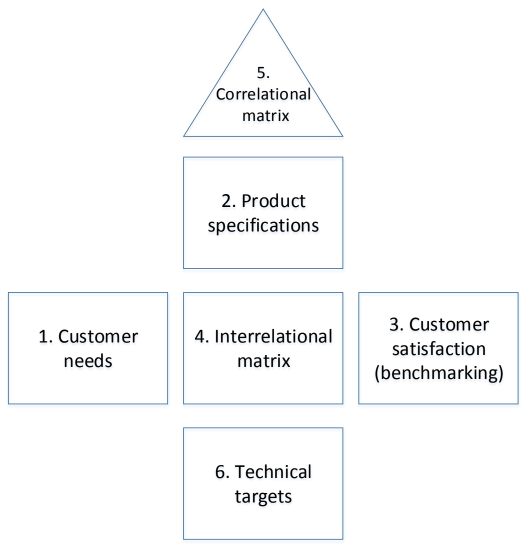

Figure 3-4. Diagram of the House of Quality (adapted from (Roberts, 2007) (Webducate.net, 2018))

1. Customer needs: This part includes the customer needs organization resulting from the step needs identification. They are organized in groups of similarity, with their corresponding importance and Kano category. Groups of similarity can be formed using an affinity diagram, where needs are written in cards and are organized in categories according to their likeness by the design team (Franceschini, 2002b). Need importance (NIC) can be obtained through a customer survey. A common scale to ask for the importance is a five level scale: not important – 1, slightly important – 2, important – 3, very important – 4, extremely important – 5) (Roberts, 2007). Kano categories can be defined as explained in sub-section 3.1.2.

2. Product specifications: In this part the design group has to agree a list of product specifications. It is, a list of product properties or characteristics that better measure the achievement of customer needs. These specifications should be possible and preferably easy to measure. They are not definitive but are the goals that will guide the design process (Roberts, 2007). Some possible types of specifications are:

- Product properties: It is possible to express some needs in terms of chemical, physical and transport properties of the product. Examples are: thermal conductivity, electrical conductivity, pH, viscosity, density, melting point, transport coefficients, among others. Product functionalities can be translated to product properties if there is a model that connects them or if the phenomenon causing the desired effect is well understood.
- Instrumental measurements: Some needs are expressed in terms of instrumental measurements. The relation between them is normally established empirically and validated through experimentation and data analysis (Cussler and Moggridge, 2011). This type of translation is frequently used for needs of the type feelings and sensations. For example, texture is usually characterized with a texturometer, an equipment that measures mechanical textural parameters of the sample as cohesiveness and hardness under conditions similar to the ones of use.
- Indicators: Some needs are translated into combination of properties or performance indicators. Examples are economic, environment and safety indicators.
- Standard tests: To define how well a product performs a function, different production sectors have developed standard tests. Based on these tests, target product specifications can be defined. For example, a sunscreen should have a SPF superior than 15 and protect in a broad spectrum (UVA and UVB) in order to be legally labeled as a product that protects against skin cancer and early skin aging (FDA, 2012a). SPF can be measured with a standard test, which is technical well defined and therefore can be selected as the product specification for the need of U.V. protection. Standard tests are numerous and they are sector and product specific.
- Subjective statements: Some needs are very complex to translate and the design group may conclude that it is not possible to find a measurable specification after analyzing them carefully. In that case, these needs may remain untranslated and its evaluation can be done through a panel tests.

Annex A presents a list of standard test and instrumental measurements that can be applied to identify specifications for cosmetic products.

Product specifications, like customer needs, are organized in groups of similarity within the HoQ. This can be done using an affinity diagram.

3. Customer satisfaction (benchmarking): It is used to compare customer satisfaction in relation to existing products.

First, customers are asked about the satisfaction of each need (defined in the part 1 – customer needs) regarding an existing product that perform a similar function that the one to be design, for example a competitive product. Customers are normally asked in a five point scale: The product performance is poor - 1, fair - 2, good - 3, very good - 4, excellent – 5 (Roberts, 2007).

Second and based on the previous results, the design team can decide an improvement ratio for each need (IR_0). It is, a target customer satisfaction in relation to existing customer satisfaction with an existing product.

Third, it is possible to define a final need importance (NI) using the improvement ratios (IR_0), the need importance defined by customers (NIC) in part 1 of the HoQ (customer needs) and integrating Kano coefficients defined in section 3.1.2, as shown in equation 3-12 (Chaudha et al., 2011):

$NI = (1 + \max(|FI|, |DI|))^k * IR_0 * NIC$ [3-12]

where FI and DI are the Kano coefficients calculated with equations 3-1 and 3-2, k is an exponent that takes the values of 0, 0.5, 1 and 1.5 for indifferent, must-be, one- dimensional and attractive needs, respectively, IR_0 is the improvement ratio and NIC are need importance according to customers.

4. Interrelationship matrix: This is the main part of the HoQ. It enables the connection between previously defined customer needs (part 1) and product specifications (part 2) (Roberts, 2007). The design group agree the existence and the degree of relation between each need i and each specification j to define an interrelation coefficient (C_{ij}), according to their experience and knowledge. The relation can be measured in a four point scale: high (9), medium (3), low (1) and none (0) (Webducate.net, 2018). For the case study, the interrelationship matrix is defined with the help of a group of experts, as explained in sub-section 3.1.3.1.

5. Correlational matrix (Roof): The roof of the matrix is used to identify possible interferences between product specifications. In this part, the design group defines by consensus the existence and degree of interrelation between product specifications. The relation can be measured in a five point scale: strong positive, positive, none, negative and strong negative (Roberts, 2007). This part is not develop in the case study.

6. Target values for product specifications (technical benchmarking): In this part, weights and target values for product specifications are defined. Target values are the numerical values that result from the measurement of a product specification. For example, in the case of a sunscreen with a SPF 30, the SPF is the specification that translates skin protection against U.V radiation, and the number 30 is the target value.

For the calculation of specification weights (W_j), the final importance of each need (NI) (from part 3 - customer satisfaction) is multiplied by the corresponding interrelation coefficient (part 4 - interrelationship matrix) and the resulting values of all needs related to a specification are summed to obtain the specification weight. The same procedure is done for the entire list of specifications as shown in equation 3-13 (Webducate.net, 2018).

$$W_j = \sum_i NI_i * C_{ij} \quad [3\text{-}13]$$

For the definition of specification target values, it is possible to consult customer, experts, or to analyze technical parameters in competitive products. Specification target values are agreed by the designers after the analysis of previous mentioned aspects and the results of the other parts of the HoQ. Some criteria to select target values based on kano categories are:

- Must-be needs are normally ranked as important. However, an improvement in product performance in relation to these type of needs will not bring further satisfaction. Thus, product performance affecting must-be needs should not be increased, but kept at the same value of the competitive products.
- Improvements in one-dimension needs are highly valued by customers. Thus, product performance affecting one-dimensional needs should be at least equal or better than competitive products, overall if they are ranked as important. If they

result to be worse than competitive products, the design product could have a competitive disadvantage.

- Attractive needs, even when they are ranked as important, do not bring competitive disadvantage when they have an inferior performance in comparison to competitive products (Gérson Tontini, 2007). Some of them have to be select by the design group as differentiation factors to give identity to the product. In those cases, target values should be superior or different than those present in competitive products.

In the case study, target specifications are defined by analyzing competitive products and standards and, for those needs related to customer sensations and feelings, target specifications are established based on a customer consultation, as explained in sub-section 3.1.3.2.

3.2 Case study

3.2.1 Case study presentation

The case study is the design of a facial moisturizing cream containing calendula oil as natural antioxidant. This example was born from the need of the entrepreneurial project "Xiu Aguee – Aceites esenciales" to give added value to its products. Xiu Aguee is a Colombian entrepreneurship that produces essential oils and hydrosols (water of essential oils) by steam distillation for cosmetic use and aromatherapy since 2015. Its main product is the calendula hydrosol, from which around 80 Liters per month are produced. In addition, its installed capacity enables the production of around 1 Liter per month of calendula oil, which is not sold as fast as the hydrosol.

With the aim of producing more elaborate cosmetic products and benefit from the surplus of calendula oil production, the design of a facial moisturizing cream containing calendula oil is proposed. This cream is visualized as a daily beauty product complementary to the sun protection. Additionally, due to the fact that most current customers of Xiu Aguee are women between 30 and 40 years old, there is a great interest in the creation of a product to attract a new customers sector with the profile of women from 20 to 29 years old.

Some decisions are made together with two product engineers of Xiu Aguee, who together with the author of this study form the design team of the project.

3.2.2 Calendula oil characteristics

Calendula oil characterization as given by Xiu Aguee is shown in Table 3-3.

Table 3-3: Calendula oil characterization

CAS Nº	70892-20-5
INCI name	*Calendula Officinalis* Flower Oil
Process	Steam distillation
Part of the plant	Fresh flowers
Origin	Sogamoso - Colombia
Uses	Pure natural product. For cosmetic use
Characteristics	Raw material of vegetal origin. 100% natural
Aspect	Yellow translucent liquid
Odor	Characteristic, herbal, penetrant
Refractive index	1.457 – 1,468
Density (g/mL)	0.864 – 0.883
Inflammability point (°C)	> 95
Solubility	Insoluble in water, soluble in fats, soluble in ethanol, soluble in hexane

Variants: In addition to calendula flower essential oil, other products obtained from marigold plant that are widely used in cosmetics are *Calendula officinalis* extract, *Calendula officinalis* flower, *Calendula officinalis* flower extract and *Calendula officinalis* Seed Oil (Andersen et al., 2010).

Uses: Calendula essential oils and extracts have been traditionally used for treatment of skin wounds, burns and sun burns (Basch et al., 2006) in products to calm skin inflammation, acne, dermatitis and sensible skin. Topical activity and effects of calendula oils and extracts have been widely studied. Examples of some of them are:

Antioxidant activity: According to a study done by Fonseca et al. (2010), there is evidence of antioxidant activity of *Calendula officinalis* hydro-alcoholic extract probed with in vitro and in vivo studies.

Antifungal and antimicrobial activity: Methanolic and ethanolic extracts of *Calendula officinalis* petals, as well as calendula essential oil, have shown excellent antifungal activity (Efstratiou et al., 2012)(Gazim et al., 2008). There is also evidence of antimicrobial activity (Efstratiou et al., 2012).

Anti-inflammatory activity: Calendula anti-inflammatory activity has been well proved. A study showed this activity is proportional to the content in faradiol monoester, which can be used as indicative of the quality of calendula derived products (Loggia et al., 1994).

Collagen production and wound healing: An in vivo test showed that depending on concentration, collagen production can be enhanced by topical application of products containing calendula extract (Naeini et al., 2012). Additionally, it was shown that ethanolic calendula extract enhances proliferation of fibroblasts by an in vitro test (Fronzaa et al., 2009).

Solar protection: It was found that formulations with calendula essential oil (at 5%) give a good solar protection (in vitro SPF around 14) (Mishra et al., 2012).

Products and usage levels: According to information provided by some cosmetic producers to the FDA, calendula oil and extracts are used in many cosmetic product categories such as baby products, makeup products, personal hygiene products and skin care products (Andersen et al., 2010). Calendula usage levels depend on the nature of the extract or oil and the product in which it is included. In the case of study, corresponding to calendula flower oil and skin care products, concentrations between 0.02 and 0.1 % have been reported (Andersen et al., 2010).

Safety: In common used concentrations, all derived products from calendula plant are safe for cosmetic use (Andersen et al., 2010). They were not found toxic, genotoxic or irritating for skin (Andersen et al., 2010).

3.3 Application of framework for need stage in the study case

3.3.1 Needs definition for the study case

Needs were identified by applying an internet survey. The survey contained some questions about the customer profile, one multiple choice question asking about the main criteria for the selection of cosmetics and one open question asking about customer expectations for a moisturizing cream. The survey was shared in the social networks of Xiu Aguee and between students of the Chemical and Environmental Engineering Area at the Universidad Nacional de Colombia. In this step, the objective was to get as many ideas as possible for the product, reason why all answers were taken into account, regardless of whether or not they belong to the target customer group. The survey was answered by 213 people, from which 114 correspond to the group of interest: women of 20 to 29 years. The survey and additional information of the people who answered it can be found in Annex B.

Figure 3-5 shows the results of the multiple-choice question – "What criteria do you consider most important when selecting a cosmetic product?". The results show that the main criteria for the selection of a cosmetic are the adaptation to skin, product effectiveness and product price. This indicates that besides the expected criteria of price and function, most of the population wants products adapted to their own needs, in this case skin, showing the potential of custom products in the cosmetic sector and the importance of understand and analyze carefully customer expectations.

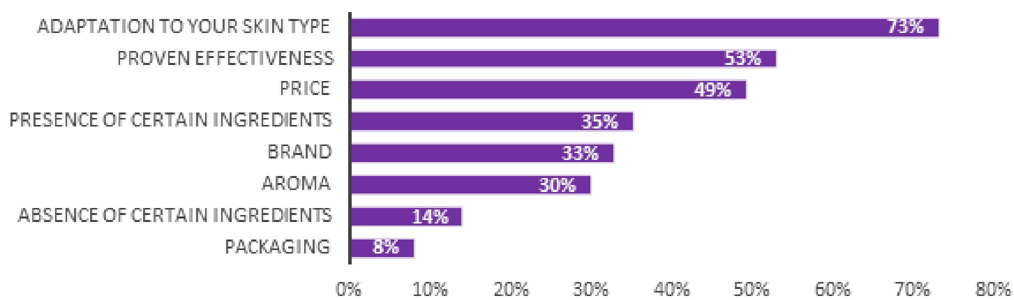

Figure 3-5. Answers of 213 respondents to the multiple choice question - What criteria do you consider most important when selecting a cosmetic product?

Based on the answer to the open question, the design team defined the needs for the case study using an affinity diagram. Needs as expressed by each survey respondent were sequentially grouped in 1) need statements and classified in 2) secondary needs categories and 3) main needs categories. Figure 3-6 exemplifies how the affinity diagram was used for the definition of the needs *effectiveness* and *soft or neutral aroma*. The same procedure was followed for the definition of all needs of the case study. The 29 resulting needs were classified into 8 secondary categories and 5 main categories. They are presented in Table 3-4.

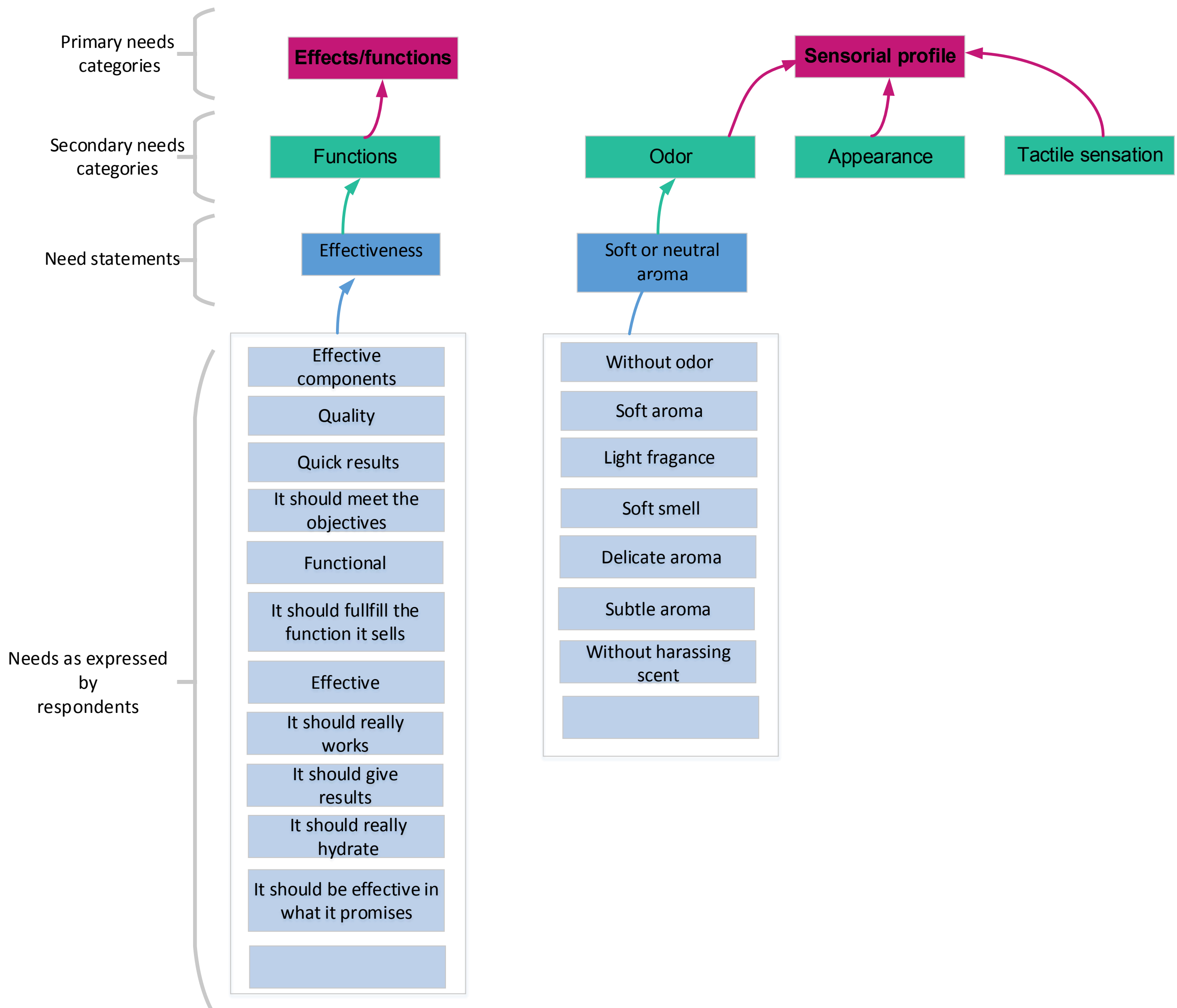

Figure 3-6. Representation of the affinity diagram used for the definition of needs for the design problem

Table 3- 4: Identified needs for the case study

Main classification categories	Secondary classification categories	Needs	Frequency
Sensorial profile	Odor	1. It has a soft or neutral aroma	49
		2. Aroma is nice	65
	Tactile sensation	3. It is not oily	99
		4. It has a light texture	30
		5. It spreads easily	20
		6. It is absorbed quickly	20
		7. It is thick, consistent	5
	Appearance	8. It is white	7
Effects/functions	Functions	9. It is effective (and it generates trust in customers)	55
		10. Leaves skin soft and hydrated	90
		11. It provides prolonged hydration	54
	Feelings	12. It gives a fresh feeling	14
		13. It gives a sensation of vitality	1
		14. It gives a relaxing sensation	1
		15. It is nutritious	12
		16. It is comfortable and practical	9
	Natural ingredients	17. It has ingredients of natural origin	18
		18. It is 100% natural	23
Additional functions	Additional functions	19. It gives solar protection	14
		20. It controls acne	8
		21. It is anti-stain	10
		22. It is mattifying	19
		23. it prevents wrinkles	4
		24. It gives protection against pollution	1
Compatibility/ non side effects	Skin type	25. it is for greasy skin	4
		26. it is for sensible skin	8
	Non side effects	27. It is not irritating or allergenic	16
		28. It is compatible with sunscreen and makeup	3
Price	Price	29. It is affordable	11

Table 3-4 shows that the more mentioned needs are: “it is not oily or sticky”, “it leaves skin soft and hydrated”, “aroma is nice”, “it is effective, “it provides prolonged hydration” and “it has a soft or neutral aroma”. Frequency shows that the conscious desire of respondents is focused on the main function of the product (effective, prolonged hydration) and the main sensations it produces in terms of texture (not oily) and aroma (nice and soft). Those characteristics will be carefully treated during design. Additionally, it is interesting that respondents were concerned about product reliability. Expressions of the type “the product should do what it says it does” were constantly expressed by users, showing the importance of design quality products (and indirectly the need of a reliable design process) to develop customer trust.

It is worth to say that the fact that some needs were mentioned only once does not mean that they are not important. Some of them may be non-conscious attractive needs that do not spring instantly to people mind, but may become a competitive advantageous when included in the design. To analyze needs effects on customer satisfaction Kano model was applied.

3.3.2 Needs analysis with Kano model in the case study

- **3.3.2.1. Questionnaire preparation**

In this step, needs were classified into Kano model categories and were organized according to their importance. This is done by applying the questionnaire of the Kano model (explained in sub-section 3.1.2) to people of the target customer group in relation to the identified needs (Table 3-4). To avoid survey fatigue in the respondents, the initial list of needs was reduced from 29 to 16 by pre-classifying those that were considered mandatory as must-be needs and by removing those that were repeated, beyond the scope of this work (for example, those related to the design of packaging) or out of the cosmetic field (as example, products to treat acne are not cosmetic but medical and are sold under a different regulatory framework). Table 3-5 shows the needs that were pre-classified as must-be needs and those that were introduced into the Kano model. Table 3-6 shows an example of the questions of the Kano model questionnaire.

Table 3-5: List of needs showing those that were pre-classified as must-be needs and those that will be analyzed with Kano model.

Need	Pre-classification	Comments
1. It has a soft or neutral aroma	To be classified using Kano model	-
2. Aroma is nice	Must-be need	Aroma has to be pleasant or absent
3. It is not oily	To be classified using Kano model	-
4. It has a light texture	To be classified using Kano model	-
5. It spreads easily	To be classified using Kano model	-
6. It is absorbed quickly	To be classified using Kano model	-
7. It is thick, consistent	Removed	It is already included as the dysfunctional question of need 4
8. It is white	To be classified using Kano model	-
9. It is effective (and it generates trust in customers)	Must-be need	-
10. Leaves skin soft and hydrated	Must-be need	-

Need	Pre-classification	Comments
11. It provides prolonged hydration	Must-be need	-
12. It gives a fresh feeling	To be classified using Kano model	-
13. It gives a sensation of vitality	To be classified using Kano model	-
14. It gives a relaxing sensation	To be classified using Kano model	-
15. It is nutritious	To be classified using Kano model	-
16. It is comfortable and practical	Removed	The design team decided to relate this need to packaging design and product presentation. This is beyond the scope of this work
17. It has ingredients of natural origin	To be classified using Kano model	-
18. It is 100% natural	To be classified using Kano model	-
19. It gives solar protection	To be classified using Kano model	-
20. It controls acne	Removed	This is a medical function that cannot be labeled in a cosmetic product.
21. It is anti-stain	Removed	This function will not be directly included in the design. Only ingredients that do not alter skin color will be used
22. It is mattifying	To be classified using Kano model	-
23. it prevents wrinkles	To be classified using Kano model	-
24. It gives protection against pollution	To be classified using Kano model	-
25. it is for greasy skin	Removed	Many people expressed their concern about oily skin and their desire of a product that does not leave and oily feeling. The product is designed for normal to greasy skin and this need is merges with need 3.
26. it is for sensitive skin	Removed	This function will not be directly included in the product, but attention is paid to allergenic ingredients.
27. It is not irritating or allergenic	Must-be need	-
28. It is compatible with sunscreen and makeup	Must-be need	-
29. It is affordable	Must-be need	A question to define an appropriated price in the concept of the customer was included in the third survey (section 3.3.3)

Table 3-6: Kano questions for the need 1 – the product has a soft or neutral aroma

Functional question: How would you feel if you use a facial cream with a soft or neutral aroma?	1. I like this way. This would be very helpful to me (+2)
	2. It must-be this way. This is a basic requirement for me (+1)
	3. This would not affect me (0)
	4. This would be a minor inconvenience, I can live with it that way (-1)
	5. This would be a major problem for me and I can't accept it (-2)
Dysfunctional question: How would you feel if you use a facial cream which does NOT have a soft or neutral aroma?	1. I like this way. This would be very helpful to me (+2)
	2. It must-be this way. This is a basic requirement for me (+1)
	3. This would not affect me (0)
	4. This would be a minor inconvenience, I can live with it that way (-1)
	5. This would be a major problem for me and I can't accept it (-2)
From 1 to 5, how important do you rate that the product has a soft or neutral aroma? [1] [2] [3] [4] [5]	

3.3.2.2. Kano model results

As for the first survey, the Kano questionnaire was shared in the social networks of Xiu Aguee and between students of the programs of the Chemical and Environmental Engineering Area at the Universidad Nacional de Colombia. This time only answers from the target customer group that have experience with similar products were accepted, i.e., women of age between 20 to 29 years that use a similar product at least 2 to 5 times per week. Questions were presented randomly.

Based on answers of respondents, the Functional score (FI), Dysfunctional score (DI) and Reverse score (RI) for each need were calculated using the equations 3-1, 3-2 and 3-3. Table 3-7 shows the results of the three scores and the normalized importance for the 16 needs under analysis. Needs are classified in their corresponding Kano category according to their location quadrant in the plot FI-DI (Figure 3-7).

Table 3-7: Kano model results for the case study

Needs	FI	DI	RI	Kano categories	Normalized average of importance
1	0.52	0.50	0.02	One dimensional/ attractive	0.71
3	0.72	0.88	0.03	One dimensional	0.88
4	0.67	0.25	0.03	Attractive	0.73
5	0.77	0.61	0.02	One dimensional	0.74
6	0.66	0.61	0.02	One dimensional	0.73
8	0.16	0.09	0.13	Indifferent	0.38
12	0.64	0.53	0.00	One dimensional	0.64
13	0.72	0.53	0.00	One dimensional	0.58
14	0.59	0.45	0.02	Attractive	0.58
15	0.80	0.61	0.00	One dimensional	0.67
17	0.78	0.61	0.00	One dimensional	0.69
18	0.72	0.42	0.02	Attractive	0.63
19	0.80	0.55	0.02	One dimensional	0.76
22	0.72	0.47	0.03	Attractive	0.64
23	0.61	0.38	0.03	Attractive	0.56
24	0.20	0.09	0.27	Indifferent	0.61

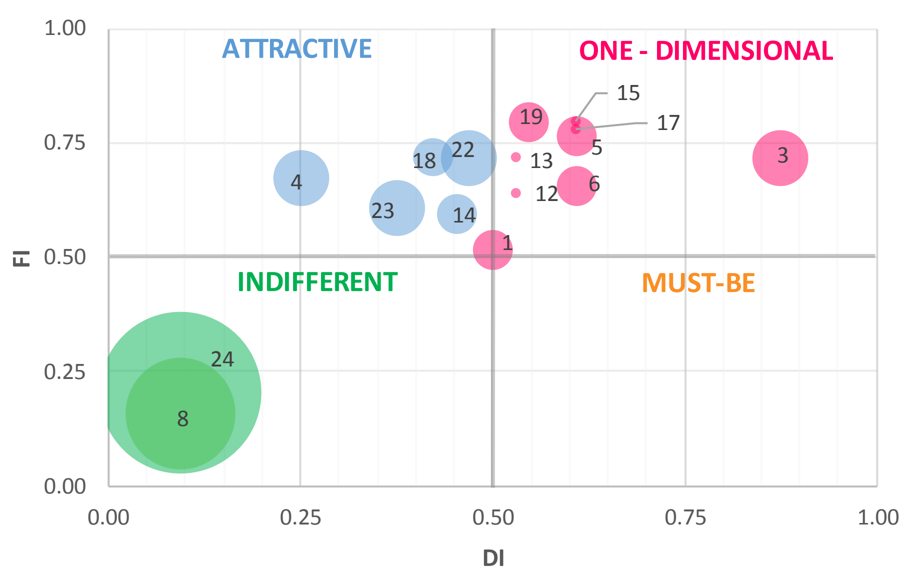

Figure 3-7. Kano model results for the case study

From the 16 analyzed needs, 9 were one dimensional, 5 attractive and 2 indifferent. In addition to the 7 needs that were previously pre-classified as must-be in Table 3-5. The two indifferent needs: 8 – "it is white" and 24 – "it gives protection against pollution", have a very large score RI in comparison to the others, which means they are not perceived as desired but rather as undesired functions by customers. Need 24 has the higher RI score. It is possible that the advantage of this function was not well understood or that this function is more related to cleansing and not to moisturizing products. Need 8 may be perceived negatively, because users may relate white color with a non-natural cream or with a cream that left a white layer on the face. None of these two needs were further included in the design because they are classified as indifferent.

From the needs classified as one-dimensional, the need 3 – “It is not oily” has the highest DI score (it has the rightmost location in the Figure 3-7), which indicates that customers would be more dissatisfied if the product does not reach this need in comparison to the others. The same need is ranked as the most important one.

Need 1- “It has a soft or neutral aroma” is located in the plot almost in the middle and, as a consequence, its classification is not clear. The design team decided to classify it as an one-dimensional need after considering the frequent reference to aroma given by users in the first survey (see Table 3-4) and the role it plays together with product texture in the generation of product identity.

Analyzing the classification of needs according to their main categories (identified in Table 3-4 with an affinity diagram), it can be seen that most of the needs related to the sensory profile and to feelings are one-dimensional except for the need 4- “light texture” and the need 15- “it is nutritious” which are attractive. Needs related to product main functions, non-side effects and price are must-be needs. Needs related to additional functions are most of them attractive, except for need 19- “it gives solar protection” which is one-dimensional. The latter, despite its classification, will not be longer included in the product, because, as it was pointed in the introduction of the case study, the objective is to create a moisturizing product of daily use complementary to the sunscreen.

Table 3-8 shows the needs used to drive the design process. All must-be needs and almost all one-dimensional needs were included. Two attractive needs were also selected: Need 4-“light texture”, because it was ranked as the most important of them, and need 23 –“it prevents wrinkles”, because the product contains calendula oil and this material is an important source of antioxidants.

Table 3-8: Final list of needs to drive the design process. They are presented with their respective Kano category and importance level

Main classification categories	Secondary classification categories	Needs	Kano category	Importance
Sensorial profile	Odor	1. It has a soft or neutral aroma	One dimensional	0.71
		2. Aroma is nice	Must-be	1*
	Tactile sensation	3. It is not oily or sticky	One dimensional	0.88
		4. It has a light texture	Attractive	0.73
		5. It spreads easily	One dimensional	0.74
		6. It is absorbed quickly	One dimensional	0.73
Effects/functions	Functions	9. It is effective (and it generates trust in customers)	Must-be	1*
		10. Leaves skin soft and hydrated	Must-be	1*
		11. It provides prolonged hydration	Must-be	1*
	Feelings	12. It gives a fresh feeling	One dimensional	0.64
		13. It gives a sensation of vitality	One dimensional	0.58
	Natural ingredients	17. It has ingredients of natural origin	One dimensional	0.69
Additional functions	Additional functions	23. it prevents wrinkles	Attractive	0.56
Compatibility/ non side effects	Non side effects	27. It is not irritating or allergenic	Must-be	1*
		28. It is compatible with sunscreen and makeup	Must-be	1*
Price	Price	29. It is affordable	Must-be	1*

*The importance level of all must-be needs were rated with 1

3.3.3 Needs translation into specifications for the case study

Two steps were used for needs translation into specifications. First, experts were asked about the relationship between customer needs and suggested product specifications found in a literature review. Second, specification target values were defined based on the characterization of competitive products, the consultation of customers and a literature review.

- **3.3.3.1. Needs translation – expert consultation**

As explained in sub-section 3.1.3 experts are consulted to find product specifications that better represent customer needs. This is done in three steps: 1) Preparing a list of product specifications based on a literature review. 2) Consulting experts about the relation of customer needs with the product specifications. 3) Analyzing the results of previous steps with multivariate methods. This development is shown for the case study. It was done in collaboration with the PhD student Javier Andrés Arrieta Escobar.

1) A list of customer needs frequently found in the design of a moisturizing cream and a complete list of possible product specifications are proposed in Table 3-9 and 3-10, respectively. Needs were agreed by the design team and product specifications were summarized from:

- The recommendations from the program Safe+ program of United Nations Industrial Development Organization (UNIDO) for stability tests in cosmetics (ONUDI, 2018)
- The guidelines from the European Cosmetic and Perfumery Association (Colipa) (COLIPA, 1997); (COLIPA, 2004); (CTFA and COSMETICS EUROPE, 2004)
- Explanation of clinical test, sensorial test and instrumental test in (Pensé-Lhéritier, 2016)
- Explanation of rheological and texture test (Gilbert et al., 2013)

Needs in Table 3-9 were classified into 4 groups applying an affinity diagram: Performance, Usability, Safety, Sensations and Appearance. Product specifications in Table 3-10 were classified in five groups: Safety and Regulation (SR), Sensorial Tests (ST), Clinical Test (CT), Instrumental test (IT), and Price. Additionally, they are explained in Annex A. The objective is to define the representativeness of each specification in relation to each need in order to select those that are easier to measure and better describe those needs.

Table 3-9: Customer requirements frequently found in the design of a moisturizing cream to be analyzed by experts.

Groups	Customer needs		Abbreviation	Correspondence to needs of the case study (Table 3-8)
Performance	1	It provides an immediate moisturizing effect	Moist0	Need 9 and Need 10
	2	It provides a prolonged (8h) moisturizing effect	Moisth	Need 11
Usability	3	It is easy to dose and spread	Spreadability	Need 5
	4	It has a pleasant appearance	Appearance	It was not included in previous step, but it is a must-be need that has to be added to the design problem
	5	It has a pleasant aroma	Fragrance	Need 2
	6	It is affordable	Affordability	Need 29
Safety	7	It is safe and reliable	Safety	Needs 9 and 27
Sensations and appearance	8	It does not leave an oily texture	Oiliness	Need 3
	9	It does not feel sticky	Stickiness	Need 3
	10	It has a soft/light texture	Light texture	Need 4
	11	It is natural	Naturality	Need 17

Table 3-10: Test and measurements that can be used to define product specifications.

Groups	Product specifications		Abbreviation
Safety and Regulation	1	Physical/chemical stability of the cosmetic product ()	SR - PC Stability
	2	Physicochemical, toxicological, and eco-toxicological profile of the substances ()	SR -Toxicity
	3	Microbiological quality ()	SR - Mbiology
	4	Use of allowed substances (Annex II to VI)	SR - allowsubs
	5	Dermal tolerance and non-irritability	SR - irritation
Sensorial test	6	Sensory panel (stickiness)	ST - stickiness
	7	Sensory panel - product appearance	ST - appearance
	8	Sensory panel - peak (stringiness)	ST - stringiness
	9	Sensory panel - product odor	ST - fragance
	10	Sensory panel (oil on skin)	ST - oiliness
	11	Sensory panel - spreadability	ST - spreadability
Clinical test	12	Clinical test (skin appearance before and after product application)	CT - appearance
	13	Clinical test (skin appearance before and 8h after product application)	CT - appearance8
	14	Clinical test - Allergenic test	CT - allergenic
	15	Clinical test - Transepidermal water loss (TEWL)before and after application	CT -TEWL
	16	Clinical test - TEWL before and 8h after application	CT -TEWL8
	17	Clinical test - skin conductivity before and after application	CT-corneometer
	18	Clinical test - skin conductivity before and 8h after application	CT-corneometer8
Instrumental tests	19	Rheological profile	IT - Rheo
	20	Instrumental measurement (oil on skin)	IT - oiliness
	21	Spreadability test in Texturometer	IT - spreadbility
	22	Extrusion test in Texturometer	IT - extrusion
	23	Penetration test in Texturometer	IT - penetration
	24	pH	IT -pH
Price	25	Product price (production costs + company profit)	Price

2) A group of 50 experts were asked to assess the relationship between product specifications and customer needs with a scale between 1 to 9, where 1 means a weak relationship, 3 a moderate relationship, 5 a medium relationship, 7 a strong relationship and 9 a very strong relationship. To reduce respondent fatigue, the number of questions was limited by screening out the pairs of specification – need in which it was considered there is not an important relationship as it is presented in Table 3-11. The complete survey can be found in Annex C.

Table 3-11: Pair of specification – need to be consulted with the experts. (Only the relation between the pairs in white were asked to experts)

		1	2	3	4	5	6	7	8	9	10	11
		Moist0	Moisth	Spreadabil	Appearan	Fragance	Affordabilit	Safety	Oiliness	Stickiness	Light texture	Naturality
1	SR - PC Stability											
2	SR -Toxicity											
3	SR - Mbiology											
4	SR - allowsubs											
5	SR - irritation											
6	SP - stickiness											
7	SP - appearance											
8	SP - stringiness											
9	SP - fragance											
10	SP - oiliness											
11	SP - spreadability											
12	CT - appearance											
13	CT - appearance8											
14	CT - allergenic											
15	CT -TEWL											
16	CT -TEWL8											
17	CT-corneometer											
18	CT-corneometer8											
19	IT - Rheo											
20	IT - oiliness											
21	IT - spreadbility											
22	IT - extrusion											
23	IT - penetration											
24	IT -pH											
25	Price											

3) The results of the survey were analyzed. The survey was answered by 20 of the 50 consulted experts in a period of 75 days. Figure 3-8 shows the level of experience of the respondents, from which 60% have more than 5 years of experience.

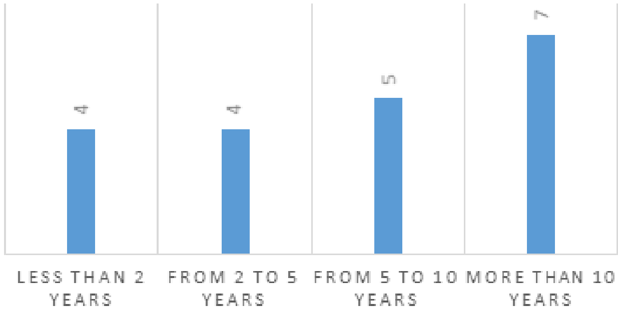

Figure 3-8. Level of experience of experts that answered the survey to translate needs into product specifications

The representativeness of each product specification according to each expert was computed as the average value of the representativeness of the specification in relation to assessed needs. In turn, the representativeness of each group of specifications of Table 3-10 is computed as the average of its components. Complete values are presented in Annex C.

The representativeness of the five groups of specifications along with a factor indicating the effect of the level of expertise of respondents is evaluated with PCA using the software PAST (Hammer et al., 2001). Figure 3-9 shows the result of the analysis. The first two principal components represent the 67% of the variance, and with the addition of the third principal component, it is possible to explain the 80% of the variance, as it is shown in Table 3-12. Principal component 1 is highly correlated with the level of expertise of respondents and with the price, while principal component 2 is more correlated with the other four groups of specifications. The fact that price and level of expertise are negatively correlated indicates that as experts gain experience, they rate product price as less representative of customer needs.

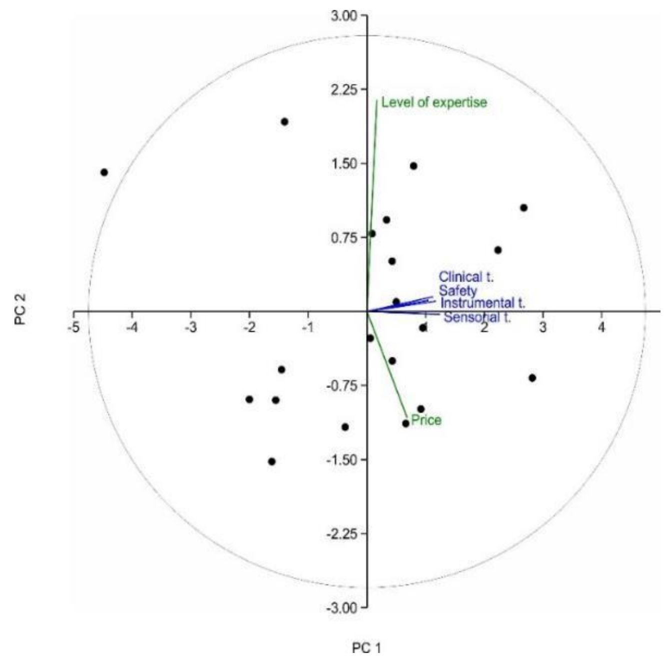

Figure 3-9. PCA for the groups of product specifications price, clinical tests, safety and regulations, instrumental test and sensorial test according to expert with different level of experience

Table 3-12: Numerical results of principal component analysis

PC	Eigen value	Variance (%)	Correlation of variables with principal components: Level of expertise	Safety and Regulations	Sensoral t.	Clinical t.	Instrumental t.	Price
1	3.0	49.9	0.07	0.43	0.52	0.47	0.49	0.28
2	1.0	17.4	0.89	0.05	-0.01	0.06	0.04	-0.45
3	0.8	13.4	0.44	-0.05	0.08	-0.28	-0.3	0.08
4	0.7	11.1	0.10	-0.74	-0.25	0.43	0.37	0.22
5	0.3	5.3	0.01	0.34	-0.49	0.64	-0.47	0.11
6	0.2	2.9	0.05	0.37	-0.64	-0.32	0.56	0.16

Based on the results of PCA, the use a weighting factor related to the level of expertise of respondents was selected to give a relative weight to their answers to calculate the interrelation between the pairs of needs and product specifications. A weighting factor of 1 was given to respondents with less than 2 years of experience, 2 for respondents with an experience from 2 to 5 years, 4 for respondents with an experience from 5 to 10 years and 8 for respondents with an experience of more than 10 years. Using these weights, the interrelationship matrix of needs and specifications was created. It is shown in Table 3-13.

Table 3-13: Relationship between needs and specifications for a moisturizing cream, defined based with the help of experts - QFD*

		Product specifications																								
		SR - PC Stability	SR - Mbiology	SR -Toxicity	SR - allowsubs	CT - allergenic	SR - irritation	SP - stickiness	SP - stringiness	IT - Rheo	SP - spreadability	SP - oiliness	IT - oiliness	CT-corneometer	CT -TEWL	CT - appearance	CT - appearance8	CT -TEWL8	CT-corneometer8	IT - spreadbility	IT - extrusion	IT - penetration	SP - appearance	SP - fragance	IT -pH	Price
Needs	Moist0													7.3	8.2	6.8									5.4	5.9
	Moisth																7.6	7.8	7.3						5.4	6.8
	spreadability							7.4	6.6	7.9	8.5									7.4	5.7	5.7	6.3			5.5
	Appearance	8.2	7.2	5.4	4.3																		8.1			7.2
	Fragance	7.5	7.8	6.1	5.2																			8.5		7.1
	Affordability					3.6				3.3			2.8	3.0	3.6	3.7	3.4	3.8	2.9	3.2	2.6	2.5				5.9
	Safety	7.5	8.0	7.0	8.5	7.4	8.6							5.5	6.3	6.9	6.9	6.7	5.4						7.9	
	Oiliness							6.0	5.1	4.7	5.4	7.9	6.8										7.2			5.5
	Stickiness							7.8	5.9	6.0	6.6	6.5								5.4	4.1	3.7	6.5			5.7
	Light texture							7.1	7.2	7.5	7.3	7.2	5.5							6.6	4.1	5.6	7.2	3.0		5.5
	Naturality	4.5	3.7	4.6	5.4	5.2	6.2																3.1	3.9	2.4	6.6

*Interrelation between the elements was calculated after consulted 20 experts of the cosmetic field from which 60% have more than 5 years of experience. The interrelation scale goes from 1 to 9, being 1 a low level of interrelation and 9 a very high level of interrelation

Finally, and with the aim of find the most representative product specifications, a clustering analysis based on Euclidian distance was applied to the data presented in Table 3-13. The result is shown in Figure 3-10, where groups of product specification are organized in successive clusters with a correlation coefficient of 0.92. Product specifications that form groups at small distances are very similar, i.e., they can be used to describe similar needs. For example, the clinical test of appearance, the corneometer test and the Transepidermal water loss test (TEWL) are relative near among them within the plot. This happens because the three of them are used to measure hydration. The same happens with the sensory panel test of stickiness, spreadability, stringiness and the instrumental test of rheology, which indicates that the latter can be used to represent sensorial properties of the cream. By its part, price seems to be located very far from other product specifications. Product specifications (with a distance less of 4) are shown with the same color tone in Table 3-13.

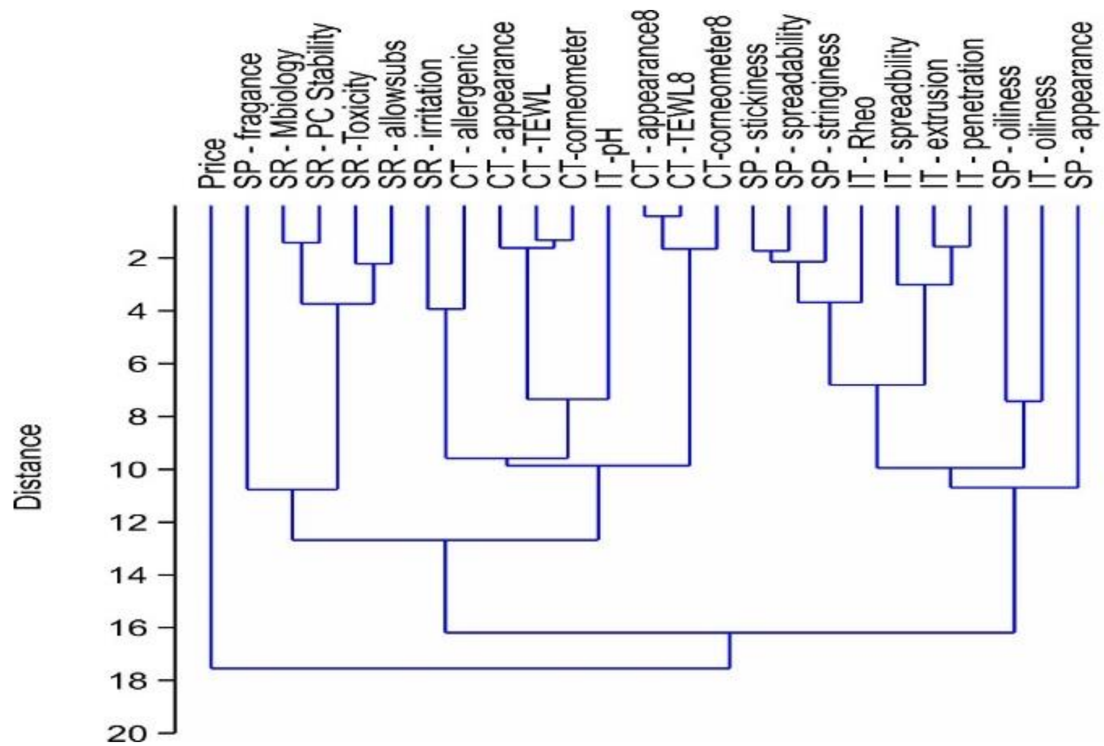

Figure 3-10. Clustering of product specifications

3.3.3.2 Needs translation into specifications – customer consultation

As explained in sub-section 3.1.3, customers are consulted to find target values for properties that translated needs related to sensations and feelings. Consultation was done following eight steps: **1)** Definition of the main idea of the design, **2)** Collection of customer words describing needs related to sensations, **3)** Selection of a semantic scale for needs related to sensations **4)** Definition of a list of product properties, **5)** Collection of product samples**, 6)** Characterization of product samples by: a) measuring product properties selected in step 4 and b) assessing product performance with the semantic scale defined in step 3, **7)** Statistical analysis **8)** Definition of target values. These steps were applied to the case study as described below:

1,2) Steps 1 and 2 were already done in section 3.2.1, where the design problem was presented, and in section 3.3.1, where customers were consulted and needs were identified and analyzed as shown in Table 3-8. From that list, seven needs were consulted with customers to assign to them the target values, because they are related to customer sensations. Those needs are listed in Table 3-14.

3) Semantic scale for evaluation: A five points scale was selected to assess product samples in relation to customer needs. Scales for the seven needs under analysis are presented in Table 3-14.

Table 3-14: List of needs to be consulted with the customers with the semantic scale

Needs	Sensation type	Semantic scale for evaluation*
1 - It has a soft or neutral aroma	Aroma	It has a very intense aroma (1), It has an intense aroma (0.75), It has an intermediate between intense and soft (0.5), It has a soft aroma (0.25), It has a very soft aroma (0)
3 - It is not oily*	Tactile sensation	It is very oily (0), It is oily (0.25), It is intermediated between oily and non-oily (0.5), It is not oily (0.75), It is not oily at all (1)
4 - It has a light texture*	Tactile sensation	It has a very thick texture(0), It has a thick texture (0.25), It has a texture intermediated between thick and light(0.5), It has a light texture (0.75), It has a very light texture (1)
5 - It spreads easily*	Tactile sensation	It spreads very slowly (0), It spreads slowly (0.25), It spreads between slowly and easily (0.5), It spreads easily (0.75), It spreads very easily (1)
6 - It is absorbed quickly	Tactile sensation	It absorbs very slowly (0) It absorbs slowly (0.25), It absorbs between quickly and slowly (0.5), It absorbs quickly (0.75), It absorbs very quickly (1)
12 - It gives a fresh feeling	Tactile sensation + Aroma	It is very fresh (1), It is fresh (0.75), It gives a feeling between fresh and non-fresh (0.5), It gives a low fresh feeling (0.25), It does not give a fresh feeling at all (0)
13 - It gives a sensation of vitality	Tactile sensation + Aroma	It gives a high feeling of vitality (1), It gives a feeling of vitality (0.75), It gives an intermediated feeling of vitality (0.5), It gives a feeling of low vitality(0.25), It does not give a feeling of vitality at all (0)

4) Product specifications: A texture test, two rheological tests (viscosity and oscillaroty) and a spreadability test were selected to represent specifications for the needs of Table 3-14. It was done, because, as it was established by experts in Table 3-13, the needs of spreadability, oiliness and light texture correlate well with rheological and instrumental measurements. Additionally, it was considered that the sensation of absorption is highly correlated to spreadability, reason why the same tests were used for its characterization. Conditions for the tests were similar to those proposed by Gilbert et al. (2013) in their study about sensory texture properties of cosmetic emulsions.

Needs related to product fragrance were linked to a categorical variable describing three fragrance types: floral, herbal, woody, and to an ordinal variable describing two levels of fragrance intensity: low and high.

The needs of feeling of vitality and fresh sensation were described by both, tactile sensations and fragrance, due to their complexity. Table 3-15 shows the tests and the properties measured. Tests conditions are explained in numeral 6 of this section.

Table 3-15: Product specifications to represent product properties

Properties	Test	Instrument of measure	Measured variables
Properties describing tactile sensations	Viscosity test	Rheometer	In this test it is possible to measured viscosity (η) and shear stress (σ) at different shear rates ($\dot{\gamma}$). Both dependent variables were measured at shear rates of 0.1, 1, 11, 111, 360 and 1000 s^{-1}
	Oscillatory test	Rheometer	In this test, viscoelastic properties of materials are studied at a constant frequency by varying the strain. Representative viscoelastic properties are: The elastic modulus (G') at the lineal viscoelastic region, the viscous modulus (G'') at the lineal viscoelastic region, the critical strain γ_{cr}, i.e., the point at which the lineal viscoelastic region is exceeded.
	Penetration test	Texturometer	In this test, the penetration force versus distance is measure when introducing a cylindrical probe under determined conditions. Representative variables are: penetration work, which is the area under the curve of force vs distance and the maximal penetration force which is the highest peak in the curve
	Spreadability	-	In this test, the displacement speed of a sample under a force is measured. In this case, a sample placed between two glasses is pressed with a determined weight and its displacement is measured after a determined period.

Properties	Test	Instrument of measure	Measured variables
Properties describing fragrance	-	-	Two variables are used to describe fragrance:- Categorical variable of fragrance: floral, herbal, woody - Ordinal variable for fragrance intensity

5) Collection of product samples:

To make easier the communication with customers, six samples with different tactile sensations and six samples with different fragrances were selected. The first group of samples were commercial lotions and creams with different textural properties. The second group of samples were mixtures of unscented cream with three different combination of essential oils (representing the fragrance type) in two proportions (representing fragrance intensity). Table 3-16 and Table 3-17 contain information about the 12 samples.

Table 3-16: Characteristics of product samples used to define desired tactile sensation of the moisturizing cream with the help of customers

Sample	Name and brand	Description	Picture
T1	Refreshing cleansing lotion Nivea – normal skin	Body lotion. It is light and very liquid. Flows easily	
T2	Johnson's body lotion suavidad prolongada - 24hours – normal skin	Body lotion. It is light and flows easily	
T3	Lubriderm extra hidratante – 24hours – crema hidratante corporal	Body cream. It is thick and leaves an oily sensation on skin. It is very moisturizing	
T4	L'oreal Hidra – total 5 Crema hidratante día	Facial moisturizing cream. It is thick and soft	
T5	Nivea regenerating night cream	Night facial cream. It is thick and rich	
T6	Personal choice Oatmeal with cooling action	Very thick cream with cooling effect when applied	

Table 3-17: Characteristics of product samples used to define the desired fragrance of the moisturizing cream with the help customers

Sample	Fragrance	Intensity level	Composition*
F1	Musky, woody - high intensity	High	0,4 % calendula oil
F2	Musky, woody - intermediate intensity	Low	0,2% calendula oil
F3	Musky, woody + herbal citric – high intensity	High	0,4 % calendula oil 0,2% lemongrass oil
F4	Musky, woody + herbal citric - intermediate intensity	Low	0,2% calendula oil 0,1% lemongrass oil
F5	Musky, woody + floral – high intensity	High	0,4 % calendula oil 0,2% geranium oil
F6	Musky, woody + floral - intermediate intensity	Low	0,2% calendula oil 0,1% geranium oil

* All essential oils were mixed within a cream without fragrance (Vasenol – intensive care – unscented). Essential oils were given by *Xiu Aguee*

6) Evaluation of product samples:

a) Instrumental evaluation:

Rheology tests: Two type of rheological test were applied to the samples: viscosimetry and oscillatory using a Bohlin C-VOR rheometer. Conditions of the tests were similar to those proposed by Gilbert et al. (2013).

The viscosimetry tests were done at 25°C using a geometry of cone and plate of 4°, 40 mm of diameter and a gap of 150μm. This geometry was selected considering the rheology of the majority of the samples (fluids with relative high viscosity that do not flow easily). The shear rate was varied in a continuous increasing ramp from 0.01 to 1000 s^{-1} in a period of 150s. 40 points were measured in a logarithmic scale. Each sample was evaluated by triplicate.

The oscillatory test was done under de mode amplitude sweep. The test was done at 25°C using a geometry of cone and plate of 4°, 40 mm of diameter. The gap was settled in 150μm as indicated by the rheometer fabricant. The frequency was fixed at 1 rad/s, the strain was increased from 0.01 to 100% and 40 equidistant points were measured in logarithmic scale. Each sample was evaluated by duplicate.

Texture test: A penetration test was done to all samples with a Brookfield CT3 texture analyzer. A normal test mode was implemented with similar conditions of those proposed by Gilbert et al. (2013). Each sample was loaded in a container of 70mm of diameter up to a high of 25 mm. A plastic probe of 12.7 mm was introduced 15 mm into the sample at a speed of 1m/s. The penetration work (area under the positive curve) and the maximal force (maximal positive peak) were measured by triplicate.

Spreadability test: Spreadability was measured as suggested by Montenegro et al., (2015). 0.5 g of each sample was placed between two glass slides (12 cm diameter) and a weight of 0,5 kg was put on the upper glass slide for 1 minute. The spread area of the sample after the weight is removed was measured.

b) Customers assessment: Fifty eight women students at the Universidad Nacional de Colombia in the age group from 20 to 29 years, who regularly use a moisturizing cream for at least 2 up to 5 times per week were asked to test the 12 product samples showed in Tables 3-16 and 3-17. Before the samples were given to participants, they were explained about the objective of the experiment, the needs under evaluation and the rating scale. The respondents were instructed to observe and apply a small portion (around 0.1 mL) of each of the first six samples (Table 3-16) in different areas of their hands and arms and to assess them with the needs related to tactile sensation of Table 3-14. Subsequently, they were instructed to smell the other six samples (Table 3-17), using a neutralizing aroma between each and to assess them with the needs related to fragrance of Table 3-14. Every sample was identified with a random number and tested in a random order, always first those related to tactile sensation and secondly those related to fragrance. For each sample, each need was evaluated in a semantic scale of 5 points as indicated in Table 3-14. The complete questionnaire is presented in Annex D.

7) Statistical analysis:

a) Results are summarized in Tables 3-18 and 3-19 and in Figures 3-11 and 3-12. A Friedman test was used to determine if there was any difference in sensory data with a significance of $p<0.05$. This test was selected because it is suitable for ordinal data with repeated measures. For data presenting a significant difference, a post hoc analysis of Wilcoxon signed-rank tests with a Bonferroni correction was done. Details are shown in Annex E.

Table 3-18: Customer assessment of samples T1-T6

	Lightiness	Spreadability	Fresh feeling	Feeling of vitality	Rapid absorption	Oiliness	Total (without oiliness)
Sample T1	0.75 a	0.75 a	0.75 a	0.75 a,b	0.50 a,b	0.75 a	3.50
Sample T2	0.50 b	0.75 a	0.75 a	0.75 b	0.75 a	0.50 a	3.50
Sample T3	0.25 c,d	0.25 b	0.50 b,c	0.50 a	0.25 b	0.50 a	1.75
Sample T4	0.50 b,c	0.50 c	0.75 a,c	0.50 a,b	0.50 a	0.50 a	2.75
Sample T5	0.25 d	0.50 b,c	0.50 b,c	0.50 a	0.50 a,b	0.50 a	2.25
Sample T6	0.25 d	0.50 b,c	0.75 a,c	0.50 a,b	0.50 a,b	0.38 a	2.50

Table 3-19: Customer assessment of samples F1-F6

	Fragrance intensity	Fresh fragrance	Feeling of vitality
Sample F1	0.63 b,d	0.50 a	0.50 a
Sample F2	0.38 c	0.50 a	0.50 a
Sample F3	0.75 a,b	0.75 b	0.75 b
Sample F4	0.50 c,d	0.75 b	0.75 b
Sample F5	0.75 a	0.50 a	0.50 a
Sample F6	0.50 b,c	0.50 a	0.50 a

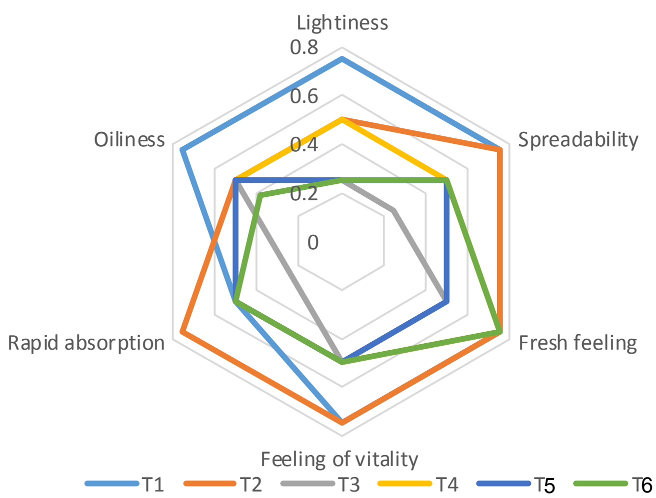

Figure 3-11. Customer assessment of samples T1-T6

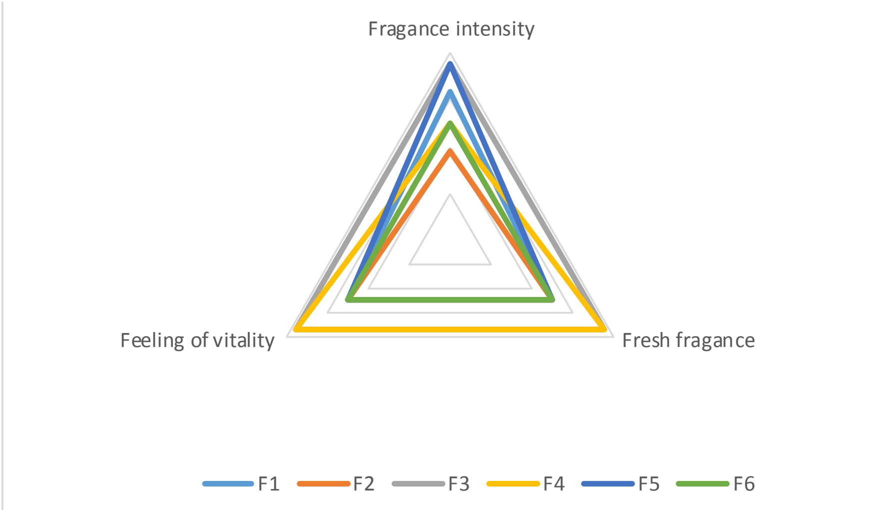

Figure 3-12. Customer assessment of samples F1-F6

The results of the tactile sensation experiments in Table 3-18 and Figure 3-11 show that:

- Customers found differences between the analyzed samples, except for the characteristic of *oiliness,* which does not show any statistical difference.
- It seems that there is a correlation between the characteristics *spreadability* and *feeling of vitality*, because the median for both are equal for five of six samples.
- Considering that, except for oiliness, all characteristics in Table 3-18 are seen positively by customers (as it was established with Kano model). Samples 1 and 2 showed the highest results in relation to customer satisfaction than other samples and sample 3 showed the lowest. Therefore, the product to be designed has to be similar to the first two samples and different to the third.

The results of the fragrance experiments in Table 3-19 and Figure 3-12 showed that:

- Customers found differences between the analyzed samples
- The mixture of calendula oil and lemongrass oil (samples F3 and F4) showed the highest level of fresh sensation and feeling of vitality, reason why this mixture will be used in the product to be designed.
- Intensity was high for almost all samples except for F2 (see Figure 3-13). This is not desired by customer, because they expressed to prefer soft to neutral fragrance according to Kano model results (section 3.3.2). Concentration of the essential oils should not be higher than the used in sample F2.

b) Results of texture analysis and spreadability are shown in Table 3-20. When possible, ANOVA analysis was applied to determine if there were differences between samples. For data with a significant difference, a post hoc Turkey analysis was done. Details can be found in Annex E. Rheological results are shown in Figures 3-13 and 3-14. Figure 3-13 compares the viscosity of the samples at different shear rates. All test were done by triplicate except for the oscillatory tests, which were done by duplicate. Results of oscillatory test are shown in Figure 3-14.

Table 3-20: Instrumental assessment of samples T1-T6

Sample	Penetration_work (P-work)*						Maximal_force (p-max)*						Spreadability			
	mean [mJ]	Error					mean [mJ]	Error					mean [mm]	Std		
T1	0.5	+	0.1	-	0.1	a	7.7	+	0.6	-	0.6	a	72.4	±	1.3	a
T2	1.1	+	0.2	-	0.2	b	13.1	+	1.1	-	1.0	b	59.8	±	0.8	b
T3	1.4	+	0.0	-	0.0	b	13.2	+	0.3	-	0.3	b	85.3	±	4.1	b
T4	2.2	+	0.0	-	0.0	c	24.2	+	0.3	-	0.3	c	62.7	±	1.9	c
T5	3.7	+	0.1	-	0.1	d	38.5	+	0.9	-	0.9	d	56.3	±	1.7	d
T6	5.7	+	0.7	-	0.7	e	64.5	+	8.2	-	7.3	e	56.3	±	2.0	e

* Anova were applied to square root transformed data

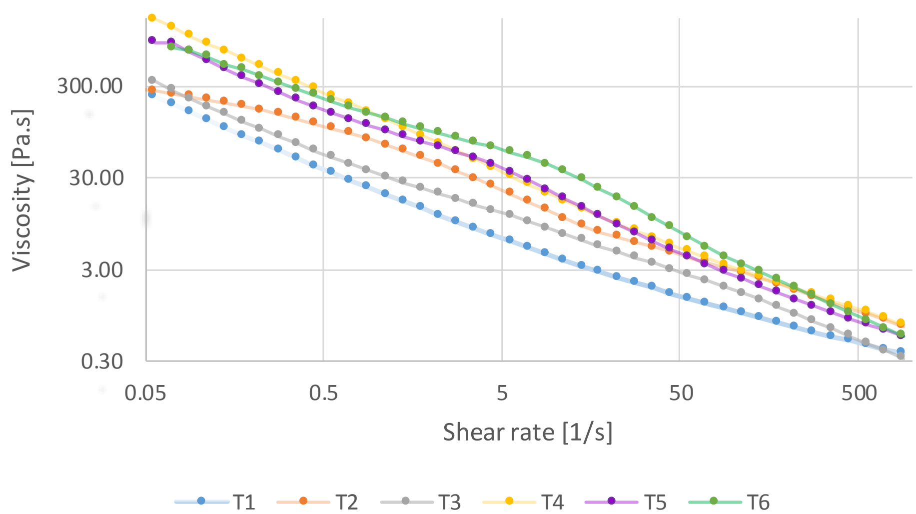

Figure 3-13. Viscosity as a function of shear rate for the six samples employed to translate needs into specifications by consumer consultation. Test were done by triplicate and the mean is plotted.

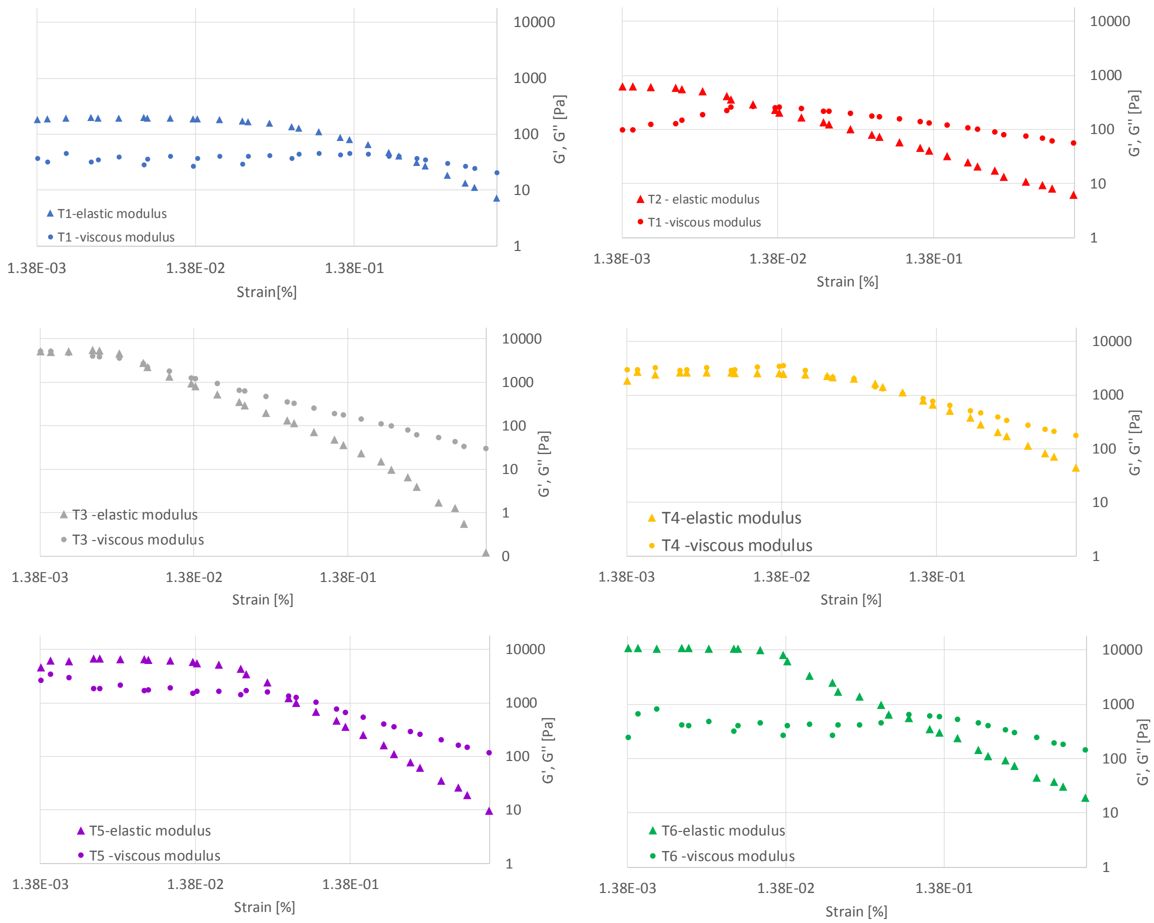

Figure 3-14. Oscillatory test for the 6 T samples (T1-blue, T2-red, T3-gray, T4-yellow, T5-purple, T6-green). Triangles correspond to elastic modulus G' while circles correspond to viscous modulus G''.

The results of the penetration test show that:

Sample 6 exhibited the highest penetration work and the firmest aspect, while sample 1 and 2 showed the lowest penetration work and tend to be more fluid. Additionally, samples 1 and 3 showed higher spreadability than the others.

Viscosity test results in Figure 3-13 showed that samples 1, 2 and 3 had the lower viscosity in the complete range of shear rate in comparison to the others. Sample 2 had the lowest shear tinning behavior with the smallest change in viscosity within the range of shear rate for all of analyzed samples.

Oscillatory results presented in Figure 3-14 showed that in almost all samples, except for samples 4, the elastic modulus (G') is higher than the viscous modulus (G'') in the lineal viscoelastic range, which means that samples had an important elastic behavior. Samples 1 and 2 exhibited the lowest values for G' and G'', and in samples 3 and 4, G' and G'' were very close to each other in the linear viscoelastic region.

PCA was applied to instrumental variables in order to observe any correlation between them and to simplify the multidimensionality of the problem.

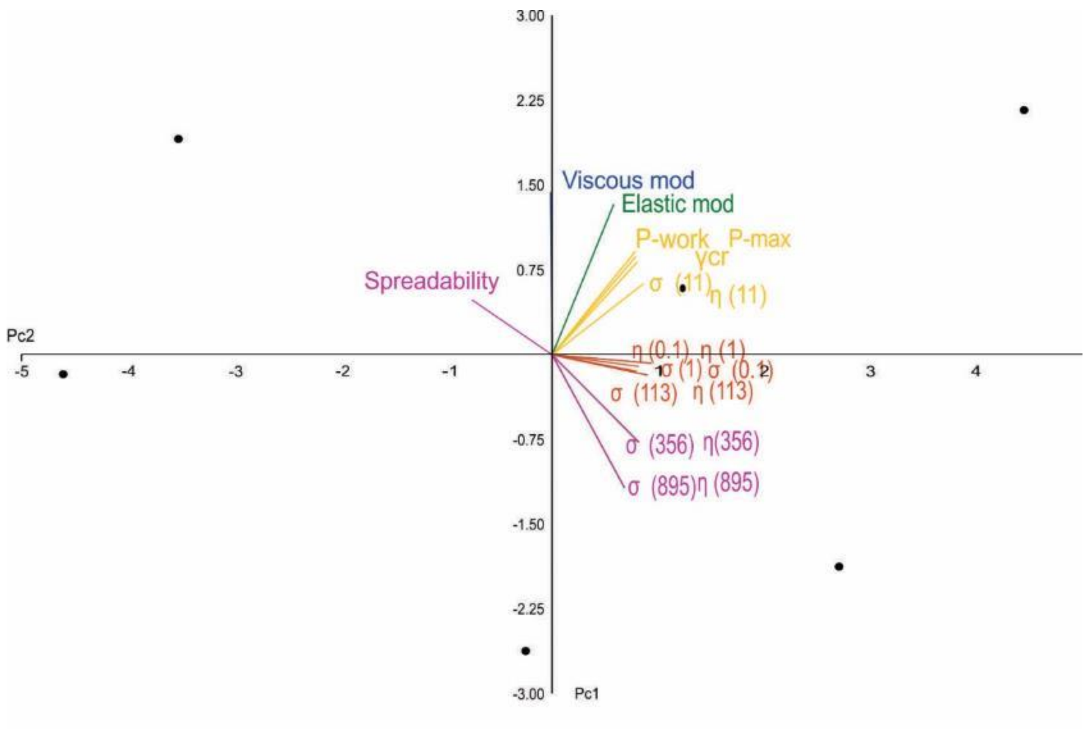

Figure 3-15. PCA of product specifications, the two first components explain around the 90% of the variance

Instrumental variables showing correlation in the PCA plot were grouped forming five groups of variables (shown in different colors in Figure 3-15). From each group, a variable was defined as representative, trying to select for this purpose different type of variables measured in different test. Selected variables were: viscosity ($356s^{-1}$), shear stress ($0.1s^{-1}$), penetration work, elastic modulus and viscous modulus. This variables were used as specifications for representing customer needs related to sensations.

With the selected specifications, k-clustering was applied to the samples to determine similarities and differences between them, considering:

1) 2-clusters with only viscosity related variables (viscosity (356s^{-1}), shear stress (0.1s^{-1}))

2) 2-clusters with oscillatory and penetration test variables (penetration work, elastic modulus and viscous modulus)

3) 3-clusters with all variables together

Results are shown in Figures 3-16, 3-17 and 3-18. In these figures, it can be seen that, when only viscosity variables were considered, samples 1, 2 and 3 belonged to the same cluster, which does not correspond exactly to customer assessments, where sample 3 was rated as having a poor development in relation to all needs in comparison to sample 1 and 2. When oscillatory and penetration test variables were considered, samples 1,2 and 4 showed to be similar, which corresponds better to customer assessments as shown in Table 3-18, where these three samples had the best general rating. Figures 3-16 and 3-17 showed that it is necessary to consider more variables in addition to viscosity at different shear rates to be able to find differences between samples, as customers did. When all representative properties were (Figure 3-18) considered and three clusters were formed, samples 1, 2 merged in a cluster, sample 3 remained alone and samples 4, 5 and 6 formed a third cluster, which corresponds well with customer expressed sensations.

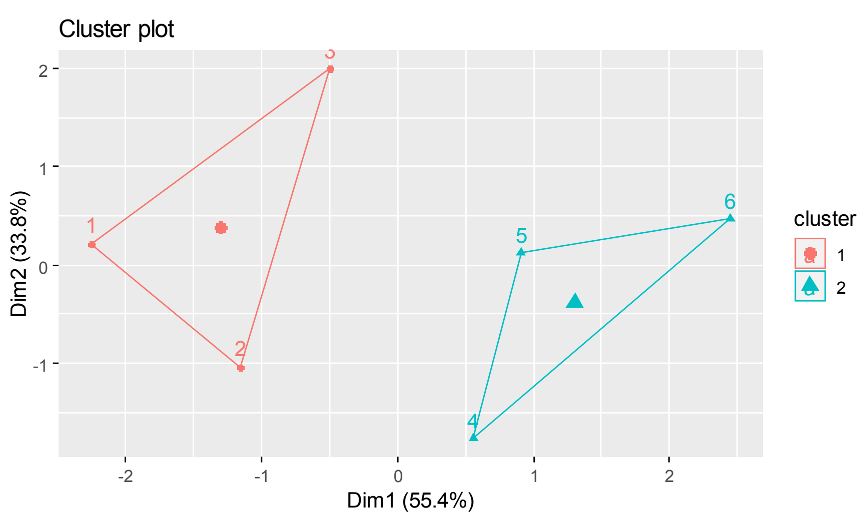

Figure 3-16. K-clustering considering rheological variables (2-centers, 25 start points)

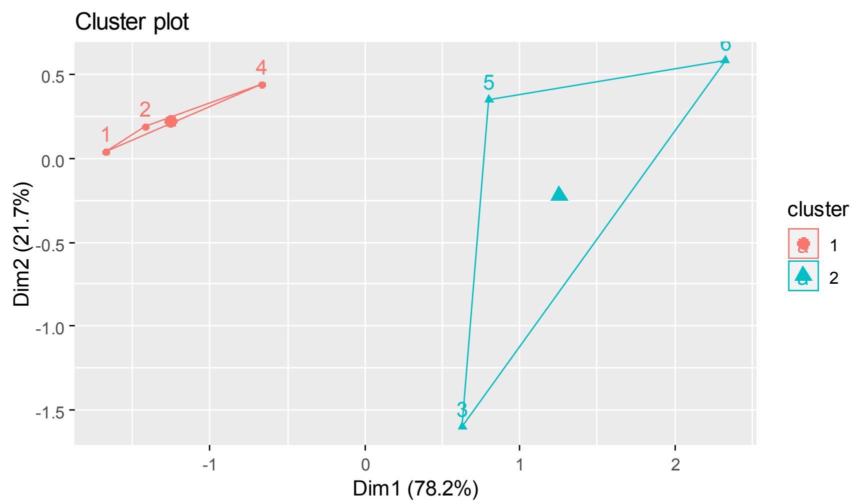

Figure 3-17. K-clustering considering oscillatory and penetration test variables (2-centers, 25 start points)

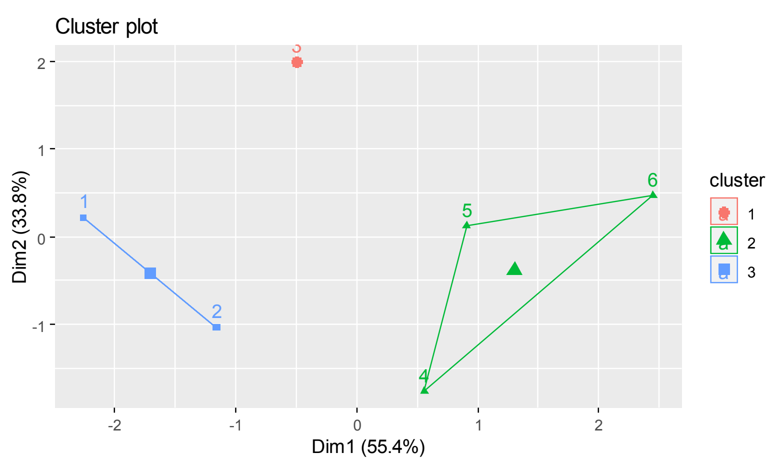

Figure 3-18. K-clustering considering all variables (3-centers, 25 start points)

Considering previous analysis, and the fact that samples 1 and 2 were the best rated in all needs assessed by customers, target values were defined as an interval where the limiting values are those measured in these two samples. Table 3-21 summarizes customer needs related to sensations with the selected product specifications and with their corresponding target values.

Table 3-21: Specifications and target values for customer needs related to customer sensations

<table>
<tr><th>Needs</th><th>Product specifications</th><th>Specification target values</th></tr>
<tr><td>Q1 - It has a soft or neutral aroma</td><td>Fragance intensity
Fragance type</td><td rowspan="7">For fragrance:
- Herbal fragrance type
- Fragance concentration < 0.2%

For rheological and texture analysis specifications
- η (356) [Pa.s] : 0.56 – 1.30
- σ (0.1) [Pa] : 14.3 – 23.9
- Penetration work: 0.5 – 1.1
- Elastic modulus: 192 – 630 far from 5260 (value of sample 3)
- Viscous modulus: 46 – 97 far from 4700 (value of sample 3)

Oiliness by a sensory</td></tr>
<tr><td>Q3 - It is not oily</td><td>Sensorial evaluation of oiliness*</td></tr>
<tr><td>Q4 - It has a light texture</td><td>Rheological, texture measurements</td></tr>
<tr><td>Q5 - It spreads easily</td><td>Rheological, texture measurements</td></tr>
<tr><td>Q6 - It is absorbed quickly</td><td>Rheological, texture measurements</td></tr>
<tr><td>Q12 - It gives a fresh feeling</td><td>Rheological, texture measurements
Fragance intensity
Fragance type</td></tr>
<tr><td>Q13 - It gives a sensation of vitality</td><td>Rheological, texture measurements
Fragance intensity
Fragance type</td></tr>
</table>

* The need of oiliness remains untranslated because it was not possible to find a statistical significant difference between customer assessments of samples. To correct this it is possible to a) survey new customer b) assess more samples, b) left the need untranslated and test product prototypes in a sensory sensorial test.

3.3.4 Partial results of the needs stage

Results from the previous three sub-sections are summarized in the structure of QFD presented in Table 3-22.

Table 3-22: QFD of the case study

				Safety and Regulation					Sensorial evaluation						Performance evaluation							instrumental tests						Price	Additional
				1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26
				Physical/chemical stability	Toxicology	Microbiological quality	Use of allowed substances	Dermal tolerance and non-irritability	Stickiness	Product appearance/odor	stringiness	Product odor	Oil on skin	Spreadability	Skin appearance	Skin appearance 8h after application	Allergenic test	TEWL	TEWL 8h after application	Corneometer	Corneometer 8h after application	Rheological profile	Instrumental measurement - oil	Texturometer - Spreadability	Texturometer - extrusion test	Texturometer - penetration test	pH	Product price	Antioxidant test DPPH
Needs		Kano category	Importance																										
Apperance	0. Pleasant appearance	must-be	1	8.2	5.4	7.2	4.3			8.6																		7.2	
Odor	1. It has a soft or neutral aroma	One dimensional	0.71	7	7	7	5			9																			
	2. Aroma is nice	must-be	1	7.5	6.7	7.8	5.2					8.5																7.7	
Tactile sensation	3. It is not oily or sticky	One dimensional	0.88						6.0	7.2	5.1		7.9	5.4								4.7	6.8					5.5	
	4. It has a light texture	Attractive	0.73						8.0	7.2	7.2	3.3	7.2	7.3								7.5	5.5	6.6	4.1	5.6		5.5	
	5. It spreads easily	One dimensional	0.74						7.4	6.3	6.6			8.5								7.9		7.4	5.7	5.7		5.5	
	6. It is absorbed quickly	One dimensional	0.73						5				5	7								7	5	7	3	5			
Functional	10. Leaves skin soft and hydrated	must-be	1												6.8			8.2		7.3							5.4	5.9	
	11. It provides prolonged hydration	must-be	1													7.6			7.8		7.3						5.4	6.8	
Feelings	12. It gives a fresh feeling	One dimensional	0.64	7	7	7	5			9												7	5	7	3	5			
	13. It gives a sensation of vitality	One dimensional	0.58	7	7	7	5			9												7	5	7	3	5			
Natural ingredients	17. It has ingredients of natural origin	One dimensional	0.69	4.5	4.6	3.7	5.4	6.2		3.1		3.9					5.2										2.4	6.6	
Functional	23. it prevents wrinkles	Attractive	0.56																										7
Non side effects	27. It is not irritating or allergenic/safe and reliable	must-be	1	7.5	7.0	8.2	8.5	8.6							6.9	6.9	7.4	6.3	6.7	5.5	5.4						7.9		
	28. It is compatible with sunscreen and makeup*	must-be	1																										
Price	29. It is affordable	must-be	1												3.7	3.4	3.6	3.6	3.8	3.0	2.9	3.3	2.8	3.2	2.6	2.5		5.9	
			Kano categories	must-be	must-be	must-be	must-be	must-be	One-dimensional	must-be	One-dimensional	must-be	One-dimensional	One-dimensional	must-be	must-be	must-be	must-be	must-be	must-be	must-be	One-dimensional	One-dimensional	One-dimensional	One-dimensional	One-dimensional	must-be	must -be	attractive
			Impotance	39.8	35.8	39.3	31.3	12.9	20.2	44.3	14.7	13.7	15.9	21.5	17.5	18.0	14.6	18.0	18.2	15.7	15.6	32.5	22.5	27.2	15.7	20.5	20.4	51.0	3.9
			Normalized importance	0.78	0.70	0.77	0.61	0.25	0.40	0.87	0.29	0.27	0.31	0.42	0.34	0.35	0.29	0.35	0.36	0.31	0.31	0.64	0.44	0.53	0.31	0.40	0.40	1.00	0.08
			Test	Shelf stability	Information search	Count of miscroorganim	Information search	Information search	Sensorial test	Sensorial test	Sensorial test	Sensorial test	Sensorial test	Sensorial test	Sensorial test	Sensorial test	Information search	-	-	hidration index -corneometer	hidration index -corneometer	Rheolica test test	-	-	-	-	-	-	
			Targert values	6 months	Only allowed substances	less than 103 cfu/g	Only allowed substances	Use of substances	3 over 5	4 or 5 over 5	3 over 5	4 or 5 over 5	4 or 5 over 5	4 or 5 over 5	Skin dryness absent	Skin dryness absent	-	-	-	HI over 50	HI over 50	*Values in Table 3-12	-	-	-	*Values in Table 3-12	6-7*	5 euro - 10 euro*	

Notes

The relations that were no defined by the design experts, were agreed by the design team./ Need 8 is correlated with 6 and 3. It is assume that if these two are achieved, need 8 will be also achieved./ Need 9 is correlated with needs 10 and 11. It is assumed that if these two are achieved, need 9 will be also achieved./ pH is defined to be slightly acid to neutral because to protect essential oils from hydrolysis./ Price is defines based on benchmarking and customer consultation./ In this example, instead of calculating an importance using kano categories as suggested in equations 3-12, Kano categories were transferred from needs to product specifications to keep their meaning during the design stage. An specification took a kano category when it has an interrelation with a need with this kano category higher than 5.If a specification is related by an index superior than 5 with more than one need, and the needs have different Kano categories, the specification is first classified as must-be specification, if there is a must-be need. And secondly, it is classified as one-dimensional, if there is a one-dimensional need./Test are explained in AnnexA

3.4 Conclusion

In this chapter, methods for need analysis and translation of needs into product specifications were presented and applied to the case study. The needs stage begins with customer needs identification, which are described in non-technical terms, and ends with product specifications expressed mostly with measurable target values. For this transformation three steps and two methods are used: First, customer needs are analyzed using Kano model, a method based on customer responses to a questionnaire, that classifies needs into four categories: one-dimensional needs (optimization goals of the design problem), must-be needs (constrains of the design problem), attractive needs (optional needs to be included into the design problem) and indifferent needs (needs to be excluded of the design problem). Second, based on the information structure of QFD, needs are transformed into specifications by asking experts to assess the relationship between analyzed needs and product specifications. Third, target values are assigned to product specifications based on customer consultation and a literature review. Figure 3-20 shows the information connection.

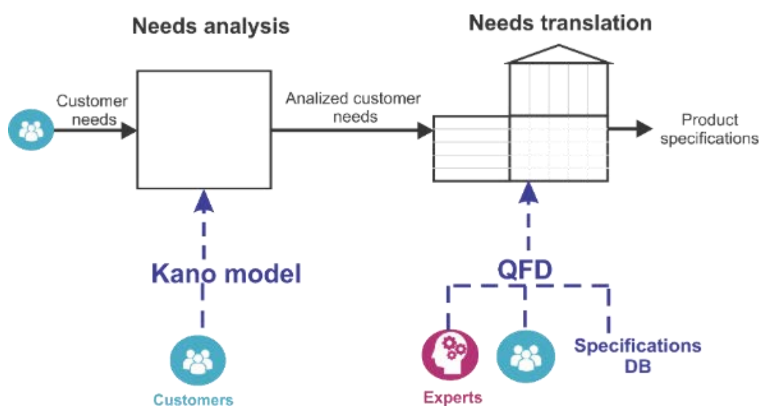

Figure 3-19. Information connection – Need stage

The case study evidences the important role played by both, experts and customers, to analyze and translate customer needs. The communication with customers is easier with the use of product samples, a flexible tool that enable their active participation in the design process and a better understanding of their needs. Besides, experts have a huge knowledge not only related to technical procedures but also about customer and their needs. The formalization of this knowledge is an imperative that can be achieved by expert consultation and data analysis, as it was shown in the case study.

4. Product design

In product design stage, designers' work is to devise product prototypes meeting the specifications defined in the previous stage. As described before, this is not a simple task because emulsions are complex systems in which its components, structures, phenomena and processes are highly interrelated. Thus, any design decision has to be made considering its multiple effects in final product properties.

To overcome that difficulty, this study proposes a methodology that considers the multivariate nature of the problem enabling product designers to explore systematically the solution space and to create possible design options. The methodology workflow comprises the following three steps and uses two matrix data bases as shown in Figure 4-1:

- In the first step, product specifications are classified according to a list of 21 general sub-problems, which were previously defined based on emulsion science principles. Sub-problems are phenomena or interactions that are wanted to happen or not. Examples of them are emulsion viscosity, emulsion viscoelasticity behavior and emulsion stability, among others.
- In the second step, sub-problems are connected to a list of 34 general solution strategies. Solution strategies are general solution paths predefined based on emulsion science principles and related to emulsion structure and nature but at first not directly related to a specific compound or processing technology. Examples of them are: the use of a type of emulsifier system, increasing/decreasing droplet or particle size, changing emulsion pH, among others. The connection between sub-problems and solution strategies is possible thanks to a first relational matrix that was previously filled taking advantage of expert's knowledge. Each solution strategy works as a building block for the product concept. In this way, the designer can define sets of compatible solutions strategies for a specific product design problem, identifying their interrelations, trade-offs and synergies.

- In the third step, solutions strategies are connected to ingredients and processing conditions thanks to a second relational matrix. This matrix links solution strategies to a database of compounds and processing conditions in order to create possible design concepts.

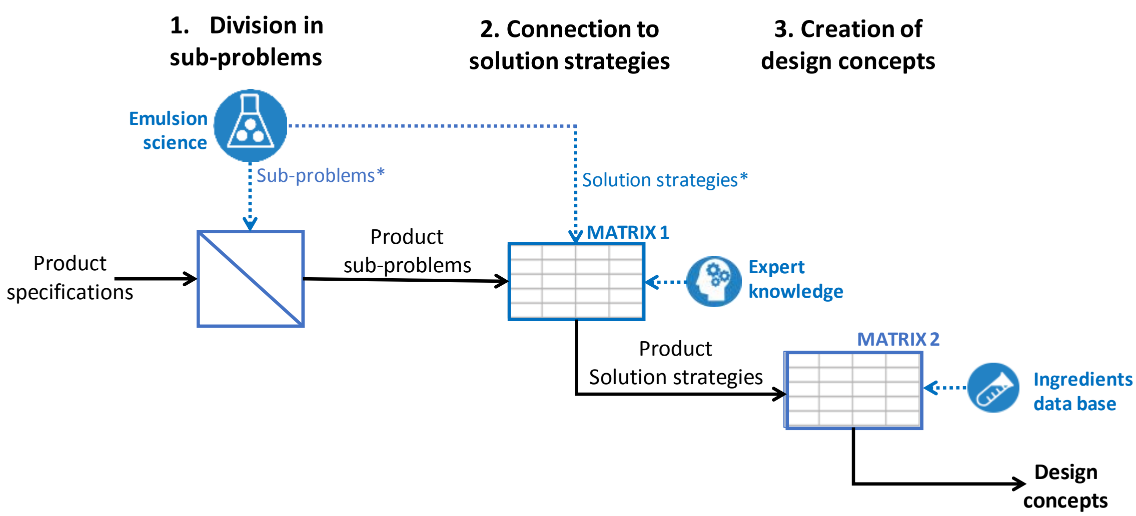

Figure 4-1. Product design stage workflow

This chapter begins presenting the elements of the methodological framework: the list of sub-problems, the list of solution strategies the first relational matrix and the structure of the second relational matrix. Subsequently, it explains how these elements can be used to make design decisions. Finally, the methodological framework is applied to solve the case study and based on the results, product prototypes are prepared and analyzed. This approach was inspired by a decision methodology applied in the field of process intensification (Commenge and Falk, 2014).

4.1 Methodological framework for product design stage

4.1.1 Sub-problems and solutions strategies for emulsion based product design

The lists of sub-problems and solutions strategies were defined based on a literature review. The search was focused on physicochemical aspects of O/W emulsions of low and intermediated concentration (maximum 30% oil concentration). The objective was to be as exhaustive but as general as possible. Therefore, publications containing emulsions science basic principles were prioritized. Emulsions science is a huge and complex discipline and there are many non-typical examples of emulsion behavior that could not be covered in the method presented here. Table 4-1 explains sub-problems classified into five categories: appearance, rheology, stability, transport phenomena, special functions. This last category corresponds to those functions connected to special ingredients, as for example U.V. protection or antioxidant effects and it is directly connected to the data base. Table 4-2 shows solution strategies classified into seven categories: aqueous phase, oily phase, interface and relations between phases, colloidal forces, emulsion structure, environmental conditions and functional ingredients.

Table 4-1: List of general sub-problems

Sub-problems	Phenomena/causes	Factors affecting sub-problems (possible solution strategies)
Appearance		
1. Emulsion lightness	Emulsion lightness (emulsion whiteness or milky appearance) is caused by light scattering, a phenomenon in which light is driven into multiples directions different from the incident angle when it meets a surface (McClements, 2016). Light is scattered by both particles and droplets. Raleigh theory models this phenomenon for one droplet as shown in equation 4-1 (McClements, 2016). $I = \frac{8\pi^4 r^6}{d^2\lambda^4}\left(\frac{\left(\frac{\eta_1}{\eta_0}\right)^2-1}{\left(\frac{\eta_1}{\eta_0}\right)^2+2}\right)(1+cos2\theta)$ [4-1] ,where I is the Raleigh scattering intensity, which depends on the angle r is the droplet radius λ is the wavelength of light d is the distance from the droplet to the detector η_0, η_1 are the refractive indices of continuous and disperse phase θ is the scattering angle Although Eq. 4-1 is valid just for small droplets, it shows that light scattering depends on the incident light characteristics, droplet size and the relation of refractive indices of phases.	Observing equation 4-1, it is possible to deduce that emulsion lightness can be changed by modifying the following parameters: **- Difference between refractive index**: Light scattering increases with the difference between the refractive indices of the continuous and dispersed phases. Emulsion turns transparent if they are equal. **- Droplet size:** The appearance of an emulsion goes from transparent to opaque and then again to transparent as the particle size is increased (McClements, 2016): Nano-emulsions are transparent (Mcclements, 2010). As diameter increases emulsions tend to be opaque. Maximum lightness can be found in diameters between 0.1 and 1.5µm, depending on concentration (Chantrapornchai et al., 2008). As diameter increases more, emulsions turn transparent again and droplets become observables. **- Light source:** Emulsion appearance depends on light source (day light, lamp light, etc.). This condition has to be considered for emulsion design. Other factors affecting emulsion lightness are: **- Dispersed phase volume fraction (ϕ):** Light scattering increases with volume fraction because light can be multiple- scattered by the increasing number of droplets. Dilute emulsions are transparent. **- Induce/ avoid weak flocculation:** There is evidence that flocculation has a slightly effect on emulsion lightness, because flocs are aggregates of droplets with higher diameters than its constituents (Chantrapornchai et al., 2008). **- Dye concentration:** if dyes are added to the emulsion, its increment causes a decrease in lightness because more of the light is absorbed by the chromophores within the dye (Chantrapornchai et al., 2008).

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2. Color hue	Color hue (spectrally pure color without considering intensity) is caused mainly by the structure of colorants. Colorants absorb some wavelength more than others, which results in different colors when different molecules are used.	The main factor affecting color hue is the identity of the selected colorant.
3. color intensity	Color intensity can be characterized in terms of absorbance (A), which is proportional to the concentration (c) of colorant and its absorptivity (α) (McClements, 2016). $A \propto c\alpha$ [4-2] ,where A is the absorbance, c is colorant concentration, α is colorant absorptivity	As shown in equation 4-2, strategies to modify color intensity are: **-Selection of colorant:** Absorptivity α is a property of the specific colorant molecule. Colorants with a greater absorptivity will generate more intensity at the same concentration than the others. **- Colorant concentration** **- Modification of emulsion lightness:** In general, the behavior of color intensity is inverse to emulsion lightness (Chantrapornchai et al., 2008), when lightness increases color intensity decreases.
4. Special color features	Different phenomena can be considered to drive a desired special color feature.	- **Additives:** Select additives with functional principles that bring color special features. Examples are thermo- chromic pigments and pearl pigments, among many others. Phenomena behind these additives have to be analyzed in order to select the better conditions for their used.
Rheology		
5. Viscosity	**- Viscosity (η) and dispersed phase volume fraction (ϕ)**: Emulsion viscosity augments progressively with dispersed phase volume fraction (Derkach, 2009). For low concentrations ($\phi < 0.05$), viscosity increases linearly with ϕ (equation 4-3) (Tadros, 2010) and for intermediate and high concentrations, viscosity increases more rapidly, as indicated by Dougherty and Krieger model (equation 4-4) (McClements, 2016). It is to note that an increase in volume fraction also causes a deviation from the Newtonian behavior (Tadros, 2010). $\eta = \eta_0(1 + [\eta]\,\phi)$ [4-3]	Solution strategies that can be visualized to modify viscosity are: - **Volume fraction:** As observed in equations 4-3 and 4-4, the increment of volume fraction produces a more viscous emulsion. The effect is more important at higher concentrations. - **Effective volume fraction** (ϕ_{eff}) and repulsive forces: Increasing the magnitude of repulsive forces augments the effective volume fraction and consequently the viscosity of the system. Strategies to enhance/reduce repulsive forces and their effect on viscosity depend on their nature: Electrostatic interactions are stronger at low electrolyte concentration and change with the pH depending on the isoelectric point of surfactant (Tadros,

Sub-problems	Phenomena/causes	Factors affecting sub-problems (possible solution strategies)
	$\eta = \eta_0 \left(1 - \frac{\phi}{\phi_c}\right)^{-[\eta]\phi_c}$ [4-4] ,where η_0 is the viscosity of the continuous phase, $[\eta]$ is the intrinsic viscosity, ϕ_c is the packing parameter **- Viscosity and repulsive forces:** Surfactants create an interfacial layer that separates droplets from the continuous phase. When the thickness of this layer (δ) is comparable with the droplet radius (r), there is an increase in the effective volume fraction (ϕ_{eff}) that causes an increase in viscosity (McClements, 2016). **- Viscosity and flocculation**: Emulsions with flocs have a higher viscosity than non- flocculated systems due to their higher effective volume fraction, caused by the formation of agglomerates having a part of the continuous phase inside them (McClements, 2016).	2010). For its part, steric forces are affected by the relation between the solvent and the solvated molecule segment (Tadros, 2010). -**Effective volume fraction and flocculation:** Flocculation increases effective volume fraction and emulsion viscosity (McClements, 2016). - **Viscosity of the continuous phase:** The effect of the viscosity of the continuous phase on emulsion viscosity is multiplicative as reflected in equation 4-3 and 4-4. Rheological additives or temperature changes vary significantly emulsion rheological behavior (Barnes, 1994). - **Droplet size** does not have an important effect on emulsion viscosity at low concentrations. However, as volume fraction increases droplet size begins to play an important role. For small particles, when $\delta \approx r$ the effective volume fraction increases and emulsion viscosity also increases substantially. - **Droplet size distribution:** increasing the width of the distribution increases the maximum packing fraction and reduces viscosity in comparison to systems with a narrow distribution (Barnes, 1994).
6. Shear thinning behavior	In fluids with this behavior, viscosity decreases as the shear rate increases. Equation 4-5 shows a model for this behavior. $\tau = k\dot{\gamma}^n$, with $n < 1$ [4-5] , where τ is the shear stress, $\dot{\gamma}$ is the shear rate, k is a proportional constants and n is an exponent smaller than 1. Shear thinning behavior may appear at intermediate and high concentrations ($\varphi > 0.2$) (Derkach, 2009), when hydrodynamic and Brownian interactions and their relation gain importance. At low shear rates, Brownian forces predominate and concentrated emulsions show a high viscosity. At high shear rates, hydrodynamic forces predominate and particles flow in a more organized manner, causing a decrease of viscosity (McClements, 2016). Thanks to this effect, viscosity goes from a constant maximal value at low shear	Shear thinning behavior may become noticeable at high Peclet numbers, i.e., at high shear rates, large particles and high continuous phase viscosity (McClements, 2016). Other factors affecting this behavior are: - **Volume fraction (ϕ):** An increase in volume fraction may generate shear thinning behavior due to enhance of hydrodynamic interactions between droplets. The behavior becomes more pronounced at higher volume fractions, causing viscosity from low to high shear rates to be of various orders of magnitude (McClements, 2016). Volume fraction can be increased by adding more disperse phase, or by increasing effective volume fraction. The latter can be increased by enhancing repulsive interactions or flocculation in the system (See viscosity row). - **Rheological modifiers:** Additives can be used to generate a shear thinning behavior. Examples are xhantan gum, guar gum, carbomers and polyethylenes (Laba, 1993). - **Form of the particles/soft droplets**: suspensions with non-spherical particles or emulsions with soft droplets (for example, droplets that were

Sub-problems	Phenomena/causes	Factors affecting sub-problems (possible solution strategies)
	rates to a minimal constant value at high shear rates (McClements, 2016). Péclet number (Pe) compares hydrodynamic and Brownian forces (McClements, 2016): $Pe = \frac{\dot{\gamma}}{D_R}$ [4-6] where $\dot{\gamma}$ is the shear rate and D_R is the rotational Brownian diffusion coefficient (equation 8 for spheres(McClements, 2016))	electrostatically stabilized an can be deformed at high shear rates) may show shear-thinning behavior, even at low volume fractions (McClements, 2016).
7. Thixotropic behavior	A thixotropic fluid is one in which the apparent viscosity decreases reversibly with time when the fluid is subjected to a constant shear rate (Tadros, 2010). After the shearing is retired, the fluid needs some time to recover its original higher viscosity (Tadros, 2010).	Possible solutions strategies to enhance this behavior are: - **Volume fraction:** An increase in volume fraction may lead to an structure formation that can be destroyed and restore at different shear rates (Derkach, 2009) - **Flocculation:** Flocculation at relative high volume fractions create structures with thixotropic behavior (McClements, 2016). If this is used as strategy to achieve this behavior, attention should be pay to emulsion stability. - **Rheological modifiers**: Additives can be used to enhance this behavior. Examples are: cellulose gum, clays, fumed silica (Laba, 1993).
8. Viscoelastic behavior	A viscoelastic material behaves solid-like and liquid-like simultaneously. This means that when a force is applied, part of the energy is stored and part is dissipated (McClements, 2016). Viscoelastic behavior is characterized by a complex elastic modulus (G^*), which comprises an elastic (G') and a viscous (G'') contribution (McClements, 2016). $G^* = G' + iG''$ [4-7] Solid-like emulsions present a yield stress (σ), which is the onset of flow (Tadros, 2010).	Possible parameters to consider in relation to viscoelastic behavior are: - **Volume fraction (ϕ):** Viscoelastic behavior becomes evident as volume fraction increases and nears the packing parameter (ϕ_c). This behavior can also be achieved at lower concentrations when the value of the packing parameter is low, for example when colloidal forces are important (McClements, 2016). At this conditions, the elastic modulus (G') becomes higher than the viscous modulus (G'') and emulsions can be treated as elastic materials and characterized in terms of the elastic modulus and yield stress (Derkach, 2009)(Francois Lequeux, 1998). In general terms, the elastic modulus increases with increasing volume fraction, decreasing droplet size, and increasing strength and range of repulsive interactions (McClements, 2016).

Sub-problems	Phenomena/causes	Factors affecting sub-problems (possible solution strategies)
		- **Rheological modifier:** Viscoelastic behavior is also observed in solutions and emulsions containing polymeric rheological modifiers. - **Effective volume fraction and flocculation**, to the extent that they help to increase effective volume fraction, can also be used as solution strategies to enhance viscoelastic behavior.
	Stability	
9. Gravitational forces	Creaming or sedimentation happens when droplets or particles move upwards or downwards within emulsion and form a visible layer. The driving force of this phenomenon is the difference of density between the phases, which enhance separation by gravity (Tadros, 2009). For O/W emulsions, density of droplets is normally smaller than density of the continuous phase, which causes creaming. The velocity at which droplets cream (ν) depends on the balance of difference forces: gravity, hydrodynamic, Brownian forces and colloidal interactions, which are stronger or weaker depending on emulsion concentration and particle size. - **For dilute emulsions** ($\phi < 0.01$) with no interacting particles, stokes' equation can be implemented to calculate ν (Tadros, 2009). $\nu = \nu_0 = \frac{2}{9}\frac{\Delta\rho g r^2}{\eta_0}$ [4-8] , where ν_0 is the stokes' velocity, $\Delta\rho$ is the difference of densities of the droplets and the medium, η_0 is the viscosity of the medium and r is the droplet radious. - **For moderate concentrate emulsions** ($0.2 < \phi < 0.1$), hydrodynamic interactions between the droplets reduces stokes' velocity (Tadros, 2009), as shown in equation 4-9. $\nu = \nu_0(1 - k\phi)$ [4-9] ,where k is a constant equivalent to 6.55, which means a reduction of stokes velocity of 65% by increasing droplet concentration(Tadros, 2009). - **In concentrated emulsions,** velocity of gravity separation decreases rapidly as volume fraction increases. It reaches a value	Creaming/sedimentation is affected by many factors that enhance or retard it. Actions to avoid them are: **- Match the density of phases** in order to decrease the driving force of the phenomena. Possible actions in this direction are the use of weighting agents for the oily phase, variation of the solid fat content of the oily phase, and the use of emulsifiers forming a thick interlayer (McClements, 2016). **- Decrease droplet size**: According to Stokes' equation, the velocity of creaming/sedimentation decrease with the squared of the particle radius, which means that size is a main factor to be considered. **- Volume fraction**: As volume fraction increases interaction between droplets become important, countering the effect of gravity. At moderate concentrations, stokes' velocity is reduced by 65% (equation 4-9). **- Repulsive interactions**: Repulsive interactions (electrostatic and steric), when strong, may decrease gravitational separation because they increase the effective volume fraction of emulsion (ϕ_{eff}) (see viscosity row) **- Control of flocculation**: In dilute and moderate concentrated emulsions, flocculation has to be prevented to avoid gravitational separation. Weak flocculation can be controlled for electrostatically stabilized emulsion by changing the amount of electrolytes and for sterically stabilized emulsions, by varying the thickness of the absorbed layer (selection of surfactant system) (Tadros, 2009). **- Control continuous phase rheology:** Viscosity can be augmented by increasing droplet concentration or adding rheological modifiers, which reduces gravitational separation. Rheological modifiers can also generate a

Sub-problems	Phenomena/causes	Factors affecting sub-problems (possible solution strategies)
	around cero as ϕ reaches the packing parameter (ϕ_c) (Tadros, 2009). **- For emulsion with weak flocculation:** At low and intermediate concentrations, gravitational separation is enhanced by flocculation (McClements, 2016). Flocs are larger than individual droplets and they have a density similar to continuous phase density (because they are a mixture of droplets and medium), being more important the first effect according to Stokes' equation (where the size is squared). Contrary to the previous case, in concentrated emulsions, flocculation can decrease gravitational separation. **- For emulsions with small droplets:** When droplet size is small, Brownian forces become important. This forces favor the random distribution of droplets reducing instability by gravitational forces (McClements, 2016).	yield stress that avoid gravitational separation (Tadros, 2009). In this case, is important to select an appropriated rheological modifier. **- Poly- dispersity:** Poly- disperse emulsion have higher ϕ_c and are less stable against gravitational forces than monodisperse emulsions. - When just a small fraction of droplets (the biggest) sediment/cream and just a small layer is formed, it can be hidden by increase emulsion lightness (McClements, 2016) and eventually by user agitation.
10. Flocculation	Flocculation is the process whereby droplets associate without merging with each other (McClements, 2016). It can be weak (reversible) or strong. A representation valid for spherical particles, is shown in equation 4-10 (McClements, 2016). $\frac{dn_T}{dt} = -\frac{1}{2}FE$ [4-10] where n_T is the total number of particles per volume (which are reduced as flocculation happens), F is the collision frequency, E is the collision efficiency Collision frequency (F) is the total number of droplets encounters per time and Collision efficiency (E) shows how many of those encounters lead to flocculation (McClements, 2016). Factors affecting F, E and consequently flocculation are: **- Brownian motion,** which enhances F and in turn flocculation, can be reduced by decreasing volume fraction (ϕ) (less concentration drivers to less encounters), increasing droplet size (r) (which reduced the number of particles per volume), and increasing the viscosity of the continuous phase (η_0)(McClements, 2016).	Strategies to avoid flocculation can be divided in 1) those controlling collision frequency and 2) those controlling collision efficiency (McClements, 2016): 1) According to previous explanation, actions to control collision frequency (F) are: to increase viscosity of the continuous phase (η_0), to decrease volume fraction (ϕ), and to decrease density difference between phases. 2) Strategies influencing collision efficiency (E) are those affecting colloidal interactions. **In the case of electrostatic interactions, strategies to control them are:** **- Selection of surfactant:** Surfactants, proteins or polysaccharides are used to electrostatically stabilize the emulsion (McClements, 2016) For stable emulsion, a surfactant with following characteristics is preferred: i) it should generate a high surface potential (ii) It should absorb efficiently on interface and dissociates (which depends on its pKa and pH and temperature of continuous phase). (iii) Its isoelectric point (pI) should be different of the pH of the product (at least by 2 points) (McClements, 2016). **- Control electrolyte concentration**: It is important to assure a electrolyte concentration below the minimum amount required to cause flocculation

Sub-problems	Phenomena/causes	Factors affecting sub-problems (possible solution strategies)
	- Gravitational separation enhances F and flocculation, because more encounters occur by the collision between moving particles (McClements, 2016). - **Attraction forces** as Van der Waals forces increase E and flocculation increase (McClements, 2016). Equation 4-11 shows Van der Waals forces between two droplets (Tadros, 2009). $G_A \propto \frac{A\,r}{h}$ [4-11] , where r is the droplet radius, h the distances between droplets and A the Hamaker constant of the droplets in the medium According to this equation, van der Waals forces are stronger at short distances, large droplet radius and are proportional to the Hamaker constant (McClements, 2016). As an approximation, it can be considered that this constant increases as the difference between the dielectric properties of the medium and the droplets increases (Claesson et al., 2006). **- Electrostatic repulsion interaction** decrease E and control flocculation. They are generated by the presence of absorbed ionic compounds on the droplets surface (Tadros, 2010). Equation 4-12 shows a model of the intensity of these forces (Tadros, 2009): $G_{el} = 2\pi r \varepsilon_r \varepsilon_0 \psi_0^2 \ln[1 + e^{-\kappa h}]$ [4-12] , where r is the droplet radius, ε_0 is the permittivity of the free space, ε_r is the relative permittivity of the medium (or dielectric constant), ψ_0 is the surface potential, h is the distance between particles and $1/\kappa$ is the double layer extension. According to equation 4-12, electrostatic repulsion increases with the particle size (r), the surface potential (ψ_0) and the dielectric constant of the medium (ε_r), and it decreases when the extension of the double layer ($1/\kappa$) is reduced. ψ_0 depends on the number of absorbed surfactant molecules and the number of ionized groups in these molecules (McClements, 2016). $1/\kappa$ decreases with an	(McClements, 2016). This can be done by (i) avoiding the use of ingredients with multivalent ions, (ii) using deionizing water, (iii) adding ingredients that sequester multivalent ions (McClements, 2016). **In the case of steric interactions, strategies to control them are:** - **Selection of non-ionic surfactant** with (i) an efficient absorption and (ii) good solvent -chain interaction in relation to the continuous phase (Tadros, 2010). *The affinitive of nonionic surfactants for the continuous phase may decrease with temperature changes. Additionally, surfactants should generate a complete and thick layer. It is, (iii) the concentration of the surfactant should be enough to assure a complete coverage of the droplets and (iv) a chain of high molecular weight is preferred (Tadros, 2010). - **To avoid high temperatures** because they can drive to hydrolysis of some polymeric chains of the surfactant and/or dehydration and low affinitive for the continuous phase of the soluble part of the surfactant chain. **Strategies for other interactions:** **- Depletion interactions:** depletion interactions increase attraction between droplets due to an osmotic effect caused by the presence of non-absorbed colloidal molecules (surfactants and biopolymers) (McClements, 2016). Depletion interactions can be avoided by reducing the molecules causing this effect to a concentration lower than the limit when flocculation occurs (McClements, 2016).

Sub-problems	Phenomena/causes	Factors affecting sub-problems (possible solution strategies)
	increase on the number of ions in solution (Tadros, 2010), and more if they are multivalent (McClements, 2016). **- Steric repulsion**: This interaction is caused by the repulsion generated between the chains of absorbed molecules at the interface. Steric repulsion has two contributions: elastic and mixing (Tadros, 2010). Elastic contribution increases with the thickness of the interfacial layer (δ) and the droplet radius (r) (McClements, 2016). Mixing contribution is favored when surfactant chains are in good solvent conditions, i.e., when the Flory–Huggins interaction parameter (χ) is below 0.5 ($\chi < 0.5$) (Tadros, 2009). **- Other interactions** that may also affect stability are: depletion interactions, Hydrophobic interactions and hydration interactions (McClements, 2016).	
11. Coalescence	Coalescence is the process whereby two or more droplets merge together and form a single droplet (McClements, 2016). This process is thermodynamically favorable, but the time it takes to happen can be controlled. The phenomena that occur during coalescence are: 1. Droplets come in closed contact for a period either in a floc, in a cream layer or in concentrated emulsions (Tadros, 2010), due to mechanism as Brownian motion, gravity, turbulence, applied shear (McClements, 2016). 2. The film between droplets, which is composed of continuous phase and surfactants, is thinned and droplets coagulate (McClements, 2016). For this to happen attractive interactions between droplets have to be stronger than repulsive interactions (McClements, 2016). 3. The film is ruptured and droplets merge together (McClements, 2016). This is controlled mainly by short range forces and the resistance of the inter-droplet-film (McClements, 2016). Each of these phenomena has its own kinetic. The two first phenomena were already presented in flocculation and	The main factors controlling coalescence are the surfactant system and environmental factors that control its performance (McClements, 2016). Considering this, actions to avoid coalescence are: - To prevent droplets to come close together, it is, avoiding creaming and flocculation as explained in previous sections. - To prevent rupture of the inter-droplets-film by increasing repulsion between droplets, both steric and electrostatic (Tadros, 2010). Surfactants with polymeric chains provide higher protection against coalescence (McClements, 2016). Attention should be given to environmental conditions (pH, temperature, ionic strength), because they determined in a great measure the effectiveness of surfactants. - To prevent rupture of the film by avoiding droplet deformation: This can be done by decreasing droplet size and increasing interfacial tension as indicated in the Weber number (equation 4-13). - To prevent rupture of the film by controlling its characteristics: Experimentally, it has been observed that emulsions are more stable if Gibbs elasticity of the inter-droplets-film is increased (Tadros and Vincent, 1983). This can be done using mixture of different surfactants, such as anionic and

Sub-problems	Phenomena/causes	Factors affecting sub-problems (possible solution strategies)
	gravitational separation sections. Factors affecting the dynamic of film rupture are: **Droplet deformation:** The film separating two droplets becomes flatted, when the external stress acting on the droplets (colloidal, gravitational, hydrodynamic, shear forces) is larger than the internal Laplace pressure (the force responsible to keep the spherical shape of droplets) (Walstra, 1996)(McClements, 2016). The relation between these forces can be evaluated with the Weber number (McClements, 2016): $We = \frac{r^2 \sigma_{ext}}{2\gamma h}$ [4-13] ,where, r is the droplet radiuos, h is the interdroplet distance, σ_{ext} is the external force acting on the droplet (can be colloidal, gravitational, mechanical, etc), γ is the interfacial tension When $We < 1$, Laplace pressure is more important than external forces and the droplets remain spherical. Otherwise, they tend to be deformed. As shown by Weber number, small droplets are more stable. **Film rupture:** In addition to the forces, it is necessary to consider the tendency of the film to rupture. Film rupture mechanism are not perfectly known, but experimental researches have shown some indications **- Fluctuations waves:** Once droplets surface are closed, thermal fluctuations may form surface waves in the film and the content of droplets may get in contact in the apices of the waves (McClements, 2016). In this case, film rupture can be reduced by dampening the fluctuation by enhancing Gibbs elasticity of the film and repulsion forces (Tadros, 2010). **- Holes formation:** Small holes may form spontaneously because of thermal disturbances on the film. Hole formation is more favorable for systems with low interfacial tensions and thin films between droplets (McClements, 2016). It depends highly on the molecular geometry of emulsifier molecule and on the so called	nonionic surfactants or a mixture of anionic surfactants and long chains alcohols (Tadros, 2010)). - To select surfactant systems with a curvature that do not favor emulsion coalescence (McClements, 2016). For example, if an O/W emulsion is desired to be stable, a surfactant soluble in water is preferred (Binks, 1998). Selection criteria as the HLB can be used to find the most appropriated system (Binks, 1998). - To control environmental conditions according to the selected surfactant system: Environmental conditions of the emulsion have to be considered in the selection of an appropriated surfactant system, because the curvature of the surfactant may change with the pH, temperature and ionic strength (Binks, 1998)(McClements, 2016). Some nonionic surfactants stabilize droplets against coalescence at low temperatures, but coalesce when they are heated due to dehydration of the head groups (McClements, 2016). Emulsion droplets stabilized by relatively thick cohesive interfacial layers (e.g., proteins and polysaccharides) are relatively resistant to coalescence, but may become unstable when mechanical forces are applied to the system (McClements, 2016).

Sub-problems	Phenomena/causes	Factors affecting sub-problems (possible solution strategies)
	spontaneous curvature of emulsifier (McClements, 2016)(Leal-Calderon et al., 2007)(Binks, 1998). An emulsifier that is oil soluble (form micelles in oil), tends to curve toward oil and form W/O emulsions. Conversely, an emulsifier that is water soluble tends to curve toward water and form O/W emulsions (Leal-Calderon et al., 2007)(Binks, 1998).	
12. Phase inversion	Phase inversion is the phenomenon in which the emulsion structure inverts. That is, the continuous phase becomes the disperse phase and the disperse phase becomes the continuous phase (Leal-Calderon et al., 2007). This phenomena can be desirable during emulsification, because it may drive to emulsions with very small droplet sizes (Brooks et al., 1998)(Leal-Calderon et al., 2007). However, once the emulsion is formed, phase inversion is unwanted, because it changes emulsion structure and may conduct to coalesce (McClements, 2016). Conditions that may produce phase inversion are: **- Increase of the disperse phase concentration** until a critical level. Inversion caused by a change in dispersed phase concentration are normally non-reversible (McClements, 2016). **- Change in surfactant spontaneous curvature** due to a change in emulsion environmental aspects (Brooks et al., 1998) (McClements, 2016). This kind of inversion is reversible if the conditions that led to a change in the curvature of surfactant are reverted (McClements, 2016). Conditions that may lead to a transition from a W/O to a O/W emulsion are: **Increasing salt concentration** for systems with nonionic surfactant, i**ncreasing HLB** of the surfactant (HLB can be changed by mixing surfactants with different HLB together), **increasing the Temperature of nonionic** surfactants until its PIT (Phase Inversion Temperature), **the addition of alcohols and solvents** (Brooks et al., 1998).	Possible strategies to avoid phase inversion are (McClements, 2016): - Controlling that the volume fraction do not reach a critical value in which inversion may occurs. - **Selection of a surfactant system that do not undergo phase inversion under the conditions that emulsion experience during its lifetime** (McClements, 2016). With this purpose, the next properties of the surfactants can be checked: The surfactant mixture has to have an HLB that favors the desire type of emulsion. Low HLB forms W/O emulsions while high HLB forms O/W emulsions. Intermediate HLB may form emulsions with a tendency to phase inversion (McClements, 2016). **- Selection of surfactants with a PIT** higher than the temperatures experience by the emulsion during its time life. - Test carefully the effect of alcohols, salt and other additives in surfactant behavior (Brooks et al., 1998). - Prefer surfactants that do not undergo a change (as example proteins can only form O/W emulsions (McClements, 2016)) over systems that may undergo phase inversion (nonionic and ionic surfactants). **- Avoid the changes in temperature**. Cooling an O/W emulsion may conduct to partial coalescence and phase inversion and heating an emulsion stabilized by nonionic surfactants beyond its PIT will conduct to phase inversion (McClements, 2016).
13. Ostwald ripening	This phenomenon consist in the diffusive transfer of the disperse phase from smaller to larger droplets, because the solubility of the disperse phase increases as the size of the particles decreases (Leal-Calderon et al., 2007). The transport can be characterized	Measures to control Ostwald ripening are: **- Select a disperse phases with low solubility:** The phenomenon decreases when the disperse phase components are poorly soluble in the

Sub-problems	Phenomena/causes	Factors affecting sub-problems (possible solution strategies)
	according to the limiting stage: 1) if it is controlled by the diffusion through the continuous phase (diffusion-controlled ripening) or 2) if it is controlled by the diffusion through the interfacial layer (surface-controlled ripening) (Leal-Calderon et al., 2007). The driving force causing the phenomena is the difference of solubility (chemical potential) of the disperse phase which is larger in small than in large droplets (Tadros, 2010). 1) Diffusion controlled ripening: If the phenomenon is controlled by the diffusion through the continuous phase, the variation of droplet size with time can be represented by equation 4-14 derived from the Lifshitz–Slyozov–Wagner (LSW) theory (McClements, 2016). $r^3 = \frac{4}{9}\left(\frac{2\gamma V_m}{RT}\right) S(\infty)\ D\ t$ [4-14] ,where D is the diffusion coefficient of the disperse phase through the continuous phase According to this equation, the mean radius of particles augment linearly with time proportionally to bulk solubility of the disperse phase, the diffusion coefficient of the disperse phase in the continuous phase and the interfacial tension. Additionally it have been found experimentally that when volume fraction (ϕ) is increased or the movement of droplets due to Brownian motion is considerable (which is important for small radius) droplets encounters increase and Oswald ripening rate is higher than the predicted by equation 4-14 (Binks, 1998). 2) Interface controlled ripening: Sometimes the limiting step is the diffusion of the disperse phase through the interfacial layer. In this cases the main measures to control it are related to a change in the interfacial characteristics (Mcclements, 2007).	continuous phase. It has been found experimentally that Ostwald ripening is not significant in O/W emulsions for oils with a negligible solubility in water such as long chain hydrocarbons or triacylglycerols, but it becomes important for more soluble oils as short chain hydrocarbons, short chain triacylglycerols, essential and flavor oils (Binks, 1998)(Mcclements, 2007). - **Add components with low solubility to the disperse phase:** In case the product has to content oils with high solubility in water, the Ostwald ripening effect can be controlled by adding insoluble oils into the disperse phase (Tadros, 2010). In this case, an equilibrium between the difference of solubility due to droplet size and due to the partitioning of the components is achieved, with the component having a low solubility expected to be concentrated in the smaller droplets (Tadros, 2010). - **Avoid the presence of components in the continuous phase** that increases the solubility of the disperse phase as alcohols and micelles. - **Size distribution:** If droplets have the same size and composition, the Ostwald ripening phenomena will not happen. Mono-sized distributions are difficult to generate industrially, but measures to create narrow distributions may reduce de phenomenon. - **Increase the Gibbs** elasticity modulus in order to increase resistance to transport can help to reduce Ostwald ripening when it is controlled by the diffusion through the interfacial layer rate. This can be achieved with polymeric and biopolymers emulsifiers as proteins and polysaccharides(Tadros, 2010)(McClements, 2016).
14.	Lipid oxidation is a complex sequence of chemical reactions that result from the interaction of lipids with oxygen-active species	Strategies that can be used to avoid lipid oxidation are:

Sub-problems	Phenomena/causes	Factors affecting sub-problems (possible solution strategies)
Lipid oxidation	(McClements and Decker, 2000). Lipid oxidation in O/W emulsions can be represented by a three steps mechanism: initiation, propagation and termination (McClements and Decker, 2000): **- Initiation:** Oxidative instability is originated by the interaction between lipid hydroperoxides present at the interface (and formed due to the presence of oxygen) and transitional metals present in the aqueous phase as Fe^{2+}, Fe^{3+}, Cu^{+}, Cu^{2+} (McClements and Decker, 2000). Due to this interaction highly reactive radicals are formed. **- Propagation:** Radicals formatted at the interface react with the unsaturated lipids within drops leading to the formation of lipid radicals that propagate the reaction within oil droplets (McClements and Decker, 2000). **- Termination:** Some of the lipid radicals find other lipid radicals and the reaction is terminated (McClements and Decker, 2000). To promote the reaction the reactive species have to be in enough quantity and come in contact. In an O/W emulsion pro-oxidants are normally located in the water phase, hydroperoxides are at the interface and lipids are within the droplets (McClements and Decker, 2000). Therefore, the reaction is initiated at the interface and after initiation it keeps going within the droplets.	**- Oxygen concentration:** Oxidation is avoided or reduced if oxygen concentration over the product is controlled. This can be done, for example, by packing under vacuum or nitrogen atmosphere (McClements and Decker, 2000). **- Selection of oils**: The chemical structure of the oil determines its trend to oxidation. Saturated lipids are more resistance to oxidation than unsaturated, and for the latter, those with the double bond located far from the carboxylic group are more stable (McClements and Decker, 2000). Additionally, the polarity of the lipid determines its location within the emulsion and consequently its trend to oxidation (McClements and Decker, 2000). Nonpolar lipids trends to locate deep inside the droplets and in turn they are more resistant against oxidation (McClements and Decker, 2000). - Low concentration of hydroperoxides, transition metals, or other pro-oxidants. This can be achieved by purchasing high-purity ingredients and maintaining very good storage conditions (temperatures, reduced oxygen, low light) or by purifying ingredients before use (McClements and Decker, 2000). - Prevention of hydroperoxides from coming into close proximity to pro-oxidants or by inactivating pro-oxidants(McClements and Decker, 2000). This can be done by adding chelating agents that inactive transitions metals (McClements and Decker, 2000), using cationic surfactants that charge the oil droplets positively and protect them electrostatically against pro-oxidants, using a surfactant that forms a thick interfacial layer and prevent the contact of pro-oxidants (aqueous phase) with the hydroperoxides (interface), inactivating pro-oxidative enzymes by heating, adding denaturants or changing the pH (McClements and Decker, 2000). **- Incorporation of antioxidants:** Antioxidants are substances capable of accepting free radicals and in this form they can retard oxidation until its depletion (McClements and Decker, 2000). Their effectiveness depends on its chemical nature and its location within emulsion (they tend to be more protecting when located at the interface or in the oily phase, where oxidation initializes and propagates (McClements and Decker, 2000)), being the latter mainly defined by the polarity of the antioxidant (McClements and Decker, 2000).

Sub-problems	Phenomena/causes	Factors affecting sub-problems (possible solution strategies)
15. Biological stability	Contamination with biological agents can happen during product elaboration, storage or use. To prevent biodegradation it is necessary to protect the product and raw materials during its entire life cycle. According to FDA, some of the ways cosmetics may become contaminated are (FDA, 2017): Contaminated raw materials, water or other ingredients, poor manufacturing conditions, ingredients that encourage growth of microorganisms without an effective preservative system, packaging that doesn't protect a product adequately, poor shipping or storage conditions, consumer use, such as the need to dip fingers into the product. Antiseptic effects must last long and secondary pollution after opening the pack also needs to be prevented (Iwata and Shimada, 2013).	It is fundamental to protect the product during its entire life cycle by: - Using decontaminated raw materials. It is also possible to disinfect them prior used with antimicrobial additives, heating, and UV radiation or membrane filtration, among other techniques, according to the specific nature of the material and product (Brannan, 1996). Maintain good storage conditions to prevent microbiological contamination. Use of hygienic or sterile processing conditions (Brannan, 1996). Design a product with a hostile environment using a preservative system either of the type preservative-self or adding preservatives (Brannan, 1996). Design a package system that prevent or even eliminate contamination during product use (Brannan, 1996). In relation to the preservative system, they can be of two types: preservative substances and the creation of an hostile environment Preservative substances: There are preservatives of different nature. General groups are: organic acids as benzoic acid, parabens as methyl paraben, essential oils as eucalyptus oil, aldehydes as formaldehyde, phenyl compounds as phenol, and quaternary ammonium as benzethonium (Draelos, 2011). For their selection it is necessary to consider some factors such as: The protection they offer against different microorganism, if they are allergenic, safety, water solubility (microorganism growth in water), compatibility with other ingredients, synergies with other preservatives, effectiveness, etc. (Draelos, 2011). - Hostile environment due to pH, water activity, nutrient availability, surfactant concentration, sequestering agents, alcohols (Kabara and Orth, 1997)

Sub-problems	Phenomena/causes	Factors affecting sub-problems (possible solution strategies)
Transport phenomena		
16. Release of a relative nonpolar molecule (Kow>1) to a relative nonpolar medium	For the release of an active molecule from the formulation to other medium, it is important to consider the partition coefficient and the rate of transport of the active. For example, for skin penetration, minimum three steps have to be considered: 1) diffusion of the active molecule through the emulsion, 2) partitioning of the molecule from the emulsion into the first skin layer, the stratum corneum, 3) diffusion through the stratum corneum and partitioning into the second skin layer, the epidermis, and so on (Wiechers et al., 2004). Equation 4-15 shows a simplified one dimension model of flux through the stratum corneum, where the role of partition and diffusion coefficients is shown (Wiechers et al., 2004). $J = \frac{KD}{L}\Delta C$ [4-15] ,where K is the partition coefficient between the formulation and the stratum corneum, D is the diffusion coefficient of the stratum corneum, L corresponds to the stratum corneum thickness, and ΔC is the difference of concentration of the molecule of interest through the stratum corneum In all release cases, it is very important to consider the difference in polarity of the active and the formulation in relation to the difference of polarity of the active with the target medium (Wiechers et al., 2004), because partition coefficient and in consequence release are largely influenced by this factor.	When transferring a non polar molecule from emulsion to a nonpolar medium, if the difference of polarities between the active and the oily phase (where the active is mostly concentrated in formulation) is larger than the difference between the active and the target medium, the release is favored (Wiechers et al., 2004). Attention should be also given to the active solubility in the formulation because it is reduced (and enough active may not be solubilized in the emulsion), when the difference of polarities is increased (Wiechers et al., 2004). Other factors affecting this transfer are: concentration of the active in emulsion (more concentration means more active transferred to the target medium), the volume fraction (more oil content means less transfer because more active can be solubilized), droplet size (if the limiting step is the diffusion of the active through the droplet, larger and more viscous droplets will retard the transfer. However, in emulsions with relative small droplets, this is not usually the limiting step, but the partition of the active in the emulsion – medium interface). Some molecules can bind to active components through physical or covalent interactions, what reduce the released rate significantly (McClements, 2016). Additionally, the presence of surfactant micelles in the oily phase may increase the solubility of the active and the formation of oily crystals may decrease its solubility (McClements, 2016).
17. Release of a relative nonpolar molecule (Kow>1) to a polar medium	Non polar actives are more soluble in the oily phase. The active has to diffuse through the droplet and partition to the aqueous phase and then diffuse to the polar medium. Nonpolar molecules tend to prefer the oily phase, transferring just in low proportion to the aqueous phase.	Factors that may enhance or retard this release are: the partition coefficient of the active between emulsion and the medium (polarity of emulsion can be changed to control this factor), the concentration of the active in the emulsion (more active enhance the release), the volume fraction (more oil content retard the release), droplet size (it may influence if limiting transfer step is the diffusion through the oily phase), the possibility of the active of binding physically or chemically with the interface or some component within emulsion, the presence of inverse micelles or oil crystals (McClements, 2016)(Wiechers et al., 2004).

Sub-problems	Phenomena/causes	Factors affecting sub-problems (possible solution strategies)
18. Release of a relative polar molecule (Kow<1) to a relative unpolar medium	Polar molecules are mostly solubilized in the aqueous phase. The active has to partition to the non-polar medium. The volume fraction has no effect on the concentration of highly polar actives. However, as the polarity of the active decreases, volume fraction gain importance and its increases cause a change in the concentration of the active in the aqueous phase decreases, which direction depends on its partition coefficient (McClements, 2016).	Factors affecting this partition are: active molecule ionization or binding with components in the aqueous phase (which retard the release), change in the polarity of the aqueous phase. Additionally, attention to factors as pH or presence of acids or alkalis has to be consider, because they may change active molecule behavior.
19. Release of a relative polar molecule (Kow<1) to a polar medium	In the release of a polar molecule from an O/W emulsion to a polar medium, it is expected that this molecule is mostly in the aqueous phase. The medium will dilute the emulsion and the active molecule will diffuse due to the difference of chemical potential created by the dilution. This is for example the case of polar flavors in a O/W emulsion food diluted by saliva when eaten and transported by diffusion to the flavor receptors (McClements, 2016).	In this case partitioning is not relevant and diffusion is favored. Factors that may decrease transport are for example an increase in continuous phase viscosity.
20. Release of a relative polar volatile molecule to the air	The properties of the volatile molecule are the main factor determining its release (McClements, 2016).	Factors affecting their transport are: polar molecules that can dissociate in aqueous medium, tend to reduce its volatility when they are ionized (due to pH change, for example) (McClements, 2016). Equally, the presence of molecules that can bind to the volatile molecules reduce the transport of this component. Droplet size and volume fraction have a minimum effect for O/W emulsion of low and intermediate concentration on the release, because the polar molecule is mainly in the aqueous phase.

Sub-problems	Phenomena/causes	Factors affecting sub-problems (possible solution strategies)
21. Release of a relative nonpolar volatile molecule to the air	The properties of the volatile molecule are the main factor determining its release (McClements, 2016). For example, as the molecular weight of the active increases, its volatility decreases (McClements, 2016).	Formulation factors affecting the transport of nonpolar volatile actives are(McClements, 2016): -The presence of binding molecules at the interface or micelles that solubilize nonpolar molecules and reduce their partitioning. -The volume fraction, which when increased, decrease partitioning to the air. This effect is stronger as the polarity of the molecule decreases, and it also affects intensity and transport rate. When volume fraction decreases, intensity and rate of release also decrease. -The interface composition that may bind the active molecule and reduce its partitioning to air. - The droplet size because the vapor pressure of a molecule within a droplet increases as the droplet size decreases (this is relevant for nano emulsions).

Table 4-2: List of solution strategies

Solution strategies	Solution strategies and their application
Aqueous phase	
1. Water activity	Water activity is related with the capability of organism to survive and growth. The smaller the water activity, the less are the possibilities of organisms to live in the media (Russell et al., 2003). Water activity can be changed by adding solutes as sugar, salt, glycerin, propylene glycol, rheological modifiers, among others. It also decreases with temperature.
2. Polarity of the aqueous phase	Polarity of the aqueous phase can be changed by the addition of solvents. For example, the addition of glycerin, propylene glycol and/or ethanol reduces polarity of the aqueous phase, and in turn reduces solubility of highly polar compounds and increases solubility of nonpolar compounds.
3. pH	pH has an important effect in almost all emulsion characteristics. It can be changed by the addition of an acid or an alkali and it can be controlled with a buffer. For cosmetic applications, when it is required to reduce the pH, it is suggested to use a weak acid such as lactic or citric acid. When it is required to increase the pH, sodium hydroxide, potassium hydroxide and triethanolamine are of commonly use in the cosmetic industry.
4. Electrolyte concentration aqueous phase	Electrolyte is any compound that dissociates in water, i.e., salts. Its concentration has important effects on the behavior of electrical charged species within the emulsion, especially when the emulsion is stabilized with ionic surfactants. In the case when it is necessary to increase electrolyte concentration, for example when a rheological modifier is controlled with electrolytes or an active molecule that is also an electrolyte has to be introduced, special attention has to be taken of not introducing a concentration higher than the minimum amount required to cause flocculation.
5. Multivalent electrolyte concentration	Multivalent ions have a much bigger effect on emulsion stability than monovalent ions. Thus, actives with multivalent electrolyte should be avoided or used in very small concentrations in an emulsion stabilized with anionic surfactants.
Interface	
6. Surface charge density (σ)	The electrical charge of a droplet is expressed in terms of the surface charge density and the electrical surface potential. The first is defined as the amount of electrical charge on the droplet surface, while the second is defined as the free energy required to increase the surface charge density from cero to its actual value (McClements, 2016). It is mainly affected by the nature of the ionic compounds adsorbed on the droplet surface (ionic surfactants as phospholipids, fatty acids, multivalent ions as Ca^{2+}, Cu^{2+}, charged biopolymers and nanoparticules as titanium dioxide) as well as by the characteristics of the continuous phase as the pH (which change molecules dissociation), ionic composition, temperature, among others. Depending on the nature of the adsorbed ion, electrical charge of droplets may increase, decrease or be inverted (McClements, 2016). Monovalent ions in moderate concentrations screen electrostatic interactions but do not affect the electrical charge. Multivalent ions do affect electrical charge (McClements, 2016).
7. Quality of the solvent – surfactant (steric repulsion)	Steric repulsion has two contributions: elastic and mixing. The mixing contribution is enhanced when surfactants chains are in good solvent conditions, it is, when the interaction surfactant – solvent is favored over the interaction polymer-polymer. For example, polyethylene oxide chains in water at moderate electrolyte concentrations and low temperature are in good solvent conditions (Tadros, 2009). When surfactant chains are not in good solvent conditions, polymer - polymer interactions may be preferred, which drives to an attraction between droplets and flocculation. For example, the same surfactant in the same solvent but at high temperatures is not in good solvent conditions and it may even precipitated (cloud point). Good solvent conditions can be enhanced by selecting an appropriated surfactant with a suitable HLB, by keeping low temperatures, or by changing the composition of the aqueous phase to enhance solvation (for example by adding a solvent in which the surfactant has a higher solubility in comparison to water).
8. Thickness - steric interaction	Steric repulsion has two contributions: elastic and mixing. In a rough simplification, elastic contribution can be described by equation 4-16 (McClements, 2016) $w_{elastic} = \left(\frac{2\delta}{h}\right)^{12} kT$ [4-16] , where δ is the thickness of the interfacial layer, h is the distance between the droplets and kT is the thermal energy. The range of steric interactions increases with the thickness of absorbed layers, which in practice can be increases by surfactants with a longer hydrophilic chain. In addition, the strength of steric interactions increases with droplet radio and depend on the interfacial layer characteristics as viscosity and flexibility (McClements, 2016).
9. Gibbs elasticity -	The interfacial dilatational (Gibbs) elasticity, is very important in determining emulsion stability, because it gives resistance to the interfacial layer against deformation and coalescence. Interfacial elasticity can be improved with polymeric emulsifiers, and biopolymers as proteins and polysaccharides(Tadros, 2010)(McClements,

Solution strategies	Solution strategies and their application
steric interaction	2016). It is also improved when the packaging of the interface is tight, reason why the use of mixture of surfactants with different polymer length (different HLB) is suggested (Tadros, 2010).
10. Interfacial tension (γ)	Interfacial tension indicates the free energy required to increase the interfacial area (McClements, 2016). It is decreased when surfactants or polymers are adsorbed. It is also decreased when temperature is increased, meeting a minimal value at a temperature point know as PIT. When emulsions are prepared at PIT, droplets are smaller in comparison to those prepared at lower temperatures (Tadros, 2009).Additionally, the concentration of polyoils change also interfacial tension (Benichou et al., 2001)
Oily phase	
11. Polarity of oily phase	Polarity of the oily phase can be changed by selecting different type of oily compounds. Hydrocarbons have low polarity, esters have an intermediate polarity between hydrocarbons and fatty alcohols. Fatty alcohols tend to have high polarity.
12. Degree of unsaturation of the oils	The degree of unsaturation can be controlled by selecting an oily phase with the desire degree of unsaturation. Normally, to avoid oxidation, a low degree of unsaturation is preferred. It is measured through the iodine number, which results to be high, when the degree of unsaturation of the compound is high. This value is easy to find and it is normally registered in the datasheet of oily compounds.
Oily phase - aqueous phase	
13. Refractive index difference	Refractive indices difference can be modified by changing the nature and/or composition of the continuous and disperse phases. This is difficult to do in practice because the entire product properties will change if the composition is modified. The refractive index of water is normally lower than the refractive index of the oily phase. Thus, in order to turn the emulsion transparent, the refractive index of the aqueous phase has to be increased and/or the refractive index of the oily phase has to be decreased. It is possible to increase water refractive index by adding solutes to the aqueous phase such as salts, polysaccharides, alcohols and polyols (McClements, 2016). This will also change other aqueous properties such as viscosity, density and freezing point (Lide, 2004) and some properties of the emulsion such as interfacial tension (it has been found that there is an optimal concentration of polyols that reduce interfacial tensions and helps to obtain smaller droplets during homogenization (Benichou et al., 2001)). It is possible to change oily phase refractive index by modifying oily phase composition. The refractive index is different for different type of oils, mixtures of oils and molecular structures. It is possible to relate refractive index to the molecular structure of oils (chain length, degree of unsaturation, degree of conjugation) (Gunstone, 2002): Refractive index increases with the chain length of the oil molecule and with the number of unsaturations (Gunstone, 2002). Additionally, it is higher for monoacylglycerols than for triacylglycerols and for the latter in comparison to fatty acids (Gunstone, 2002). Refractive index is also affected by temperature. It decreases as temperature increases. It is closed related and has an inverse behavior in relation to density (Budwig, 1994). It is also related to the dielectric constant and consequently to colloidal interactions(McClements, 2016).
14. Density difference	Density difference between phases can be decreased by: Selecting an oil with a relative high density: This solution is not directly applicable because most fats and oils have densities smaller than water. Example of components that can be used with this purposed are waxes as carnauba wax, candelilla wax, beeswax, which show relative high specific gravities (in comparison with oils and fats) of around 0.96 to 1 (Iwata and Shimada, 2013). Natural oil and fats have densities of around 0.91 (McClements, 2016). The presence of this components affect oily phase density, but also other important properties as the sensorial ones. It is to remark that density change with temperature. Densities can be equated by changing composition, but this solution is only valid at a temperature (Tadros, 2010). Using weighting agents: This solution is frequently used in food emulsions of low concentration to avoid separation by gravity (McClements, 2016). Weighting agents are molecules with a gravities greater than 1 that are soluble in the oily phase. Examples are brominated vegetable oil (BVO $\rho \approx 1330 kg\, m^{-3}$), sucrose acetate isobutyrate (SAIB $\rho \approx 1146 kg\, m^{-3}$), ester gum (EG $\rho \approx 1080\, kg\, m^{-3}$), damar gum (DG $\rho \approx 1050 - 1080\, kg\, m^{-3}$) (McClements, 2016). Avoiding the use of heavy agents in the aqueous phase that may increase its density. Increasing the portion of solid fat: This can be done by changing oil composition with ingredients with high melting points (McClements, 2016). Oils with high molecular weight and without unstaurations tend to be solids at room temperature. It is to note that crystalline droplets are more susceptible to partial coalescence (McClements, 2016). Using emulsifiers that form a thick interlayer, which may increase droplet density.

Solution strategies	Solution strategies and their application
15. Solubility of the disperse phase components in the continuous	Ostwald ripening is caused by the increase on the solubility of the disperse phase in the continuous phase. It has been found experimentally that for O/W emulsions, the presence of components as alcohols, or micelles in the continuous phase increase the solubility of oils in water and in turn the Ostwald ripening rate(Mcclements, 2007). The effect of micelles formed by nonionic surfactants tend to be higher than for those of ionic surfactants, apparently because the last generate an electrostatic repulsion (Binks, 1998). Solubility of the disperse phase can be reduced by selecting a low polar oily phase, i.e., by hydrocarbons and silicons instead of esters and fatty acids.
Colloidal forces	
16. Depletation interaction -	This force is attractive and it enhances flocculation, reason why it may be detrimental to stability. It is originated when there are small colloidal particles (as polymeric surfactants and biopolymers) in the continuous phase. These particles nears the droplets and generate an osmotic pressure between droplets, which increases their attraction(McClements, 2016). Depletion interaction can be avoided by reducing the concentration of the molecules causing this effect (McClements, 2016).
17. Polyvalent ions - ion bridging	When there are polyvalent ions in a emulsion, it is possible that they interact with two or more droplets at the same time, which increase their attraction and can enhance flocculation (McClements, 2016). Example of polyions are Ca^{2+}, Mg^{2+}, Al^{3+}, polysaccharides or proteins (McClements, 2016).
18. Electrostatic interaction	Electrostatic interactions are generated in the emulsion by adding ionic surface active agents. Ionic surfactants adsorb on the oil-water interface and if they are in their ionized form (which depends on their pKa and pH of aqueous phase) a surface potential and a double layer is formed. This layer generates a repulsion between droplets with the same charge (Tadros, 2010). -Advantages: Ionic surfactants have to be used in lower quantities in comparison to nonionic surfactants (McClements, 2016). -Disadvantages: their performance depends on pH and electrolyte concentration. Flocculation may occur when surfactant isoelectric point is closed to emulsion pH, they have poor stability when emulsions is frozen and thawed (McClements, 2016). -Ionic surfactants and stability: Special attention has to be given to the factors that affect the spontaneous curvature of the surfactant, because it has important repercussions in emulsion stability. Factors that increase the curvature toward the oil droplets and consequently the stability of O/W emulsions are: reduction of the electrolytes concentration and increase of temperature. Factors that decrease the spontaneous curvature are: increase of the size of the surfactant chain, branching of the surfactant chain, presence of desorbing neutral species (sugar), oils with high polarity (Binks, 1998).
19. Steric interaction	Steric interactions are generated when nonionic surfactants are added to the emulsion. It is important to select a group of surfactants in a proportion that guaranties that the curvature of the droplets under the existing conditions are correct to form an O/W emulsion. - Working principle: Nonionic surfactants have two parts, one of them is highly soluble in the medium, and define the curvature and the thickness of the interfacial layer (block A). The other has a high surface activity and should absorb efficiently on droplet interface (block B) (Tadros, 2010). Nonionic surfactants can have these parts in different configurations, for example A-B, A-B-A, BA_n (for nonionic surfactant polymers) (Tadros, 2010). Characteristics of interfacial layer can be controlled by selecting surfactants with an specific structure and molecular weight. - Advantages: Nonionic surfactants are relative stable to pH changes and high electrolyte concentration (McClements, 2016) -Disadvantages: They are needed in larger quantities in comparison to ionic surfactant, many of them are unstable at high temperatures although they may present a relative good stability to freeze and thaw (McClements, 2016). -Nonionic surfactants and stability: Special attention has to be given to factors that affect the spontaneous curvature of the surfactant, because it has repercussions in emulsion stability. Factors that increase the curvature toward the oil droplets and consequently the stability of O/W emulsions are: higher size of polar group and oils with a large chain (Binks, 1998). Factors that decrease the curvature and may destabilize emulsions are: a rise in temperature when the surfactants are dehydrated (this happens for example in ethylene oxide groups) (McClements, 2016). Special molecules: Some molecules can generate electrostatic and steric repulsion. This is the case of proteins, polysaccharides and mixture of surfactants. Proteins are very effective against coalescence and they generate emulsions with very small droplets and thick interfacial layers (McClements, 2016). Careful has to be taken if they are used in systems exposed to high shear rates or high or very low temperatures, because they can be damaged and emulsion stability can be affected (McClements, 2016). Polysaccharide have a similar behavior as protein emulsifiers. Polymeric surfactants, such as the Tweens, have polymeric hydrophilic head groups that generate a better steric protection than the provided by small molecules (McClements, 2016).

Solution strategies	Solution strategies and their application
20. Weak flocculation	Weak flocculation is generated by the interrelation of attractive and repulsive forces. It is possible when forces acting between droplets create a configuration in which two potential energy minimums are evidenced. One of them is very deep and corresponds to a very close distance between droplets (primary minimum) and the other one corresponds to a larger distance between droplets and it is known as a secondary minimum. In the secondary minimum, droplets are sufficiently close to agglomerate reversibly (weak flocculation) but not enough to aggregate irreversible (strong flocculation) and approach to a possible coalescence. Actions that may conducted to avoid weak flocculation are: - For electrostatically stabilized systems it is possible to generate weak flocculation by controlling electrostatic repulsion. For example, by adding small amounts of electrolytes to the emulsions system (Tadros, 2009). - For sterically stabilized emulsion, it is possible to generate a weak flocculation by a controlled reduction of the protecting layer. This can be done by reducing the molecular weight of emulsifier or changing the relation between the surfactant chains and the medium (for example by adding electrolites) (Tadros, 2009) - The addition of a non-absorbed polymer or surfactant. This action increases the osmotic pressure outside droplets and generate and attraction between them to compensate the pressure change(Tadros, 2009). The attraction is known as depletion interaction and it increases as polymer concentration and/or molecular weight increases as polymer concentration increases and generate a controlled attraction between droplets, which is known as depletion flocculation. Osmotic pressure (and consequently attraction of droplet) increases with the concentration and molecular weight of polymer (Tadros, 2009). Examples of molecules that aid to induce depletation are surfactants such as Tween 20, sodium dodecyl sulfate, polysaccharides such as xanthan gum, and proteins, such as whey and caseinate (McClements, 2016).
Structure	
22. Droplet size	Factors affecting droplet size are: Surfactant properties: At equilibrium conditions (when emulsifier is already adsorbed) and considering that energy input is sufficient and oil, water and emulsifier concentrations are constant, the minimum droplet size depends on surfactant nature and concentration: - Surfactant concentration: when energy input is constant, an increase of surfactant concentration tends to decrease droplet size. - Surfactant – interfacial packing: A droplet protected with a surfactant having high interfacial packing requires the addition of a high amount of energy to be disrupted, which results in the generation of emulsions with larger droplets at constant energy input (McClements, 2016). A measure of interfacial packing can be given by excess surface concentration at saturation (Γ_{sat}) (Rosen and Dahanayake, 2000). - Emulsifier molecules that adsorb rapidly generate emulsions with smaller droplets (McClements, 2016). A measure of adsorption rate can be given by the surface tension change over time (Rosen and Dahanayake, 2000).Usually surfactants with low molecular weight tend to adsorb more rapidly because they diffuse rapidly in the media - Surfactant - adsorption efficiency: At a constant surfactant concentration, more efficient surfactants generate smaller droplets, because they can reduce in a greater degree the interface tension (McClements, 2016). Oil/water phase composition: - Viscosity ratio (η_D/η_C): Variations on the oil and water phase composition to change viscosity ratio may affect droplet size. During homogenization under turbulence conditions experimental evidence have shown a minimum in droplet size when viscosity ratio is between 0.05 and 0.5 (Chevalier et al., 2016) (McClements, 2016). - Viscosity of the disperse phase (η_D): As the viscosity of the dispersed increases, droplet size also increases. This happens because cohesive forces of the droplet are enhanced and gain importance in comparison with disrupting forces (Chevalier et al., 2016) - Interfacial tension: Lower interfacial tension favors droplet disruption during homogenization and the generation of smaller droplets. Interfacial tension can be reduced by adding surfactants, by changing oil phase nature (increasing its affinity to water) or due to impurities present in one or both phases. As example, impurities of fatty acid in the oil phase, biopolymers, alcohols, sugar, bubbles, particles, among others, can affect interfacial tension (McClements, 2016). Temperature: - Heating reduces emulsion viscosity, which in turn increases Reynolds, favoring homogenization and the reduction of droplet size (McClements, 2016). Additionally, because oils viscosity decreases more quickly than water viscosity, viscosity ration is also reduced by heating which favors the generation of smaller droplets (McClements, 2016). Heating reduces slightly interfacial tension, which also reduces droplet size (McClements, 2016). Energy input (ε): If enough emulsifier is added, droplet size is decreased by increasing energy input. Energy input depends on homogenizer and operating conditions(McClements, 2016). It can be increased by increasing

Solution strategies	Solution strategies and their application
	rotation speed (for example in a rotor-stator homogenizer), increasing applied pressure (for example in high pressure valve homogenizer) or increasing residence time (for example in batch homogenizers) (McClements, 2016). It is to highlight that an increase in energy input also increases manufacturing cost and over- processing should be avoided. Relation between surfactant and emulsification conditions: To decrease droplet size, both energy and emulsifier should be considered simultaneously. When emulsifier concentration is constant, there is a maximum limit in which energy input generates a reduction in droplet size. Over it, more energy does not conduct to droplet size reduction. Similarly, if energy input is constant, there is a maximum emulsifier concentration, that once exceeded does not affect droplet size (McClements, 2016).
23. Droplet size distribution (DSD) - width	DSD is complex to be controlled, because it is affected by many factors such as homogenization conditions, surfactant properties, and other properties of the components. Some actions that can be done to control DSD are: - Homogenizer selection: DSD depends strongly on the homogenizer. Membrane and micro-channel homogenizers generate narrow distributions, while high shear mixers, high-pressure valve homogenizers, colloid mills, micro-fluidizers, and ultrasonic homogenizers generate broader distributions (McClements, 2016). Shear mixers generate a normal distribution with larger droplets than rotor stator devices, static mixers produce droplet size with a normal distribution, and rotor stator mixers produce normal and log normal distributions (Paul et al., 2004). The latter happens when very small droplet sizes are produced (for example, when a very high energy is introduce to the emulsions or when a regimen transition occurs) (Paul et al., 2004). - Operation regimen (batch – continuous): Batch systems produce wider DSDs in comparison to continuous operation systems. DSD can be narrowed in Batch systems if the agitation in the entire vessel is improved to be homogeneous (Paul et al., 2004). - Viscosity of the disperse phase: A more viscous disperse phase generates a broader distribution(Paul et al., 2004); (Vankova et al., 2007). This effect is significant and it can be avoided by heating or changing disperse phase composition. - Interfacial tension: distribution becomes broader as interfacial tension is increased (Vankova et al., 2007). Interfacial tension can be reduce by adding/changing surfactant system or by selecting an oily phase more affine to water.
24. Volume fraction (ϕ)	In practice an increase in volume fraction implies an increment of the oily phase and/or of particles concentration, in case the product contents suspended particles. When volume fraction is augmented, emulsion rheology, stability and appearance are importantly affected. For example, emulsion lightness increases, viscosity and viscoelastic behavior are enhanced, and stability against flocculation, coalescence and phase inversion may be affected. For O/W the increment of the oily phase carries higher costs. When the product contents suspended particles, it is necessary to pay attention to some conditions (Paul et al., 2004): - Agitation should be homogeneous through the vessel. For this purpose agitators with high pumping efficiency are preferred (contrary to equipment use for homogenization, where more shear is preferred). - If the solids float, a mixer must-be designed to provide downward pulling drag. -Small and flat particles are easier to suspend than large and dense solids. The use of particles is necessary when special functions are required. For example, many colorants are pigments, and they have to be dispersed to give color to emulsion. Mineral U.V. filters as titanium oxide are non-soluble solids that have to be dispersed.
Environment	
25. Packing	The packing provides protection to the product. It can be designed with U.V. protection or in a way it can limit oxygen inlet to the product. Special attention has to be given to packing material and its compatibility with the product formulation. It is advisable to perform a stability test of the product to study is compatibility with packing material.
Functional ingredients	
26. Delivery system 27. Antioxidants 28. Preservatives	This section contains special ingredients that can be used to perform a specific function. Some of them are explained below: - Delivery system: An emulsion itself is a delivery systems, because it has two phase that can be used to dilute and transport bioactive compounds. It can also contain a specific delivery system. Example of them are: multiple emulsions, multilayer emulsions, solid lipid particles, and filled hydrogel particles (McClements et al., 2007). - Antioxidants: are compounds that prevent oxidation, the formation of free radicals and the deterioration of cells - Preservatives are substances that inhibit the growth of organism preventing the product to get damage. Careful has to be taken with this substances because many of them can be toxic or controlled with a limit concentration

Solution strategies	Solution strategies and their application
29. Chelating agents 30. Alcohols - solvents 31. Fragances 32. Colorants 33. Rheological modifier - continous phase 34. Rheological modifier - disperse phase	Chelating agents are compounds capable of remove transition metals as iron and copper and remove them from the vicinity of droplets (McClements and Decker, 2000). Examples of this agents is EDTA (McClements and Decker, 2000). -Alcohols – solvents: This solution strategy makes reference to the addition of a low molecular weight alcohol (ex: ethanol) or other solvent. In some cases this can affect the spontaneous curvature of the surfactant system (from O/W to W/O), increase solubility of oil in water, reduce surface tension, increase water refractive index, enhance emulsion preservation, amount other effects. - Fragrances naturally give aroma to emulsion. Careful has to be taken to aspects as toxicity and compatibility with other components, stability to pH and light, price, and in the case of cosmetics, compatibility with skin. - Colorants obviously give color to emulsion. In colorant selection, it is necessary to pay attention to aspects such solubility in the media (dyes are soluble and pigments are not), resistance to pH and temperature changes, stability to the light and chemical agents, price. - Rheological modifiers are substances that change the rheological behavior of the mixture. They can increase viscosity or change the rheological profile to increase shear thinning behavior or enhance viscoelasticity. Examples of rheological modifiers enhancing shear thinning behavior: xhantan gum, guar gum, carbomers, polyethylenes (Laba, 1993).Examples of rheological modifiers enhancing viscoelastic behavior are: cellulose gum, clays, trihydroxystearin, fumed silica (Laba, 1993)

4.1.2 First relational matrix

To construct the first relational matrix, three experts in emulsion science, from the academy, were consulted. They were asked to assess the interrelation between sub-problems and solution strategies using a seven points scale: -7, -3, -1, 0, 1, 3, 7, where 7, 3, 1 and 0 correspond to high interrelation, intermediate interrelation, low interrelation and no interrelation, respectively. Negative values correspond to an opposite relation. From the transport phenomena sub-problems, only those related to volatile compounds were analyzed by experts. Other values were added considering the description in Table 4-1 and 4-2. The complete first relational matrix is presented in Table 4-3.

Table 4-3*: Interrelation between sub-problems and solution strategies*

			Aqueous phase					Interfase					Oily phase		Oily phase - aquous phase			Colloidal forces					Structure			-			Functional ingredients							
			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34
			water activity -presence of	polarity of aqueous phase	pH	Electrolyte concentration aquous phase	Multivalent electrolyte concentration aquous phase	Surface charge density (σ)	quality of solvent - steric	Thickness -steric interaction	Gibbs elasticity -interfacial film	Interfacial tension (γ)	polarity of oily phase	Degree of unsaturation of the oils	Refractive index difference (|η0-η1|)	Density difference (|ρ0-ρ1|)	Solubility of the disperse phase components in the continuous (Δko/w)	Depletation interaction (attractive)	Polyions/Ion bridging -	Electrostatic interaction	Steric interaction (repulsive)	Weak flocculation	Droplet size	Droplet size distribution (width)	Volume fraction φ	T ambient	Packing	Delivery system	Antioxidants	Preservatives	chelating agents	Alcohols - solvents	Fragance	Colorant	Rheological modifier - continous phase	Rheological modifier - disperse phase
Appearance	1	Emulsion lightness (opacity)	0	0	0	0	0	0	0	0	0	0	0	0	3	0	0	0	0	0	0	1	3	+/-1	3	0	0	0,3	0	0	0	0	0	-1	0	0
	2	Color hue (chromaticity)	0	0	0,+/-3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	7	0	0
	3	Intensity of color	0	0	0,+/-3	0	0	0	0	0	0	0	0	0	-3	0	0	0	0	0	0	-1	-3	+/-1	-3	0	0	0,3	0	0	0	0	0	7	0	0
	4	Precence of special color features	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	7	0	0
Rheology	5	Viscosity	0	0	+/-3*	-3*	-3*	?	?	3	3	0,3*	0	0	0	0	0	instability	7	3*	3*	7	-1**	-3**	3	-3	0	0	0	0	0	0	0	0	7	1
	6	Shear thinning behavior	0	0	+/-3*	-3*	-3*	?	?	3	-1	0,3	0	0	0	0	0	instability	7	3*	3*	7	-1**	-1**	7	-3	0	0	0	0	0	0	0	0	7	-?
	7	Thixotropic behaviour	0	0	+/-3*	-3*	-3*	?	?	3	0	0,3	0	0	0	0	0	instability	7	3*	3*	7	-1**	-1**	3	-3	0	0	0	0	0	0	0	0	7	0
	8	Viscoelastic behavior	0	0	+/-3*	-3*	-3*	?	?	1	1	0,7	0	0	0	0	0	instability	7	3*	3*	7	-1**	-1**	7	-3	0	0	0	0	0	0	0	0	7	1
Stability against	9	Gravitational forces	0	0	0	0	0	0	0	0	0	0	0	0	0	-7	0	0	0	0	0	-3	-7	-3	3	-1	0	0,-3	0	0	0	0	0	0	7	0
	10	Flocculation	0	0	+/-3*	-1	-7	3	3	3	0	0	0	0	0	0	0	-3	-7	3*	3	-3	0,-3	0,-1	-3	-3	0	0,-3*	0	0	3	0	0	0	3	0
	11	Coalescence and partial coalescence	0	0	+/-3*	+/-3	-3	3	3	7	7	3	0	0	0	0	0	-3	-3	3	3*	-3	-7	-1	-3	-7	0	0,-3	0	0	3	0	0	0	3	?
	12	Phase inversion	0	0	0,+/-3*	+/-3*	+/-1	0	3	0	0	+/-7	-7	-1	0	0	0	0	0	0	0	0	0	0	-7	0,+/-3	0	0	0	0	+/-1	0	0	0	0	0
	13	Ostwald ripening	0	0	?	?	?	0	?	0,3	0	-7	-7	-1	0	0	-7	0	0	0	0	0	7	-7	0	-3	0	0	0	0	0	-3	0,-3	0	3	1
	14	Lipid oxidation and chemical stability of lipids	0	?	+/-7	-1	-1	0	0	0	0	0	-3	-7	0	0	-1	0	0	0	0	0	0	0	0	-1	3	0	7	?	3	0	0	0	0	0
	15	Biological stability	-3	0	0, 3	3	3	0	0	0	0	0	0	0	0	0	0,-1	0	0	0	0	0	0	0	-1	-7	3	0	?	7	?	3	0,3	0,3	0,-3	0
Transport phenomena	16	Release of a relative polar molecule (Kow<1) from emulsion to a polar medium	?	+/-3	?	?	?	0	0	0	0	0	-1	0	0	0	-1	0	0	0	0	0	0	0	0	3	0	3	0	0	0	+/-3	0	0	-3	0
	17	Release of a relative nonpolar molecule (Kow>1) from emulsion to a polar medium	?	?	?	?	?	0	0	0,-3	0,-3	0	+/-3	0	0	0	+/-3	0	0	0	0	0	-3	?	-3	3	0	3	0	0	0	0	0	0	-3	-3
	18	Release of a relative polar molecule (Kow<1) from emulsion to a relative unpolar medium	?	+/-3	?	?	?	0	0	0	0	0	-1	0	0	0	-1	0	0	0	0	0	0	0	0	3	0	3	0	0	0	+/-3	0	0	-3	0
	19	Release of a relative nonpolar molecule (Kow>1) from emulsion to a relative nonpolar medium	0	?	?	?	?	0	?	0,-3	0,-3	0	3	0	0	0	3	0	0	0	0	0	-3	?	-3	3	0	3	0	0	0	+/-1	0	0	-3	-3
	20	Release of a relative polar volatile molecule to the air	?	+/-3	?	?	?	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3	-7	-7	0	0	?	+/-3*	7	0	-3	0
	21	Release of a relative nonpolar volatile molecule to the air	0	?	?	?	?	0	0	0,-3	0,-3	0	3	0	0	0	3	0	0	0	0	0	-3	?	-3	3	-7	-7	0	0	?	+/-3*	7	0	-3	-3

Notes:

?	In this cases, there may be an interrelation between the strategy and the problem, but it is indirect or unknown
+/-number	In this cases, there is an interrelation that can be positive or negative according to the specific problem conditions. Thus, the interrelation between the strategy and the problem has a maximum or a minimum
0, number	In this cases, there is an interrelation or not according to the specific problem conditions. Thus, when product designers know there is an effect, they can select the value after the comma to characterize it, otherwise, they can assume there is not an effect with a warning
*	For these cases, the importance of the interrelation can be weak (1), intermediate (3) or very strong (7) according to experts. Intermediate (3) was taken to represent the effect, but this value has to be treated with caution.
**	For these cases, interrelations between rheological behavior and emulsion structure (droplet size, droplet size distribution) become more important as disperse phase concentration increases. For non-concentrate emulsions a value of -1 is given in the table, but it can be increased to -3 as disperse phase concentration increases
Instability	For these cases, the most important effect is the stability problem, reason why rheological behavior is not considered.

Table 4-3 presents sub-problems in rows and solution strategies in columns. It can be used to explore possible actions to solve a specific problem or possible effects when an emulsion characteristic is changed. Following, some examples are presented to explain its meaning.

- It can be seen that pH (column 3) is a variable that affects many sub-problems of the groups of appearance, stability and rheology. This happens because with pH it is possible to control dissociation of some compounds and electrical charge in relation to the isoelectric point. pH is more relevant in systems that were electrostatically stabilized. Most of the values of the column present pH as having a positive or negative effect according to the specific problem conditions. If the effect of the pH on the system according to problem conditions is known, the designers can give to the cell a value (either positive or negative) and use it as a solution. If the effect of the pH is not known, designers cannot count with it as a solution but as a condition/possible limitation that has to be checked.
- There are some cells presenting two possible values (those in pink in Table 4-3). For example, the cell relating pH with biological stability (row 15) can takes the values of 0 or 3. When the designers do not know which value is the correct for their specific problem, they cannot count with it as a solution. The cell takes the value of 0 with a warning. Otherwise, they can decide which one is the correct value. For example, when the pH is below 5, there is a hostile environment for microorganism and the cell takes the value of 3 because in this case pH contributes to the biological stability. When the pH is around 7, the cell takes the value of 0 without any warning because it is sure that pH does not contribute to the solution of the biological stability.

  Something similar happens with fragrances, colorants and rheological modifiers in relation to biological stability. There are some essential oils and colorants that have preservative function. In these cases, a positive value can be assigned to the cell because they contribute to biological stability. Otherwise, the cell takes the value of 0. In the case of rheological modifiers, those that are natural may enhance biological activity while those that are not do not contribute to biological activity. In the first case, the cell takes a negative value, while in the second case it turns to 0.
- Droplet size (column 21) is a characteristic that has effects on many emulsion sub-problems. As it gets smaller, emulsion tends to be more stable in relation to gravitational force, flocculation and coalescence, but more instable in relation to

Ostwald ripening (see column droplet size in Table 4-3). In the case it is desired to have a small droplet size to avoid the first mentioned instabilities, it is necessary to take other measures to control Ostwald ripening, for example: to select an oily phase with a low solubility in the continuous phase.

- The enhance release of nonpolar volatile molecules (row 21) can be improved by: Selecting an emulsifier that do not interact with the volatile molecules (interactions such as covalent binding). In cases where there is an interaction, the thickness and nature of the interface may generate an important effect against the release (row 21 and columns 8, 9). Selecting a polar oily phase that enhances release and decreases solubility of the nonpolar component (column 11). A similar behavior is observed in relation to the solubility of the disperse phase in the continuous phase (column 15). In general temperature increase the transport of components (column 24), and the viscosity of the media difficult it (column 33).

The matrix is proposed to be used as an aid to make product design decisions. For its use the following steps are recommended:

1) Classify product specifications according to sub-problems of the matrix. Some specifications may be related to the fifth category: special functions (for example, U.V. protection, moisturizing function, etc.).
2) Select sets of solution strategies to solve the sub-problems using Table 4-3. More than a set of solution strategies can be generated. They can be more integrated (more than a problem is addressed with the same strategies due to a synergy) or more decoupled (each sub-problem has an independent solution strategy to tune it, when possible). It is recommended to decouple at least key sub-problems related to specifications that are very important in the design problem or those that have point target values or narrow target intervals.
   Here, a score for the degree of integration is proposed as the number of problems (m) over the number of solution strategies (n). As the score increases, the solution set is more integrated
   Degree of integration-solution set: $Degree_{integration} = \frac{m}{n}$
3) Check that all sub-problems are treated by summarizing the values of all the implemented solution strategies (j) for each sub-problem (i).

Score solution Sub-problem (i)

$$sP(i) = \sum_{j}^{n} x_{ij} \quad [4\text{-}17]$$

, where $sP(i)$ is the score for sub-problem (i), x_{ij} is the value in the cell ij of matrix 4-3, j is one of the selected solution strategies and n is the quantity of selected solution strategies

4) If different set of solution strategies are formed, it is possible to compare them according to the score of key sub-problems and their degree of integration or decoupling.

4.1.3 Ingredients for application in the cosmetic sector

Following, considering that the case study treated in this study is a cosmetic emulsion, a data base of ingredients for the cosmetic sector is proposed. Ingredients are presented in four groups: oils, surfactants, polymers and other ingredients (which include glycols, preservatives, colorants, fragrances and active ingredients).

Oils: Oils are used in cosmetic emulsions with several purposes: To act as emollients and give softness to the applied area (skin, hair) (Bagajewicz et al., 2011), and serve as solvents for liposoluble active ingredients. Some of them can also act as occlusive ingredients, i.e., ingredients that create a barrier and avoid the loss of water from skin (Bagajewicz et al., 2011), and some of them are naturally present on skin, for example, ceramides, cholesterol and fatty acids (Bagajewicz et al., 2011).

Characteristics/properties that are important to be considered in their selection are:

- Polarity: it determines their compatibility with other ingredients and their capability of solubilizing active ingredients. Properties related to polarity are Hansen solubility parameters, octanol-water partition coefficient (K_{ow}) and HLB.
- Required HLB: it determines the compatibility of oils with the surfactant system. It can be measured by producing a series of emulsions with the oil of interest, using emulsifiers with different HLB. The best emulsion corresponds to the required HLB of the oil of interest (ICI AMERICAS Inc., 1980). Required HLB for mixture of oils can be calculated by the weighted sum of the HLB of oils in the formulation.
- Melting point: it determines if the oil is solid or liquid, its consistency and the possible consistency of formulations (Iwata and Shimada, 2013). It is related to the oil's molecular weight (Iwata and Shimada, 2013).

- Viscosity: it determines consistency and spreadability of the oil and its formulations
- Density: Most oils are less dense than water, with a value around 0.8.
- Sensation profile: It is particular important for cosmetic emulsions, because it determines the impressions that oils and their formulations can produce in the customer.
- Environmental and Safety properties: All cosmetic ingredients must be safe and should not affect the environment. Some environmental and safety indicators are: explosiveness, flammability, human toxicity potential by inhalation or dermal exposure and acute oral toxicity, among others. Additional indications for safety can be found in the safety data sheets of each specific compound.
- Source: Oils can be 100% vegetable, vegetable based or hydrocarbons. This is important because of the increasing concern of customers in relation to the renewable origin of the products. Stability to oxidative agents, pH, temperature
- Additional characteristics/properties of interest are: special sensory profile, solubilization of UV filters, wetting capability, film forming capacity.

Oils can be classified into groups according to their chemical nature. Table 4-4 shows groups of oils and their properties:

Table 4-4: Properties of oils classified according to their chemical nature (Iwata and Shimada, 2013), Required HLB (Croda, 2015)

Oils	Description	Melting point	Polarity	Viscosity	HLB required	Feel of use	Stability oxidation	Stability pH	Stability Temperature
Hydrocarbons	Saturated non polar molecules (do not possess oxygen)	Variable	Low	Variable. It increases with molecular weight	9-11	Variable. Light sensation increases when molecular weight decreases	Stable	Stable	-
Waxes	High molecular weight compounds. They can be fatty acids, hydrocarbons, alcohols, esters.	Less or close to room temperature	Variable (depending on chemical nature of the wax)	high	Variable	Solid consistency. It gives a waxy, lubricous, moisturizing sensation	Variable (measurable with the iodine number)	Variable (depending on chemical nature)	-
Esters	Product of reaction of fatty acid and alcohol compounds.	Variable	Between hydrocarbons and alcohols	Variable depending of molecular weight	10-12	Variable. Esters with branches give a more moisturizing and lubricous sensation than esters of straight chain. Low molecular weight esters give a lighter and dry sensation.	Variable	Instable at low and high pH because hydrolysis may occur	-
Vegetable oils	Also known as tTriglycerides. They are highly polar due to the three ester bonds and depending on the oil composition they may be resistant or not to oxidation	Variable	Tend to be high due to the three ester bond. It varies according to the extension of the alkyl group and the presence of double bonds	Tend to be high, causing a heavy sensation to touch.	5-7	It is determined by the alkyl composition: - Oils rich in lauric and myristic acid (short alkyl chains) give a light sensation. - Solid fats rich in palmitic and steric acid reduce lubrication and gives a dry light sensation - Oils rich in unsaturated acids give a high moisturizing feeling	Variable, depending on the presence of unsaturation. Oils containing high concentration of oleic, linoleic and linolenic acids can oxidize quickly.	Low at high pH, because it may oxidize or undergo saponification	-
Higher alcohols	Alcohols with a long carbon chain. This chain can be branched, straight, saturated or unsaturated	Variable	High. Decreases with molecular weight	High for cetyl and stearyl alcohols. They are used as stabilizing agents	14-15	Many of them are consistency agents and give moisturizing effect	Variable	Stable	-
Fatty acids	Fatty acids are carboxylic acids (contain the group COOH) with long carbon chain		High	They can increase the viscosity of emulsion. Examples are oleic and stearic acid	14-15	They are agents that increase consistency. They form complex with cationic surfactants, improving the feel of use	Variable	Unstable at high pH (saponification). For cosmetics, it is common the use of their salts	-
Silicons	polymers of siloxane (a group of silicon and oxygen), which are used to improve texture in cosmetic products because they can give a soft and dry pleasant texture. They are also occlusive agents and form films that retain the humidity.	Low, in general they are liquid	Low	It increases with the molecular weight of the silicon. The different viscosities generate different textures.	8-12	They give a silky and soft texture to emulsions. As their molecular weight increases, the sensation they provides pass from light and silky (20-100cp), strong silky and smooth (100-5000cp) to persistant and lubricous (5000cp -10000cp).	-	-	Many silicons are sensible to high temperatures, those with low weight may volatilize

Surfactants: Surfactants are organic compounds that have two parts: a lipophilic part and an hydrophilic part (Rosen and Dahanayake, 2000). They are used in emulsions with three purposes (McClements, 2016):

To decrease interfacial tension during emulsification, reducing the required energy in the process,

To adsorb rapidly in the interface of recently formed droplets,

To generate a barrier either electrostatic, steric or of both for the long term protection of droplets and emulsion stability

In addition, they have to maintain emulsion properties under specific conditions of pH, ionic strength, temperature, etc.

Characteristics/properties that can considered for surfactant selection are:

- HLB: The hydrophilic lipophilic balance is an indication of how soluble is a surfactant in water or in an oily phase (Akzo Nobel, 2011). Low HLB indicates that the surfactant is more lipophilic and tends to form W/O emulsions. Correspondingly, a high HLB indicates that the surfactant is more hydrophilic and tends to form O/W emulsions.

  The HLB for mixture of surfactants is calculated by the ponderation of HLB of surfactants with their respectively percentage in weight regarding the total of the surfactant system (Croda, 2015).
- Surfactant nature and the effect of environmental conditions: In general there are two main surfactant families: Ionic and nonionic surfactants. Each of them stabilize emulsion using different forces: electrostatic interactions and steric interactions, respectively.

  Electrostatic interactions depends strongly on the electrical characteristics of surfaces, which in turn depends on the electrolyte concentration and pH of the aqueous phase (McClements, 2016). Electrolyte concentration determines the range of the electrostatic interactions, which become increasingly short range at high electrolyte concentration, making droplets to approach each other (McClements, 2016). pH determines the ionization degree of ionic surfactants, which create a repulsion, only when they are dissociated. Advantage of this systems is that less quantity of emulsifier is required in relation to steric stabilized systems (McClements, 2016), and that their emulsions tend to be more resistant to temperature changes.

Steric interactions depends on the specific characteristics of the surfactant molecule: interfacial rheology and packing. Its range of action increases as the thickness of the interface increases (McClements, 2016). They are less sensible to pH and electrolyte concentration, but more amount of the surfactant is required to cover the droplet surface (McClements, 2016). Although nonionic surfactants are less sensible to pH and electrostatic interactions, it worth to mention that they are affected by these conditions to some degree. The spontaneous curvature of both ionic and nonionic surfactants are affected by environmental factors as follow (Binks, 1998):

For ionic surfactants an increase of the temperature and/or an increase of the polarity of the oily phase favors a positive spontaneous curvature and the formation of O/W emulsions. On the contrary, an increase in electrolyte or inactive species (for example sugar) concentration is unfavorable for the formation of positive spontaneous curvatures and stable O/W emulsions.

For nonionic surfactants the temperature has an inverse effect in relation to ionic surfactants. Especially for Alkyl polyglucosides and polyethoxylated surfactants, an increase in temperature favors a negative spontaneous curvature and the formation of W/O emulsions. Similarly, happens with the addition of surface inactive species that favors negative spontaneous curvature. Electrolytes may have a positive or negative effect on the spontaneous curvature.

Thus, for the selection of an appropriated surfactant, both HLB and environmental conditions of the emulsions should be taken into account.

- Solubility: Some surfactants are soluble in the oily phase while others in the aqueous phase. This characteristic is important to define in which phase the surfactant is dissolved or pre-disperse for emulsification. This information can be gotten from suppliers, who usually give recommendations of how to use the products.
- Critical micelle concentration (CMC): It is the concentration at which the surfactant molecules begin to form micelles in aqueous solution, i.e., an aggregate structure of surfactant molecules (Rosen and Dahanayake, 2000). From that point, the surface tension does not decrease appreciably by increasing surfactant concentration. CMC is greater in more hydrophilic surfactants (McClements, 2016). For ionic surfactants it decreases as ionic strength increases, because it favors the encounter of molecules in spite of the head charged groups (McClements, 2016).

- Krafft point: It is the minimal temperature from which surfactants begin to form micelles. Below this temperature, solubility of surfactant is low and it is not possible to reach a critical micelle concentration (Rosen and Dahanayake, 2000). Stable emulsions are only formed over this temperature (minimal condition for stability)
- Cloud point: Solubility of some surfactants (mostly nonionic) decreases as temperature increases, because the hydrophilic head becomes dehydrated until a point. The temperature at which the surfactants precipitate and turn the emulsion turbid is known as the cloud point (Rosen and Dahanayake, 2000). Near the cloud point, the interfacial tension decreases, which may be advantageous during homogenization. Formed emulsions are destabilized above this temperature (minimal condition for stability).
- Effectiveness of adsorption: it is a measure of the amount of adsorbed surfactant in the interface. It can be measured by the saturation surface concentration (Γ_{max}) , which indicates the maximal amount of surfactant that can be adsorbed (Rosen and Dahanayake, 2000).
- Effectiveness in reducing the surface tension: it can be measured by the surface pression at critical micelle concentration (π_{CMC}), which measures the maximal possible reduction of surface tension (Rosen, 2004).
- Efficiency of adsorption: It is a measure of the tendency of the surfactant to adsorb at the surface (Rosen and Dahanayake, 2000). It can be measured with the molar concentration of the surfactant required to reduce surface tension to a certain value (20 dyn/cm by convention (Rosen and Dahanayake, 2000)). Efficient surfactants reduces surface tension with less quantity than less efficient surfactants.
- Adsorption Kinetics: Different surfactant molecules adsorb at different rates. This can be characterized by measuring the reduction of surface tension with time (Rosen and Dahanayake, 2000). The rate of adsorption depends on two phenomena: the diffusion of the surfactant through the bulk liquid and the fixation of the surfactant at the interface (McClements, 2016). The first phenomena is determined by the diffusion coefficient and the concentration of surfactant in solution. It is improved as surfactant molecular weight decreases (because it increases diffusion coefficient) and its concentration increases (McClements, 2016). The second phenomena is controlled by an adsorption energy barrier. When emulsifiers adsorb rapidly smaller droplets are formed during homogenization (McClements, 2016).

- Sensation profile, as for oils, it is important for emulsifier selection
- Environmental and Safety indicators, as for oils, are important for emulsifier selection
- Source, as for oils, is important for emulsifier selection
- Stabilization capability: The capability of forming “stable” emulsions is maybe the most important function of surfactants. While it is true that it is possible to select a surfactant system that favors a type of emulsion (O/W or W/O) under certain pH, T and environmental emulsion conditions, to our knowledge, there is still no exact property, model or measure that predicts the capability of a surfactant system to form stable emulsions during a determinate period. It is always necessary to try it experimentally with all ingredients and under real conditions.

  There are some heuristics that can be used to create stable emulsions:

  1) It is better to select a mixture of surfactants that together have the appropriated HLB than a sole surfactant with the correct HLB (Rosen and Dahanayake, 2000).
  2) Good emulsifier have limited solubility in both, aqueous phase and oily phase (Rosen and Dahanayake, 2000).
  3) A better packing of the hydrophobic groups at the interface increases emulsion stability (Rosen and Dahanayake, 2000).
  4) Mixture of surfactants that have been already used under similar conditions than the design problem, are good options. Some examples of applications and effective emulsifiers can be found in (ICI AMERICAS Inc., 1980). Providers usually give examples of formulations with the data sheet of their emulsifiers.

Surfactants can be classified according to the characteristics of their hydrophilic head and hydrophobic tail as shown in Tables 4-5 and Table 4-6.

Table 4-5: Properties of surfactants according to their ionic nature From (Iwata and Shimada, 2013)

	Cationic	**Anionic**	**Nonionic**
Function	In addition to its capacity of producing stable emulsions. It is used as charge neutralizer (avoid freeze) and conditioning agent for hair and skin	High detergency, emulsification capability	Ester or ether emulsifiers
Uses	Use in conditioners and skin creams	They are use in soaps, shampoos, cleansers	Emulsification
Short chain (C12)	The feel of use is poor and may not be used as emulsifiers but as solubilizers (example is Laurtrimonium Chloride)	Surfactants with short chain (C12) have good detergency because they solubilize better in water than long chain surfactants.	Less viscous products with a less soft sensation
Long chain (C16-18)	The feel of use improves gets more moisturizing and soft as the alkyl chain length increases	Surfactants with long chain (C16-C18) are used as emulsifiers, because they have more affinity to oils.	More viscous products with more moisturizing sensation
Feel of use	In the case of surfactants with trimethyl ammonium as cationic head, the feel of used is determined by the length of the alkyl chain. If it is short (C12) the feeling is coarse, if it is larger (C16, C18, C22), the feeling is more moisturizing. This effect is very important in final product sensation profile. Viscosity is highly affected by the combining of the surfactant with cetyl or stearyl alcohol	Depends on, length of the alkyl chain and the anionic group. Long chains and anionic groups with less electronic charge (carboxyl, phosphate) increase hydrophobicity of the molecule, it tends to remains in skin giving a moisturizing lubricous final sensation. In shampoos they form complexes with cationic surfactants which affects greatly the viscosity of the product.	It depends on the number of polyoxyethylene groups and the characteristics of the alkyl chain (length, double bonds, and side chains). As length augment, the sensations change from coarse (C12), lubricous (C16) to soft and moisturizing (C22). The alkyl chain also determines the viscosity of the product. The larger the alkyl chain, the more viscous is the product Double bonds increase moisturizing oily sensations Branch chains also increase moisturizing silky effect. This effect is important but not that much in comparison to cationic surfactants. Alkyl chains with double bonds help to decrease viscosity. For example oleates decreases viscosity and maintain a moisturizing sensation.
pH	NA	Instable emulsions at low pH	Resistant to low pH
Polyethoxyl ene	-	Hydrophilicity is improved in surfactants with polyethoxylene or amino acid groups.	Increase the affinity to water od the surfactant
Counter ions effect	They may be chlorides, bromides, methyl sulfates, having the first the best emulsifying capacity.	Sodium and potassium salts are more soluble than triethanolamine, but this last produce less irritating products. A softer texture is achieved with triethanolamine and potassium counter ions in comparison to sodium salts. In the case that neutralized fatty acids neutralized are used as emulsifiers,	-

	Cationic	**Anionic**	**Nonionic**
		softer and less viscous products are achieved with riethanolamine than with sodium hidroxide	
T	To assure its stability at high temperature, it is recommended to add long chain alcohols (as cetyl alcohol)	Anionic surfactants have a low stability at low Temperatures, because their solubility decreases. Therefore it is recommended to use them in combination with nonionic surfactants and polymers as stabilizers	Low solubility at high temperatures (overall for those with polyethoxylated and polyglucoside groups). It is recommended to use polymers and long chain molecules.
Incompatibilities	Anionic species should be avoided that may conduct to instable emulsions. Cationic polymers are recommended to stabilize it and add viscosity.	It forms complexes with cationic species	Depends on the specific case
Examples	Mono-alkyl cationic surfactants are excellent emulsifiers. Di-alkyl and tri-alkyl surfactants have to be used in combination with other emulsifiers and are used to give different sensations.	See Table 4-6	Common examples are Glyceryl monostearate, which has a low HLB but can be used to create O/W emulsion in combination with other nonionic or anionic surfactants. Mixtures of sorbitan fatty acid Esters and polyoxyethylene sorbitan fatty acid are used as emulsifiers in O/W

Table 4-6 Properties of anionic surfactants. From (Iwata and Shimada, 2013)

	Carboxyl	**Phosphate**	**Sulfonate**	**Sulfate**
Hydrophilicity	Less hydrophilic than other anionic surfactants. Thus, if not polyethoxylated, tends to remains longer on skin in relation to other similar anionics	-	-	Most hydrophilic anionic surfactant, because it has electronic charge. Thus, it has a high detergency and a less moisturizing sensation
Effects of polyethoxilation	It augments the hydrophilicity of the surfactants, and consequently, its solubility in water	It augments the hydrophilicity of the surfactants, and consequently, its solubility in water	It augments the hydrophilicity of the surfactants, and consequently, its solubility in water	It augments the hydrophilicity of the surfactants, and consequently, its solubility in water
Effect of pH	Instable at low pH	Non-stable at low pH	Instable at low pH, but more resistant than carboxyl and phosphates	Instable at low pH, but more resistant that the other anionic surfactants, because as
Effect of salt	It is affected by salt addition	It is affected by salt addition	It is highly affected by salt addition (salting out)	It is highly affected by the addition of salts (salting out), because of their high electron density

Water solubility	Depends strongly on alkyl chain. Long alkyl chains (C16-C18) create less soluble products than short alkyl chains (C12), which have better detergency properties. Hydrophilicity is improved in surfactants with polyethoxylene or amino acid groups.	Depends strongly on alkyl chain. Long alkyl chains (C16-C18) create less soluble products than short alkyl chains (C12), which have better detergency properties. Hydrophilicity is improved in surfactants with polyethoxylene or amino acid groups.	Depends strongly on alkyl chain. Long alkyl chains (C16-C18) create less soluble products than short alkyl chains (C12), which have better detergency properties. Hydrophilicity is improved in surfactants with polyethoxylene or amino acid groups.	Depends strongly on alkyl chain. Long alkyl chains (C16-C18) create less soluble products than short alkyl chains (C12), which have better detergency properties. Hydrophilicity is improved in surfactants with polyethoxylene or amino acid groups.

Rheological modifiers:

Rheological modifiers are added to the formulation with three main purposes (Iwata and Shimada, 2013): to increase viscosity, to enhance a particular rheological behavior (pseudoplastic, thixotropic), and to enhance emulsion stability at low or high temperatures. In addition, some of them (mostly the cationics) can also improve the texture of the final product as well as to static control and conditioners (Iwata and Shimada, 2013).

Rheological modifiers can be classified according to their origin in natural or artificial. They can also be classified according to their ionize nature in anionic, cationic, nonionic or amphoteric.

Important characteristics/ properties to consider for rheological modifier selection are:

- Efficiency: This can be described as the capability of increasing viscosity using a certain quantity of the rheological modifier. Efficiency depends on polymer nature, molecular weight, branches and conformation. It may be different between same polymers with similar molecular weight but different provider, due to differences in the production process, reason why it has to be evaluated before adding it into de formulation (McClements, 2016).
- Stability with other ingredients: Rheological modifiers may cause the precipitation of other ingredients in the formula, reason why, it is necessary to evaluate their compatibility (Iwata and Shimada, 2013)
- Solubility in water: The solubility in water is important to establish how to introduce it to the formula (Iwata and Shimada, 2013). Some rheological modifiers are soluble in hot but not in cold water. Some of them dissolve at low pH and are active at high

pH. Some of them can be pre-dispersed in glycols or alcohols before they are dissolved in water.

Other ingredients

Glycols are chemical compounds that content a certain number of hydroxyl groups. They are soluble in water because they are more polar than components of the oily phase (Iwata and Shimada, 2013). They are widely used in cosmetics due to their hydration capability. Other functions are: stabilizers, solvents and dispersants of polymers.

They have also an important effect on the feeling of use. For example, glycerin, which is more polar, gives a very moisturizing sensation on skin and a sticky sensation in hair (Iwata and Shimada, 2013). 1,3-butylene glycol gives a moisturizing sensation on skin and slightly sticky. Propene glycol, which is less polar than the others and it gives a silky sensation in both skin and hair (Iwata and Shimada, 2013).

Preservatives are compounds that avoid products getting bad by controlling the growth of microorganism. Some of them cannot be used for certain product application and/or they have a maximum allow concentration in the final product.

For their selection, it is important to consider:

- Efficiency
- Maximal allowed concentration
- Toxicity
- Environmental effect
- Customer perception: For example, there is a general concern about the use of parabens in cosmetic products, reason why, unless necessary, they should be avoided.

Other ingredients are: chelating agents, antioxidants, colorants, essences, solar filters. For their selection it is important to consider: their function, ingredients efficiency, possible incompatibilities with other emulsion ingredients, toxicity, and environmental effect

4.1.4 Second relational matrix –ingredients data base

Properties of a group of cosmetic ingredients of the previous explained categories were collected in order to construct a data base for product design. This database comprise five sections: oils, surfactants, thickener agents, preservatives and solar filters. Information for its construction was collected mainly from product suppliers, technology books and cosmetics books. This database is called here the second relational matrix. Below the main three sections are introduced: oils, surfactants and thickener agents.

The proposed Oil database section contents 70 of different oils (mainly esters, but also vegetable oils, hydrocarbons, ethers and silicons) with the quantitative information of viscosity, surface tension and price, and the qualitative information of polarity, skin spreading factor, emollience, after feeling and cosmetic applications. A section of the data base is shown in Table 4.7. The complete Table can be found in Annex F.

Using this table it is possible to select emollients with a certain level of spreadability, viscosity, and polarity, properties that determine the feeling given by the product, product stability and its ability to dissolve or disperse active ingredients. It is to highlight that given this set of properties, some emollients are very similar between them (see Figure 4-2), i.e., without considering the price and/or sustainability properties, several emollients are equally good, even though this list is short in comparison to the broad market offer differentiation factors are the price, sustainability properties and the specific sensorial profile of the ingredients (which is much more complex than the characteristics presented in the Table 4.7), reason why, experts can be consulted in a subsequently step, once a sub-group of suitable emollients has been identified.

Table 4-7 Data base section - first compounds of the emollients section

INCI	Class	Polarity	Viscosity (mPa*s) (25°C)	Spreading	Surface tension at 25 °C (mN/m)	Emollience	Afterfeel	Price ($/kg)
Avocado oil	Vegetable oil	NA -	65.5 (7)	NA -	32.4 (7)	Rich (7)	NA -	16 (1)
C10-30 Cholesterol/ Lanosterol Esters	Ester	medium (3)	682.5 (3)	low (3)	NA -	Rich (3)	smooth (3)	NA -
C12-15 Alkyl Benzoate	Ester	high (2, 7)	13.4 (2, 7)	low (2)	32 (11)	medium to light (7)	low oily sensation (7)	20 (1)
Caprylic/Capric Triglyceride	Triglyceride	medium to high (2)	23.3 (2, 5, 7)	medium (6)	29 (7)	light (7)	low oily sensation (7)	16 (1)
Caprylyl Caprylate/Caprate	Ester	medium (2)	5* (2)	high (2)	NA -	-	NA -	NA -
Cetearyl Ethylhexanoate	Ester	medium (2, 7)	11 (2, 11)	medium (2)	30 (11)	medium (11)	NA -	NA -
Cetearyl Isononanoate	Ester	medium (2)	16.6 (2, 7)	medium (2)	29 (7)	medium to light (11)	smooth (11)	NA -
Cetyl Dimethicone (very high viscosity,nonpolar)	Silicone	low (-)	168 (7)	low (7)	21 (7)	Rich (7)	smooth (7)	NA -
Cetyl Ethylhexanoate	Ester	medium (7)	12.7 (7)	high (7)	30 (11)	medium to light (7)	low oily sensation (7)	NA -
Coco-Caprylate	Ester	medium (2)	5* (2)	high (2)	NA -	light (2)	NA -	NA -
Coco-Caprylate/Caprate	Ester	medium (2)	11* (2)	medium (2)	NA -	light (2)	NA -	NA -
Cocoglycerides	Triglyceride	high (2)	45* (2)	medium (2)	NA -	-	NA -	NA -
Decyl Cocoate	Ester	medium (7)	9 (11)	low (7)	29 (11)	light (7)	smooth (7)	NA -
Decyl Isostearate, Isostearyl Isostearate	Ester	medium (3)	18.9 (3)	NA (3)	NA -	medium (3)	smooth (3)	NA -
Decyl Oleate	Ester	medium (2)	17* (2)	medium (2)	NA -	-	NA -	NA -

Notes: *Viscosity at 20°C, ** Viscosity at 40°C

References: (1) Making cosmetics - ingredient supplier, (2) BASF. BASF emollients - choosing the right emollient. BASF Personal Care andNutrition GmbH. 2016, (3) Croda. Emollients Your Essential Selection Guide. Seventh Edition. 2013, (4) Technical information -Crodamol TM (spanish). Croda. NA. NA, (5) Croda. Pigment Wetting Guid DS-120R-1. Croda February 25, 1999, (6) Croda. Emollient Skin Spreading Factor DS-128. Croda. January 6, 1998, (7) M. Mentel*, S. Wiechers, A. Howe, P Biehl, J. Meyer. Senses- A Scientific Tool for the Selection of The Right Emailient. SOFW-Journal, 2014, (11) Croda datasheet, (12) Evonik datasheet

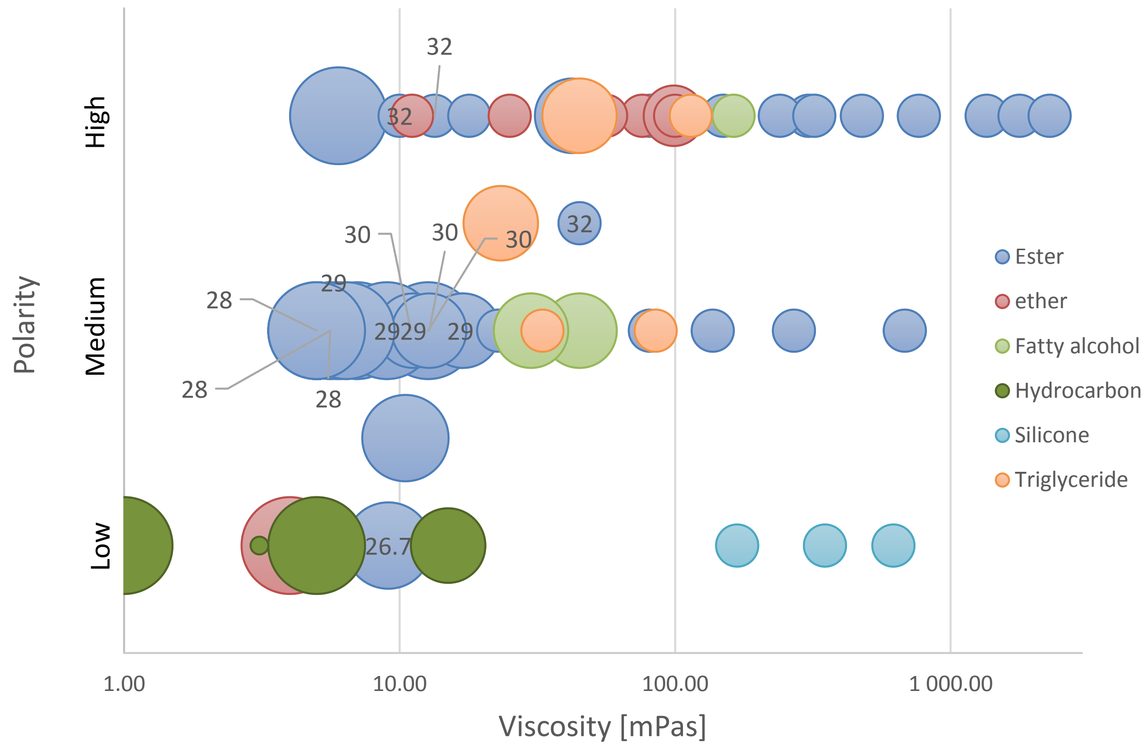

Figure 4-2: Bubble plot of Viscosity vs-polarity for emollients of Table 4-7. (The area of the bubbles represent emollient spreadability)

The surfactant database section contents 80 surfactants, most of them nonionic, of the following groups: alkyl glucosides, glycerol esters, POE alkyl ethers, polyglycerol esters, Polyoxyethylene glycerides, sorbitan and sucrose esters. Some anionic fatty acid salts and alkyl sulfates were also included. For this list, the following properties were consulted: HLB, recommended usage concentration, emulsion texture (lotion, cream, spray) and cosmetic applications (skin care, hair care, sun care). For some of them the critical micelle concentration and price were consulted. Table 4-8 shows a section of the surfactants data base. The complete Table can be found in Annex F.

Table 4-8 Data base – first 16 compounds of surfactants section

General information						Properties						Texture				
Classification 1	Classification 2	Type	INCI name	Price ($/kg)		HLB		Usage concen-tration		CMC (M) - 25°C		Cream	Lotion	Spray	Gel	
Anionic	Acylamino acid salts	O/W	Sodium Stearoyl Glutamate	NA	-	23	(3)	0.25 –2	(3)	NA	-	Yes	Yes	Yes	Yes	(3)
Anionic	Alkyl sulfate	O/W	Cetearyl Alcohol (and) Sodium Lauryl Sulfate (and) Sodium Cetearyl Sulfate	NA	-	39	(3)	3 – 10	(3)	NA	-	NA	NA	NA	NA	-
Anionic	Alkyl sulfate	O/W	Sodium Cetearyl Sulfate	NA	-	38	(3)	0 – 2	(3)	NA	-	Yes	Yes	NA	NA	(3)
nonionic	Alkylglucosides	O/W	Cetearyl Glucoside	NA	-	~13	(1)	1.0 – 1.5	(2)	NA	-	Yes	Yes	Yes	NA	(2)
Nonionic	Alkylglucosides	O/W	Cetearyl Glucoside (and) CetearylAlcohol	NA	-	11	(3)	2 –4	(3)	NA	-	Yes	Yes	-	Yes	(3)
nonionic	Alkylglucosides	W/o	Methyl Glucose Isostearate	NA	-	~5	(1)	2 –5	(8)	NA	-	NA	NA	NA	NA	-
nonionic	Alkylglucosides	O/W	Methyl Glucose Sesquistearate	NA	-	~12	(1)	2.0 – 4.0	(2)	NA	-	Yes	Yes	-	NA	(2)
Anionic	Fatty acid salt	O/W	Stearic Acid (and) Palmitic Acid	NA	-	18	(3)	0 – 2	(3)	NA	-	NA	NA	NA	NA	(3)
nonionic	Monoglycerol esters	W/O	Glyceryl Oleate	18.6	(9)	3	(3)	1 – 3	(3)	NA	-	NA	NA	NA	NA	-
nonionic	Monoglycerol esters	NA	Glyceryl Stearate	8.9	(9)	4	(7)	NA	-	NA	-	NA	NA	NA	NA	(7)
nonionic	Monoglycerol esters	O/W	Glyceryl Stearate Citrate	15.2	(9)	~12	(1)	0.3 – 2.0	(2)	NA	-	Yes	Yes	Yes	NA	(2)
nonionic	Monoglycerol esters	O/W	Glyceryl Stearate SE	8.9	(9)	~12	(1)	6.0 – 8.0	(2)	NA	-	Yes	Yes	-	NA	(2)
nonionic	Monoglycerol esters	O/W	Glyceryl Stearate; Ceteareth-20	NA	-	~12	(1)	NA	-	NA	-	NA	NA	NA	NA	-
nonionic	Monoglycerol esters	O/W	Glyceryl Stearate; PEG-100 Stearate	NA	-	~11	(1)	3 – 10	(2)	NA	-	Yes	Yes	-	NA	(2)
nonionic	POE Alkyl ethers	O/W	Ceteareth-15; Glyceryl Stearate	NA	-	~12	(1)	NA	(2)	NA	-	NA	Yes	Yes	NA	(2)
Nonionic	POE Alkyl ethers	O/W	Ceteareth-20	15.8	(9)	15	(3)	2 – 4	(3)	NA	-	NA	NA	NA	NA	-

References: (1) Evonik industries. Personal Care Catalog of products. 2015, (2) Evonik Industries. Emulsifiers for Skin Care Applications. March 2008. Essen - Germany, (3) BASF. Emulsifiers & Cream Bases. May 2016, (4) Rosen, M.J., 2004. Surfactants and interfacial phenomena, Third. ed. John Wiley & Sons, Inc, New York. doi:10.1016/0166-6622(89)80030-7, (5) Hait, S.K., Moulik S. P., Determination of critical micelle concentration (CMC) of nonionic surfactants by donor-acceptor interaction with lodine and correlation of CMC with hydrophile-lipophile balance and other parameters of the surfactants, American Oil Chemists' Society (AOCS), 2001. doi: 10.1007/s11743-001-0184-2, (6) Kim, C., Hsieh, Y-L., Wetting and absorbency of nonionic surfactant solutions on cotton fabrics, Colloids and Surfaces A Physicochemical and Engineering, 2001, DOI: 10.1016/S0927-7757(01)00653-7, (7) Croda datasheet, (8) Evonik datasheet, (9) Making cosmetics - ingredient supplier information

Figures 4-3 shows the HLB for a group of different nonionic surfactants in relation to their structures. The HLB increases as the length of the alkyl chain decreases and as the proportion of the hydrophilic part in the molecule increases, i.e., when the number of polyethylene groups (POE) increases. The most hydrophilic surfactants are those with POE groups, being able to reach values near 20. From the free-POE surfactants consulted, the sucrose monostearate presents also a relative high HLB with a value close to 15.

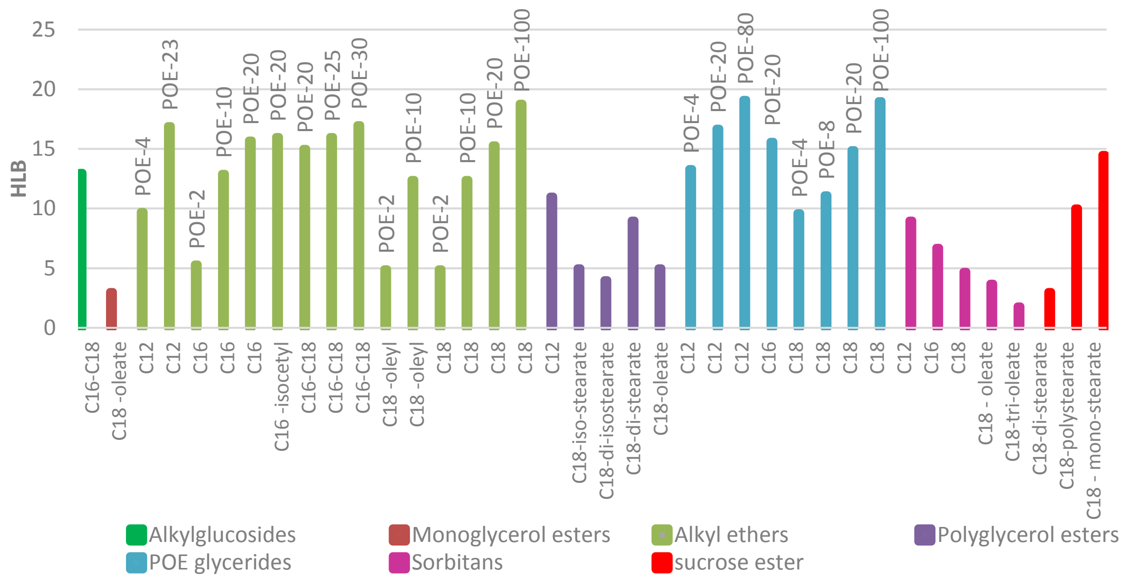

Figure 4-3: HLB of a sub-set of surfactants

For stable O/W emulsions it is recommended to use a mixture of surfactants that together gives the required HLB of the oily phase better than a unique surfactant (ICI AMERICAS Inc., 1980), (Rosen and Dahanayake, 2000). O/W emulsions are formed in an approximated HLB range between 8-15. Therefore, a surfactant with a high HLB, an intermediate HLB and a low HLB can be used in combination to create the emulsion. Attention should be given not only to the HLB but also to the type of texture the surfactants give to the emulsion, because many of them are also thickeners, Table 4-7 shows the surfactants and the type of texture in which they can be used (cream, lotion, spray).

As it happens with emollients, many surfactants have similar HLB and can be used to give similar textures. Based on this characteristics, their applications (skin care OR hair care) and their availability it is possible to pre-select a group of possible surfactants to use. This subgroup can be further analyzed considering their price, sustainability and specific sensorial profile.

The databases subsection of thickeners comprises 14 substances and information about their ionic nature, rheological behavior (newtonian, pseudoplastic, thixotropic), stability under environmental conditions and recommendations of use. It is presented in Table 4-9

Table 4-9 Data base – thickeners section

Thickener	Electrical nature (1)	Type (2)	Solvent (2)	Rheology (2)	Yield value (2)	Electrolyte stability (1)	Temperature stability (1)	Activation (1)	pH stability (1)
Cellulose gum	nonionic, anionic	Aqueous thickeners	water	thixotropic	yes	yes	excellent	NA	NA
Guar gum	nonionic	Aqueous thickeners	water	pseudoplastic	no	yes	NA	NA	Poor acid stability
Xanthan gum	anionic	Aqueous thickeners	water	pseudoplastic	yes	yes	excellent	NA	stable at low and relative high pH
Hydroxyethyl-cellulose	nonionic	Aqueous thickeners	water	pseudoplastic	no	yes	NA	NA	NA
Methylcellulose	nonionic	Aqueous thickeners	water	pseudoplastic	yes	yes	NA	NA	NA
Hydroxypropyl methylcellulose	nonionic	Aqueous thickeners	water	pseudoplastic	no	yes	NA	NA	NA
Carbomers	anionic	Aqueous thickeners	water	pseudoplastic	yes	no	NA	Alkaline agent	NA
Acrylates / VA crosspolymers	anionic	Aqueous thickeners	water	pseudoplastic	yes	no	NA	Concentration of 0.5% or less. Very efficiency rheology modifiers	stable at high pH
Polyethylene glycols	nonionic	Aqueous thickeners	water	Newtonian	no	yes	NA	NA	NA
clays	NA	Aqueous thickeners	water	thixotropic	yes	yes	excellent	NA	stable at high and low pH
Polyethylenes	NA	Non-Aqueous thickeners	oil	pseudoplastic	yes	NA	NA	NA	NA
Trihydroxystearin (organic)	NA	Non-Aqueous thickeners	oil	thixotropic	yes	NA	NA	NA	NA
Organoclays	NA	Non-Aqueous thickeners	oil	thixotropic	yes	NA	NA	Chemical (polar) activator	NA
Fumed silica	NA	Non-Aqueous thickeners	oil	thixotropic	yes	NA	excellent	NA	NA

References: (1) Braun D. B., Meyer R. R., Rheology Modifiers Handbook, 1st Edition, Elsevier, 2000 (2) Laba, D., 2001. How Do I Thicken my Cosmetic Formula. Cosmet. Toilet. 116, 35–44

It is necessary to analyze two characteristics of thickeners in addition to their main function: the ionic nature of some of them and their processability. In the case the thickener used is ionic, it will introduce an electrostatic interaction into the product, whose effects have to be evaluated for their correct use. This can be done by going back to the first relational matrix, which contents the column electrostatic interaction and enables the revision of this effect in the system (Table 4-3). This information recycle is applicable to any further design decision and it enables the revision of new sub-problems generated not from user needs but from issues that arise during the design process.

In addition to the three sections presented here, the database contains also a preservatives section and UV filter section. The first contains 10 substances with maximal allowed, typical concentration used, micro-organism against which it is effective, pH and temperature of effectiveness. The UV filter section contains 17 U.V. filters with the properties: maximal allowed concentration, SPF at maximal allowed concentration, partitioning coefficient, bioconcentration factor, ecotoxicity defined based on LC_{50} (lethal concentration 50).

4.1.5 Combining the two relational matrices to create product concepts

For the stage of product design, two tools were presented to create product concepts: a first relational matrix containing sub-problems and solution strategies and a second relational matrix containing ingredient properties and characteristics. The connection between the matrices is done in 3 steps as shown in Figure 4-4 and explained below.

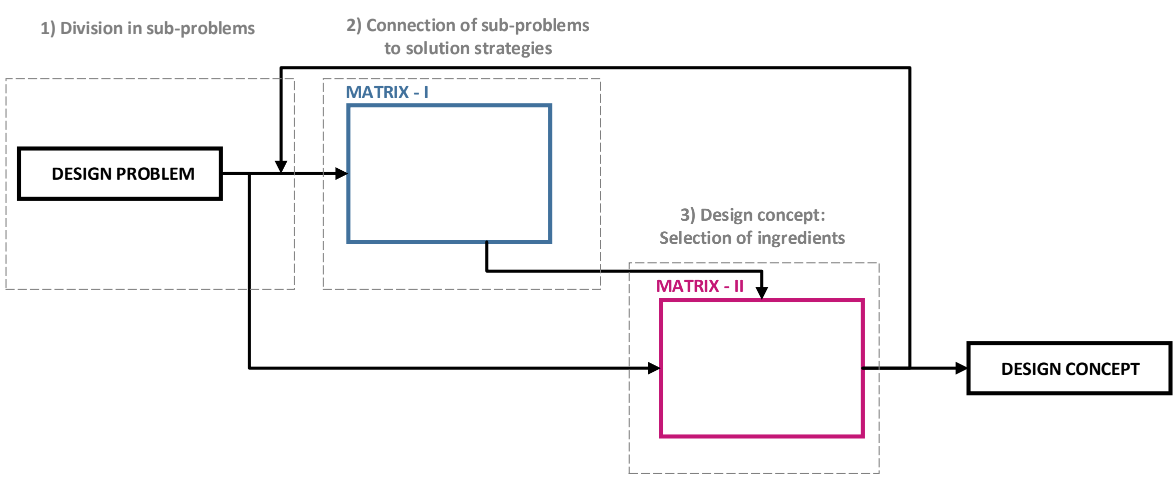

Figure 4-4. Connection between relational matrices presented for the stage of product design

1. División in sub-problems: In this step product specifications are classified, when possible, into the sub-problems presented in Table 4-1. During this classification it is possible to associate more than one sub-problem to a specification. In case any sub-problems describe a specification, the subproblem can be bypassed directly to the second relational matrix, as shown in Figure 4-4.

To illustrate this step, the design of a sunscreen is considered. The main function of this product is the Solar Protection Factor (SPF). The SPF is normally generated by the presence of molecules that either block or absorb the UVA and UVB light (Cussler and Moggridge, 2011). This function depends on the presence of active ingredients (U.V. filters) and therefore it is classified as a special function and it is bypassed to the second matrix. Additionally, it was found that the SPF factor augments when the product forms a uniform film on the user skin, because it enables the protection of the entire exposed area (Gaspar and Campos, 2003). Uniform films can be enhanced with some degree of rheological thixotropic behavior (Gaspar and Campos, 2003), because the product can spreads easily due to the reduction of viscosity and it has time to level on due to the delay in viscosity recovery (Laba, 1993). Therefore, SPF specification is also classified as a rheological – thixotropic sub-problem.

A process similar to the previously described has to be done with all specifications of the design problem.

Second step - connection of sub-problems to solution strategies:

In this step, the first relational matrix is used to connect sub-problems to possible solution strategies. As it can be seen in Figure 4-4 the input to the first relational matrix is the blend of two information flows: the sub-problems identified in the previous step and the recycle information coming from the second relational matrix.

There is a recycle when an election done with the bypassed specifications creates new sub-problems that may affect the system. For example, in the mentioned case of the design of a sunscreen, it is possible to select a mineral U.V. filter as titanium dioxide and/or zinc dioxide to achieve a desired SPF. These solids may have two effects: 1) they may precipitate due to gravitational forces 2) they affect rheological behavior because they increase the disperse phase concentration. Thus, in this case, the inlet to the first relational matrix are the sub-problem 'thixotropic behavior' identified in the previous step plus the sub-problem 'gravitational separation' coming from the recycle. Additionally, a lower limit to the solution strategy 'disperse phase concentration' has to be considered, because it is augmented due to the presence of solids, and it has to be at least equal to the quantity of UV filters required to achieve the desired SPF.

Once the flux of information is summarized, it is possible to use the first relational matrix as explained in sub-section 4.1.2. For the example of the sunscreen, and considering the sub-problems ‘thixotropic behavior’ and ‘gravitational separation’, it is possible to find the solution sets shown in Table 4-10 using the first relational matrix.

Table 4-10 Solution strategies for the example of the sunscreen (surfactant system nature is not considered in this example)

	Solution strategies	**Precaution**	**Integration degree**	**Score solution sub-problems**	
				Thixotropic behavior	gravitational separation
Set 1	Increase volume fraction	Volume fraction has a lower bound	2	3	3
Set 2	Decrease droplet size	-	2	1	3
Set 3	Use of a rheological modifier	-	2	7	7
Set 4	Enhance weak flocculation + Decrease density difference of phases	-	1	7	4
Set 5	Decrease droplet size+ Use of a rheological modifier	-	1	8	10

Apriori, all solution sets presented in Table 4-10 can be used to solve the design problem. However, some of them are easier to apply than others:

Set 1- Increase volume fraction: This implies the concentration of the disperse phase (oily phase or solids) has to be increased, which also increases the production costs. This is a solution commonly used in paints, where fillers (low cost solids) are added to the formula to control their consistency.

Set 2- Increase droplet size: This is an effective action to prevent gravitational separation. However, it may not have great impact on thixotropic behavior (this is variable according to the case). More energy has to be added during the production process and/or surfactant concentration has to be increased.

Set 3- Use of a rheological modifier: This is the most frequent measure to solve both rheological and stability problems. It is important to select an appropriate thickener and to propose an experimental design to define its concentration. This solution has a relative high degree of integration in comparison to others, because one strategy is used to solve the two considered sub-problems. This may be undesired when exact values for related product specifications are required.

Set 4- Enhance weak flocculation and decrease density difference of phases: This is the most difficult set to be implemented. Weak flocculation is difficult to control, because it increases emulsion instability. Additionally, the density difference between water and titanium dioxide cannot be changed.

Set 5- Decrease droplet size and use of a rheological modifier: This solution set is similar to set 3 but more decoupled because two solutions are used to solve two problems.

Third step – Formation of a design concept: In this step, ingredients and process conditions that enable the application of identified solutions sets are selected using the second relational matrix. In the example of the sunscreen, solution set 3 and solution set 5 are implemented. Searching in the thickeners data based two thickeners with thixotropic behavior are found: clays and cellulose gum. Based on this, four design concepts can be generated for the SPF design problem:

Design concept 1: Solution set 3 with cellulose gum - Formulation with titanium dioxide, zinc oxide and cellulose gum

Design concept 2: Solution set 3 with clay thickener - Formulation with titanium dioxide, zinc oxide and a clay thickener

Design concept 3: Solution set 5 with cellulose gum - Formulation with titanium dioxide, zinc oxide and cellulose gum/ decreasing droplet sized

Design concept 4: Solution set 5 with cellulose gum - Formulation with titanium dioxide, zinc oxide and cellulose gum/ decreasing droplet sized

An experimental design varying the thickener agent, the energy and the surfactants quantity, is required to compare experimentally the four design concepts.

4.2. Application of the approach for product design stage in the case study

4.2.1. Definition of the design problem for the case study

In chapter 3, sensorial and functional needs of the case study were translated in terms of product specifications, i.e., safety and regulation requirements, sensorial evaluation tests, performance evaluation tests, instrumental tests and price, which constitute 26 product specifications as shown in Table 3-22. A sub-group of those specifications is selected to represent the entire design problem based on the proximity of some of the tests as answered by experts and shown in Figure 3-11. Table 4-11 shows the sub-group of product specifications to begin the product design stage.

Table 4-11 Product specifications/design problem of the case study

		Product specification	Kano categories	Normalized importance	Test	Targert values
Safety and Regulation (1*)	**1**	Physical/chemical stability	must-be	0.78	Shelf stability	6 months
	2	Toxicology	must-be	0.70	Information search	Only allowed substances are used
	3	Microbiological quality	must-be	0.77	Count of miscroorganims (COLIPA)	less than 103 cfu/g
	4	Use of allowed substances	must-be	0.61	Information search	Only allowed substances are used
	5	Dermal tolerance and non-irritability	must-be	0.25	Information search	Use of substances that do not irritate skin
Sensorial evaluation (2*)	**7**	Product odor – intensity and fragance type	must-be	0.87	-	4 or 5 over 5
	10	Oil on skin	One-dimensional	0.31	-	4 or 5 over 5
Performance evaluation (3*)	**17**	Corneometer	must-be	0.31	hidration index -corneometer	HI over 50
	18	Corneometer 8h after application	must-be	0.31	hidration index -corneometer	HI over 50
instrumental tests (4*)	**19**	Rheological profile	One-dimensional	0.64	viscosimetry and oscillatory test	Values in Table 3-12
	23	Texturometer - penetration test	One-dimensional	0.40	-	Values in Table 3-12
	24	pH	must-be	0.40	-	4.7 - 8
Price	**25**	Product price	must -be	1.00	-	7-10 euro
Additional	**26**	Antioxidant test DPPH	attractive	0.08	Antioxidant test DPPH	It has to be determined with benchmark

Natural ingredients (5*)	**Need 17**	It has ingredients of natural origin	One dimensional	-	-	At least and additional to calendula oil

Notes:
(1*) All safety regulations make part of the design problem because they are clearly must-be specifications that have to be achieved.
(2*) In chapter 3, most sensorial characteristics were translated into instrumental test. However, oiliness was not easy to translate, reason why it remains as a sensorial attribute in the design problem. Product odor was described in terms of fragrance and intensity type with the aide of users.
(3*) To measure hydration a Corneometer test (immediately and 8 h after the cream application are selected. This test is clearer than an appearance test that change between skin types. It is not the same as TEWL test, but both are interrelated.
(4*) Instrumental test results are those defined with the help of users. According to them a cream relatively fluidly is desired
(5*) This need was not completely expressed in defined product specifications

4.2.2. Application of step1 of the design stage to the case study: Classification of product specifications into sub-problems

Each specification in Table 4-11 was classified according to the list of product sub-problems presented in Table 4-1. It is possible to associate more than one sub-problem to one specification. In the cases where any sub-problem can describe a specification, the sub-problem is bypassed directly to the second relational matrix. Table 4-12 shows the result of this step and Figure 4-5 shows the information flow.

Table 4-12 Classification of specifications of the case study into sub-problems

	Product specification	Sub-problems	Comments
1	Physical/chemical stability	All stability sub-problems: **9 -** Gravitational forces, **10 -** Flocculation, **11 -** Coalescence and partial coalescence, **12 -** Phase inversion, **13 -** Ostwald ripening, **14 -** Lipid oxidation and chemical stability of lipids **15 -** Biological stability	At first, all instabilities are equally considered. As the design process advances, it is possible to determine if there is one of them that is more likely to happen, thus more critical. For example, if solids are added to the formulation, instability by gravitational forces become more critical than Ostwald ripening.
2	Toxicology	**By pass** to the second relational matrix – allowed substances	Only allowed substances are used. This can be checked in CosIng Database (CosIng, 2018). In addition, the property toxicity has to be analyzed when selecting substances.
3	Microbiological quality	**15 -** Biological stability **Bypass** to second relational matrix – non contaminated raw materials and good production practices	In addition to the sub-problem 15, it is recommended to search for reliable suppliers. Specifications datasheet contents information about results of raw materials in biological tests.
4	Use of approved substances	**Bypass** to second relational matrix – allowed substances	Only approved substances are used. This can be checked in the CosIng Data Base (CosIng, 2018)
5	Dermal tolerance and non-irritability	**Bypass** to second relational matrix	The use of substances that do not irritate skin is advisable. Essential oils are potential allergenics. They will be used in low concentration to avoid adverse reactions.

7	Product odor – low intensity fragrance type – herbal/citric	Intensity: **20 -** Release of a relative nonpolar volatile molecule (oil soluble) to the air **Bypass** to second relational matrix – fragrance type	Product fragrance type was decided with customer help in Chapter 3.
10	Oiliness (to be reduced)	**By pass –** second relational matrix: selection of emollients with light to medium emollience sensation. **Oil concentration lower than 20%**	Sensations of emollients can be found in the emollients section database. If required, additional materials can be consulted with suppliers.
17	Corneometer	**Bypass –** second relational matrix: Selection of ingredients that bind water - glycols	A common ingredient used for hydration is glycerin. It is used for the development of the case study. Other glycols as 1,3-Butyleneglycol, propreneglycol, isoprene glycol, diglycerin, dipropylene glycol can also be used(Iwata and Shimada, 2013).
18	Corneometer 8h after application	**Bypass –** second relational matrix: selection of emollients with persistent or lubricous after sensation	Emollients with persistent oily sensation can be found in the emollients section database. Additional materials can be consulted with suppliers. An equilibrium between this product specification and specification 10-'oiliness (to be reduced)' skin has to be found.
19	Rheological profile	**5 –** Viscosity **6 –**Shear thinning behavior **8 –** AVOID a strong viscoelastic behavior	According to user answers, they prefer light and relative fluidly products with low viscosity and low viscoelastic modulus.
23	Texturometer - penetration test		
24	pH	**Solution 3 -** pH	Skin care products have a pH slightly acid to neutral from 4.5 to 7.5. A more narrow range can be selected according to ingredients resistant to different pH and ingredients best functional conditions. The first relational matrix shows that this variable should be decided with caution due to the multiples effects it has in emulsion general behavior.
25	Product price	**By pass-** second relational matrix: raw ingredients price: ingredients database	Product Price that users are willing to pay is relative high in relation to raw materials cost. Raw materials with intermediate cost, or of relative high cost but at low concentration can be used.
26	Antioxidant test DPPH	**By pass –** Use calendula oil plus and antioxidant ingredients	A condition of the design problem (given by product producers) is to use calendula oil as antioxidant. An equilibrium between this specification, and the specifications "product price" and "low odor intensity", has to be achieved. The last two are specifications derived from must-be needs while the antioxidant activity is derived from attractive needs, reason why the first two have a bigger priority in the case a tradeoff has to be considered. To avoid any contradiction, it is possible to use a low concentration of calendula oil plus an additional cheaper/odorless antioxidant.
Additional requirements (not completely expressed by product specifications)			
Need 17	It has natural ingredients	**By pass-** second relational matrix	Natural ingredients have to be included into the design

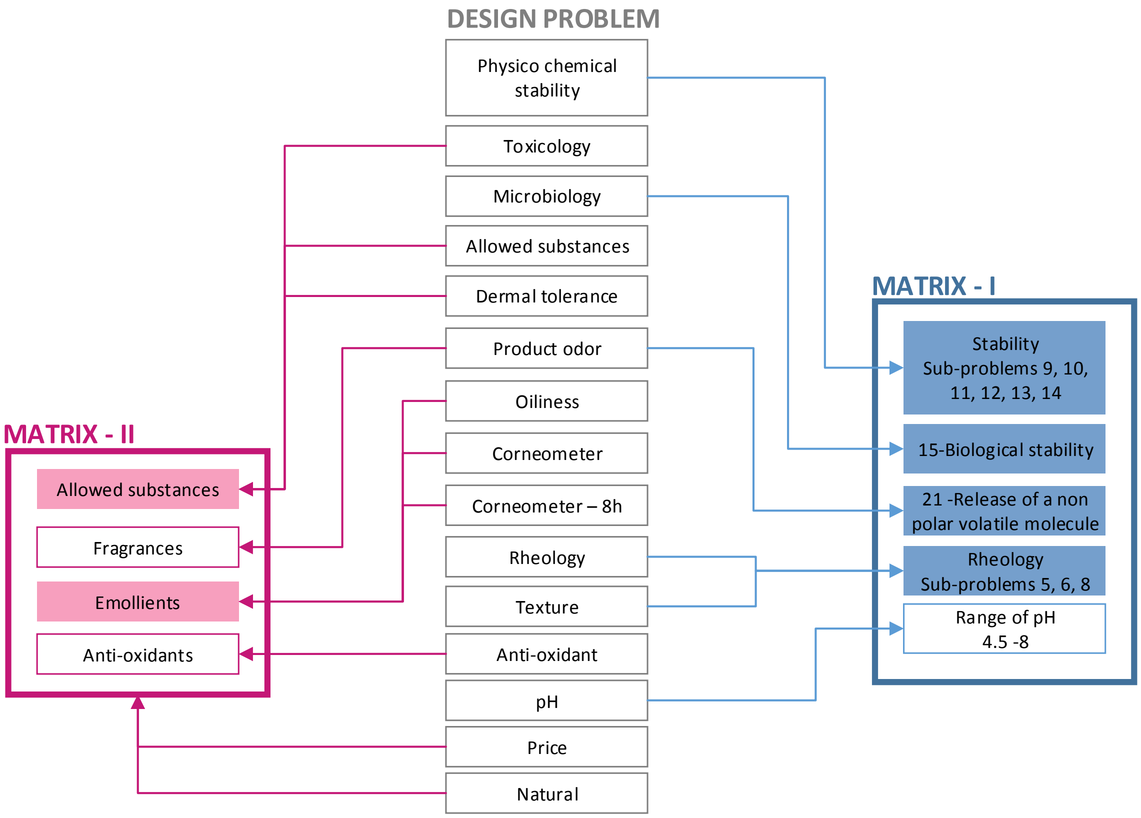

Figure 4-5. Classification of specifications of the case study into sub-problems

4.2.3. Application of step2 of the design stage to the case study: Connection to solution strategies

4.2.3.1. Substep 2-1 Selection of ingredients from bypassed specifications: Figure 4-5 shows that fragrances, emollients and antioxidants have to be selected before entry to the first relational matrix.

- Fragrance selection: As defined in chapter 3 with the aid of customer, a mixture of lemongrass and calendula essential oils in a ratio 1:2 is selected as the product fragrance, with a maximum concentration of 0.2% for the combined oils. The usual concentration of calendula oil in competitive products is between 0.02 – 0.1% (Andersen et al., 2010). A concentration of 0.09% was selected because in the criteria of the design team it was found that this concentration gives a characteristic but not intense fragrance. The fragrance intensity has to be retested with final product prototypes.

- Safety: From a literature review, it was found that calendula oil is safe under usual concentrations (Andersen et al., 2010). Lemongrass essential oil contains a high concentration of limonene, which has two reported cautions in CosIng annex III: it has to be reported as ingredient when used over 0.001% and it can only be used in cosmetic preparations when its peroxide value is less than 20mmoles/L (CosIng, 2018).

  Recycled information to Matrix I: Fragrances cannot be heated because they evaporate and/or may decompose. They are lipophilic but relative high polar oils, however, they have not a very important effect on polarity of the oily phase because of their low concentration.
- Antioxidants: According to Kano model, the specification 'antioxidant activity' is attractive, reason why it will be enhanced in the product as a market differentiation factor. In addition to calendula oil, it was decided to add another antioxidant to uncouple the specifications of 'soft fragrance' and 'antioxidant activity'. Vitamin E – tocopherol acetate is added to the formulation with this purpose at a concentration of around 0,4%, as recommended by suppliers (around 0.5% in formulations by Croda, but a less concentration is selected because it has a complementary function to the calendula oil). This vitamin was selected over other common antioxidants (alfa –tocopherol, retinol A, Q10, and vitamin C), because it has a relative low price and high stability in comparison to the others (Gianeti et al., 2012), (Making cosmetics, 2018). The antioxidant activity can be tested in comparison to a benchmark product in order to tune the final concentration of antioxidants within the product.

  Recycled information: The antioxidant should not be submitted to high temperatures because it decomposes (Gianeti et al., 2012). It is oil soluble and relative highly polar, reason why it can increase polarity of the oily phase.
- Emollients: A set of emollients are selected considering the following factors:
  (1) A light sensation is desired
  (2) A long term moisturizing effect/but also low oil sensation is desired
  (3) Customers desire that the cream contents natural ingredients
  (4) The use of at least four different emollients with different polarities and different melting points is recommended (Iwata and Shimada, 2013).

  Considering those factors, hydrocarbons and silicons are avoided, with the aim of increasing the naturalness of the cream. In the emollient database there are 22 liquid oils (ester and fatty alcohol emollients) described as having light/medium emollience (as desired by customers according to need 4 in Table 3-5) and recommended for facial care. They are presented in Table 4-13 with their spreadability, viscosity, polarity and price when available. From the oils in Table 4-13, six of them give a lubricous/smooth/oily after feeling and 12 of them give a non-oily after feeling.

Table 4-13 Sub-list of liquid emollients to use in the case study (from the database)

INCI2	Emollience	Non oily afterfeeling	Oily after feeling	Skin spreeding (qualitative)	Price ($/kg)	Polarity	Viscosity @ 25°C (mPa s)
C12-15 Alkyl Benzoate	Medium light	1		low	20	Very high	13.4
Caprylic/ Capric Triglyceride	Light		1	medium	16	Medium to high	23.3
Cetearyl Isononanoate	Medium light		1	medium		medium	16.5
Cetyl Ethylhexanoate	Medium light	1		high		medium	12.7
Coco-Caprylate	Light			high		medium	5 @20°C
Coco-Caprylate/Caprate	Light			medium		medium	11 @20°C
Decyl Cocoate	Light		1	low		medium	9
Ethylhexyl Palmitate	light		1	medium	14	medium	11.2
Ethylhexyl Stearate	Medium light	1		medium		medium	12.8
Hexyl Laurate	Light			high		medium	6 @20°C
Isoamyl Cocoate	Light	1		medium		medium	5.6
Isohexadecane	Light	1		-	22	Low	3.1
Isopropyl Isostearate	Light	1		-		Medium	7.7
Isopropyl Lanolate	Light		1	-		NA	-
Isopropyl Myristate	light	1		high	17	medium	5.6
Isopropyl Palmitate	light		1	high	17	medium	6.4
Isotridecyl Isononanoate	Light	1		medium to high		Low	9 @20°C
Octyldodecanol	Medium light	1		low	23	high	47.5
Phenoxyethyl Caprylate	Light	1		low		Very high	10
PPG-3 Benzyl Ether Ethylhexanoate	Light			low		High	11.1
Propylene Glycol Dicaprylate/ Dicaprate	light	1		medium to high		medium to low	10.5 @20°C
Stearyl Heptanoate (and) Stearyl Caprylate	Light	1		-		NA	-
Undecane (and) Tridecane	Light			high		low	1 @20°C

One emollient of each of the two previously identified sub-groups is selected with the aim of having two light oils within the formulation, with the possibility of tuning their concentration to obtain a more/less oily after sensation. This is done, because a compromise between sensation and long term hydration is to be achieved. Many combinations are possible. The selection of a specific one is done considering raw materials availability from suppliers. In this case, the Caprylic/Capric Triglyceride is selected as a light oil with an oily/smooth after feeling and Isopropyl Myristate is selected as a light oil with a dry after feeling.

In addition to these oils, it is recommended to select an emollient that imparts body to the cream (enhance creaming sensation) and helps to stabilize the cream at low to intermediate temperatures (Iwata and Shimada, 2013). Cetearyl alcohol is frequently used for this purpose, although it is also possible to use cetyl alcohol, stearyl alcohol, glyceryl monostearate and cetyl palmitate, among other stabilizing components. Cetearyl alcohol can produce from light to very thick creams. It is possible to control product consistency (considering that consumers want it to be light) by varying cetearyl alcohol concentration and/or by adding octyldodecanol (Iwata and Shimada, 2013). The concentration and effect of cetearyl alcohol in product rheology and stability is reviewed in the experimental part (section 4.3).

In addition to previous selections and with the purpose of increase natural perception of the cream, two natural oils are included within the formulation: shea butter and almond oil. Other possible ingredients are cacao butter, coco butter. Shea butter was selected because it is frequently and specifically used for face care. Natural oils oxidize more rapidly than others, therefore the sub-problem 'oxidation' should be highlighted and included in the recycle information to the first matrix.

Recycle information: Medium to high polar oils were selected. Only a component that modifies product consistency and thickens is selected (cetearyl alcohol). Oils that can oxidize rapidly are selected.

In the sub-step 2-1 the decisions made introduced new sub-problems and limit/preselect some of the solutions strategies. Table 4-14 shows the information resulting from this sub-step. Figure 4-6 shows the information flow of this sub-step.

Table 4-14 Information recycled from matrix II to matrix I for the case study

	Decisions	New subproblems	Solution strategies
Fragrance	Calendula oil 0.09% + lemon grass oil 0.045%	Fragrance cannot be heated They may oxidize –sub-problem 14	Presence of fragrance – solution strategy 31

Antioxidant	Acetate tocopherol 4%	Antioxidants cannot be heated	Presence of antioxidant – solution strategy 27 Polar compounds- solution strategy 11
Emollients	Caprylic/Capric Triglyceride, Isopropyl Myristate, Shea butter, Almond oil, Cetyl palmitate, Cetearyl alcohol	Natural oils may oxidize – sub-problem14	Polarity of the oily phase: medium to high- solution strategy 11 Presence of a rheological modifier –solution strategy 33

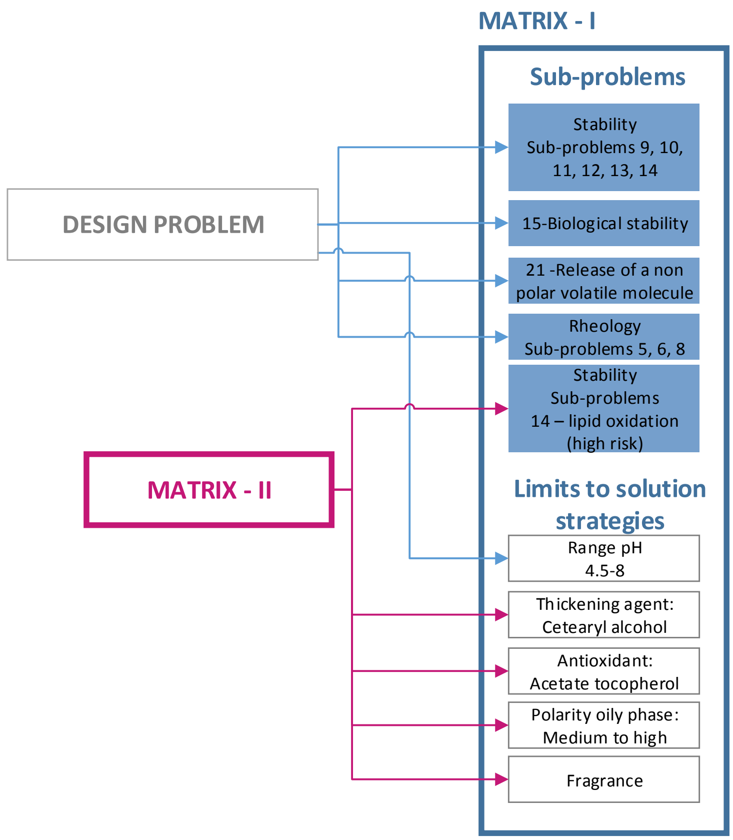

Figure 4-6. Sub-step 2-1 – input to the first matrix

4.2.3.2. Substep 2-2 Connection between sub-problems and solution strategies:

Sets of solution strategies are formed using the first relational matrix of Table 4-3. To facilitate the construction of the sets, two options were explored: (1) One using nonionic surfactant as emulsification system and (2) another one using both: ionic and nonionic surfactants. The ionic surfactant is sodium stearate due to its availability.

Table 4-15 presents three solution strategies sets in the case when a nonionic surfactant system is used (in blue). The set 1 comprises 10 solution strategies (11 considering that two thickeners were selected) in relation to the 12 sub-problems. They are shown in Table 4-15 and described below:

- The strategy 3, a pH with a slightly acid value is selected to avoid lipid oxidation (a sub-problem generated due to the selection of natural ingredients). It is assumed that raw materials resistant to this pH conditions were selected. This information goes to the second relational matrix.
- It is suggested to select a surfactant with a high HLB and with a curvature that enhanced the formation of O/W emulsions.
- The solution strategy 7- surfactant has good solvent conditions at the pH and electrolyte conditions of the problem (i.e., the surfactant should have a cloud point over the temperature of use) is selected. This information goes to the second matrix.
- The solution strategy 11- high polarity of the oily phase was set because relative polar oil ingredients were already chosen.
- Due to the presence of natural oils, oxidation can happen quickly. Protection is given with the solution strategy 3 – low pH and with the solution strategy 27- use of antioxidants.
- Because the surfactant is nonionic, the solution strategy 9 is implemented, i.e., droplets are protected with steric interactions.
- The solution strategies 25 – package-, 27 – antioxidants and 28 - preservatives are used to protect the product against environmental conditions and microorganism.
- The solution strategy 3 – fragrance- was previously set according to customer preferences.
- Rheological modifier: In addition to the cetearyl alcohol, which was selected as stabilizer and thickener, a second rheological modifier is suggested to better control the rheological behavior of the product. As previously mentioned, it should work well at the selected conditions of pH and electrolyte concentration.

In this set, two sub-problems are rated with a negative sign: phase inversion and Ostwald ripening, which indicates that attention should be given to them. Phase inversion is unlikely to happen at the oil concentration of the emulsion (20%). Additionally, Ostwald ripening can be prevented by selecting processing conditions that reduce the droplet size distribution (for example: by homogenizing at high temperature or improving the mixing conditions during homogenization). Additionally, the droplet size can be optimized to help to avoid both, Ostwald and other emulsion instabilities.

Set 2 comprises the same solution strategies as the set 1, but it introduces the droplet size as a variable to improve the solution of some sub-problems. It has two columns in the Table 4-15. The first column shows the results when droplet size is increased in relation to the base case (Set 1) and the second column shows the effects when the droplet size is decreasing. According to Table 4-15, when droplet size is increased, viscosity, and other rheological behaviors are decreased in relation to the base case. Additionally, all stability problems, with exception of Ostwald ripening, become more critical, especially gravitational separation and coalescence. The release of the fragrance may be slower in relation to the base case, because the distance of transport is increased within the droplets. When droplet size decreases the opposite effects are appreciated.

Set 3 comprises the same solution strategies of the set 1, but it introduces a surfactant system forming a thicker interface. For this purpose, a surfactant with a large polymeric hydrophilic chain can be implemented. This causes, according to the Table 4-15, an increase in viscosity and in the stability of the system.

Table 4-16 presents the set 4, which adds to the base case an ionic surfactant: sodium stearate. This combined surfactant system type, when good pH and environmental conditions are defined, shows a very high resistance to flocculation and coalescence (the score of the solution of these two problems is very high for this system in comparison to others). However, because pH must-be slightly basic for the selected ionic surfactant (sodium stearate), lipid oxidation may be enhanced. Additionally, a product with this surfactant is more irritant than the other considered (see chapert 5), which is not ideal for leave-on cosmetics. For all this reasons and given that this is the solution sets with more warnings in relation to stability, it was decided not to implement it in the experimental part.

Table 4-17 and Figure 4-7 presents the information flow of this step.

Table 4-15 Solution sets with nonionic surfactants – case study

		3- pH	7- quality of solvent - steric interaction	11- polarity of oily phase	12- Degree of unsaturation of the oils	19- Steric interaction (repulsive)	25- Packing	27- Antioxidants	28- Preservatives	31- Fragance	33- Rheological modifier - continous phase x2 (13)	**Set 1: Base solution nonionic surfactant**	21- INCREASE Droplet size (10)	21- DECREASE Droplet size (10)	**Set 2: set 1+ Increase droplet size.**	**Set 2: set 1 - decrease droplet size**	8- Thickness -steric interaction (6)	**Set 3: set 1 + thickness stearic interaction**
5	Viscosity	0(2)		0	0	3	0	0	0	0	7	**10**	-3	3	**7**	**14**	3	**13**
6	Shear thinning behavior	0(2)		0	0	3	0	0	0	0	7	**10**	-3	3	**7**	**14**	3	**13**
7	Thixotropic behaviour	0(2)		0	0	3	0	0	0	0	7	**10**	-3	3	**7**	**14**	3	**13**
8	Viscoelastic behavior	0(2)		0	0	3	0	0	0	0	7	**10**	-3	3	**7**	**14**	1	**11**
9	Gravitational forces	0	0	0	0	0	0	0	0	0	7	**7**	-7	7	**0**	**14**	0	**7**
10	Flocculation	0(2)	3	0	0	3	0	0	0	0	3	**9**	0	0	**9**	**9**	3	**12**
11	Coalescence and partial coalescence	0(2)	3	0	0	3	0	0	0	0	3	**9**	-7	7	**2**	**16**	7	**16**
12	Phase inversion	0	3	-7 (8)	-1	0	0	0	0	0	0	**-5**	0	0	**-5**	**-5**	0	**-5**
13	Ostwald ripening			-7 (7)	-1	0	0	0	0	0 (12)	3	**-5**	7	-7	**2**	**-12**	0 (4)	**-5**
14	Lipid oxidation and chemical stability of lipids	7(1)	0	-3	-7 (9)	0	3	7		0	0	**7**	0	0	**7**	**7**	0	**7**
15	Biological stability	0(3)	0	0	0	0	3		7	3 (10)	0 (11)	**13**	0	0	**13**	**13**	0	**13**
21	Release of a nonpolar volatile molecule to the air	0	0	3	0	0	-7	0	0	7	-3	**0**	-3	3	**-3**	**3**	0 (5)	**0**
											Integration degree	**1.1**			**1**			**0.9**

(1) A pH slightly acid (5.5-6) is selected to avoid the oxidation of natural oils (Iwata and Shimada, 2013)
(2) Rheological modifiers and surfactants not sensible to pH are selected (this information goes to the second matrix)
(3) The selected pH is still too high to control microorganism
(4) It is assumed that stability against Ostwald ripening is not affected by the surfactant thickness
(5) It is assume that release is not affected by surfactant thickness
(6) Thickness and Gibbs elasticity are interrelated (see the two columns in Table 4-3). They are not taken as solutions simultaneously.
(7) The effect of polarity of oils is important to Ostwald ripening, it is suggested to select at least one oil of low to intermediate polarity to avoid this effect (information to the second matrix)
(8) High polarity required a very high HLB to avoid phase inversion
(9) It is advisable to decrease quantity of oils with unsaturation in order to decreases the risk of lipids oxidation (Iwata and Shimada, 2013)
(10) Calendula oil has antimicrobial and antifugal activity (Efstratiou et al., 2012); (Gazim et al., 2008)
(11) At this stage it is unknown if the rheological modifier is natural ot not. The value of its effect on biological stability is taken as cero
(12) The effect of the fragrance is unknown in relation to Ostwald ripening. It is taken to cero with a warning
(13) A second rheological modifier is added to have more controllability of rheological problems. Thus this solution is multiply by 2 when calculation integration degree of the solution set
(14) Droplet size can be optimized to minimized instabilities

Table 4-16 Solution sets with ionic and nonionic surfactants – case study

		3- pH (1)	11- polarity of oily phase	12- Degree of unsaturation of the oils	18. Electrostatic interaction (repulsive)	19- Steric interaction (repulsive)	25- Packing	27- Antioxidants	28- Preservatives	31- Fragrance	33- Rheological modifier - continuous phase x2	**Set 4: ionic surfactant Sodium stearate**
5	Viscosity	3	0	0	3	3	0	0	0	0	7	**16**
6	Shear thinning behavior	3	0	0	3	3	0	0	0	0	7	**16**
7	Thixotropic behavior	3	0	0	3	3	0	0	0	0	7	**16**
8	Viscoelastic behavior	3	0	0	3	3	0	0	0	0	7	**16**
9	Gravitational forces	0	0	0	0	0	0	0	0	0	7	**7**
10	Flocculation	3	0	0	3	3	0	0	0	0	3	**18**
11	Coalescence and partial coalescence	3	0	0	3	3	0	0	0	0	3	**18**
12	Phase inversion	3	-7	-1	0	0	0	0	0	0	0	**-2**
13	Ostwald ripening		-7	-1	0	0	0	0	0	0	3	**-5**
14	Lipid oxidation and chemical stability of lipids	-7 (2)	-3	-7	0	0	3	7		0	0	**-7**
15	Biological stability	0	0	0	0	0	3		7	3	0	**13**
21	Release of a nonpolar volatile molecule to the air	0	3	0	0	0	-7	0	0	7	-3	**0**
						Integration degree						**1.1**

Notes:
Assumptions are done considering that the ionic surfactants is sodium stearate because of its high availability
(1)pH is set to be from neutral to slightly basic (7-7.5), because stearic has to be neutralized. At this pH the surfactant is functional and electrostatic repulsion increases rheological behavior and stability in relation to the base solution (set 1).
(2) pH is set at At high pH the oxidation is enhanced (Iwata and Shimada, 2013)

Table 4-17 Summary: solutions sets for the case study

	Decisions	Integration degree	Cautions
Solution strategies set 1	Base case: nonionic surfactants pH is slightly acid	1.1	Careful has to be taken with Ostwald ripening and phase inversion
Solution strategies set 2	Nonionic surfactants + droplet size optimization pH is slightly acid	1	Careful has to be taken with Ostwald ripening and phase inversion
Solution strategies set 3	Nonionic surfactants + a surfactants forming thick interfaces pH is slightly acid	0.9	Careful has to be taken with Ostwald ripening and phase inversion
Solution strategies set 4	Nonionic + ionic surfactant (sodium stearate) pH is slightly basic	1.1	This option is not further considered because it has more cautions than this others (Ostwald ripening, phase inversion, and oxidation) and because it was found that de product is more irritant than the others.

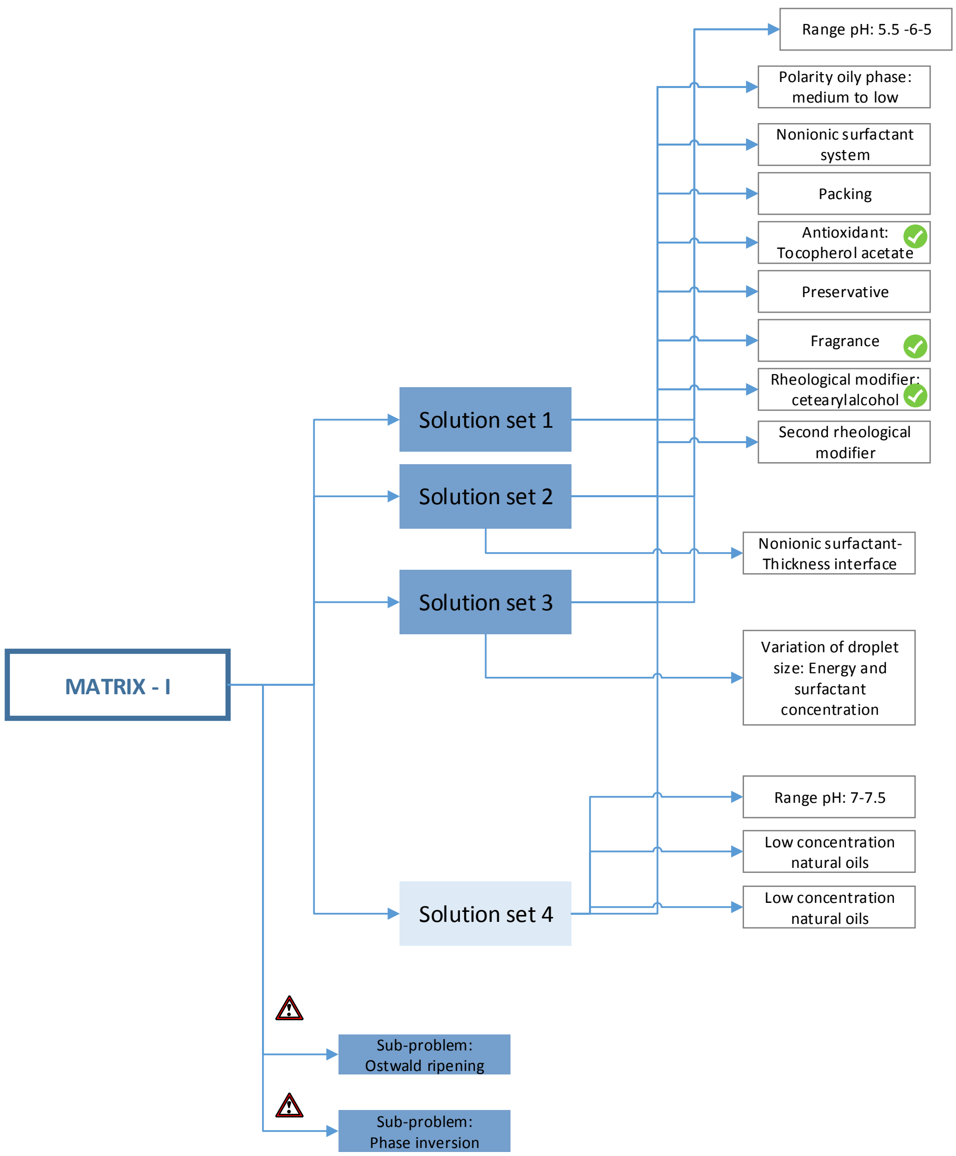

Figure 4-7. Sub-step 1 – output of the first matrix

4.2.3.3. Step 3: Connection to ingredients – Matrix II

In this step all the ingredients and some process conditions are defined with the information from steps 2-1 and 2-2 and the data base of ingredients. Table 4-18 shows the ingredients that were already selected in previous steps.

Table 4-18 Selected ingredients for the development of the case study

Ingredient type	Ingredient	Concentration	Comments	Process considerations
Antioxidant	Calendula oil Acetate tocopherol	0.09% 0.5%	Defined in step 2-1	Low resistance to high temperature
Fragrance	Calendula oil Lemongrass oil	0.09% 0.045%	Defined in step 2-1	Low resistance to high temperature
Glycol	Glycerin	3%	It is added to perform the function of hydration A percentage of 3 was defined based on a similar formulations (Iwata and Shimada, 2013)	Water soluble
Thickener	Cetearyl alcohol Cetyl palmitate	2-4% 3%	Defined in step 2-1. Percentage was selected based on a consultation of lotion type emulsions (Mitsui, 1997)	Oil soluble
Emollients – natural ingredients	Shea butter almond oil	1% 1%	Defined in step 2-1. A low concentration of them is proposed to avoid a rapid product oxidation Almond oil was selected because it is relative light and left a low oily sensation.	Oil soluble
Emollients – light sensations	Caprylic/Capric Triglyceride Isopropyl myristate	7% 2%	Defined in step 2-1. A high concentration of the caprylic/capric triglyceride is selected because it is highly recommende by providers as emollient base for multiple applications (Croda data sheet) it gives a light feeling and a smooth final sensation in skin. And it is natural based. Thus it augments the naturalness of skin.	Oil soluble

Selection of the rheological modifier and the surfactant system:

- Surfactant systems: Three different surfactant systems are suggested to implement the four solution sets.
  Set 1 and set 2: A surfactant system with a relatively high HLB is required, because the product is an O/W emulsion with a polar oily phase (ester, natural oils and fatty alcohols). Searching in the surfactants data based, it was found that nonionic surfactant groups with relative high HLB (over 10) are: POE glycerol esters, POE alkyl ethers, polyglycerol esters, sucrose esters and alkyl polyglucosides (see Figure 4-3), having the highest HLB the surfactants with high number of POE groups.

Comparing the price, sucrose esters are the most expensive surfactants in the mentioned group. Alkyl polyglucosides and polyglycerol surfactants are also expensive. All of them are completely bio-based. Thus, although they imply a relative high cost, they can create products with additional value. POE alkyl ethers and POE glycerol esters have the lowest price of the group.

Considering the previous analysis, two surfactant systems are selected to apply the solution sets 1 and 2: one based on a biobased surfactant and the other one based on a POE surfactant system.

In the case of the biobased system, a mixture based on sucrose ester and cetearyl glucoside is used. Products with these ingredients are stable at acid pH, but they have to be prepared at neutral pH and acidify only after the emulsion is already formed to avoid instability of the sucrose ester (Sisterna B.V., 2018). This surfactant system is used in combination with a low HLB surfactant: glyceryl monostearate.

In the case of the POE surfactant system, a surfactant system of the type sorbitan ester/POE sorbitan ester is selected. The system has a high HLB and can be used in acid pH. It was selected because it has been used with success in similar conditions for cosmetic creams (Iwata and Shimada, 2013).

To implement set 3, it is required to use a surfactant system with a large polymeric hydrophilic chain. For this purpose, the surfactant stearate – 100 is selected due to its high molecular weight and because it can resist low pH.

- Second rheological modifier: In addition to the already selected rheological modifier, it was decided to introduce a secondary rheological modifier to decrease the integration degree of the solution strategy sets. In this way, it is plausible to create both: stable emulsions with a desired rheological behavior.
- Xanthan gum was selected as rheological modifier of the system because, in the ingredients data base, it was found that it gives a pseudoplastic behavior, it works well at acid pH, and it is natural derived. It is used at low concentrations 0.1-0.2% because of its high efficiency (Iwata and Shimada, 2013).
- Preservative: Preservative has to be active at the working pH. According to the preservative data base, for acid pH is possible to use preservatives based on

phenoxyethanol, benzyl alcohol, benzoic acid, potassium benzoate and parabens. If possible, parabens must-be avoided, because they have a negative public image. Considering these arguments, and also availability, a preservative system based on benzyl alcohol and dehydroacetic acid is used. This preservative mixture is acid, and it decreases pH of the formulation (a pH regulator can be added to the formulation if required).

Information about the previously selected ingredients is summarized in Table 4-19. With the information from Table 4-18 and 4-19, a group of possible formulations are presented in Table 4-20.

Table 4-19 Surfactant systems, rheological modifier and preservatives for the development of the case study

Ingredient type	**Ingredient**	**Concentration**	**Comments**	**Process considerations**
Surfactant system sets 1, 2	Polysorbate 80 + Sorbitan stearate + Glyceryl monostearate	2.5-3.5%	Concentration interval was defined based on common surfactant concentrations used in skin care emulsions (Iwata and Shimada, 2013) (Mitsui, 1997)	Soluble in the oily phase
Surfactant system sets 1, 2 Second surfactant option	Sucrose palmitate + Cetearyl glucoside + Glyceryl monostearate	2.5-3.5%	Concentration interval was defined based on common surfactant concentrations used in skin care emulsions (Iwata and Shimada, 2013) (Mitsui, 1997)	Emulsification should be done in neutral pH. Sucrose palmitate is partial soluble in the aqueous phase. It can be pre-dispersed in glycols as glycerin
Surfactant system set 3	POE 100 stearate + Sorbitan stearate + Glyceryl monostearate	2.5-3.5%	Concentration interval was defined based on common surfactant concentrations used in skin care emulsions (Iwata and Shimada, 2013) (Mitsui, 1997)	Soluble in the oily phase
Surfactant system set 4	Stearic acid/NaOH (10%) +glyceryl monostearate	4% (stearic acid)+1.5%(NaOH) + 4% glyceryl monostearate	Concentration interval was defined based on common surfactant concentrations used in skin care emulsions (Iwata and Shimada, 2013) (Mitsui, 1997)	Soluble in the oily phase
Secondary rheological modifier	Xanthan gum	0.1-0.2%	(Iwata and Shimada, 2013)	Soluble in water, Dispersable in glycols as glycerin
Preservative	benzyl alcohol and dehydroacetic acid	0.6%	Concentration recommended by supplier	Soluble in polar solvents as glycerin, Decrease pH of the emulsion

Table 4-20 Formulations for the development of the case study

Phase	Ingredients	Set 1 and 2(%)	Set 1 and 2 (%)second surfactant system	Set 3 (%)	Set 4 (%)
A	Isopropyl myristate	2	2	2	2
A	Caprylic/capric trigliceride	7	7	7	7
A	Shea butter	1	1	1	1
A	cetyl palmitate	3	3	3	3
A	cetearyl alcohol	2-4	2-4	2-4	2-4
A	almond oil	1	1	1	1
A	Glyceryl monostearate	0.5*	0.5*	0.5*	2.5**
A	polysorbate 80	1.5*			
A	Sorbitan stearate	0.5*		0.9*	
A	POE100 stearate			1.1*	
B	Sucrose palmitate		1.5*		
A	Cetearyl glucoside		0.5*		
A	stearic acid				4**
B	NaOH (10%)				1.5**
C	Benzyl Alcohol and dehydroacetic acid	0.6	0.6	0.6	0.6
B	Glycerin	3	3	3	3
B	Water	76	76	76	76
B	Xantham gum	0.15	0.15	0.15	0.15
C	Acetate tocopherol	0.4	0.4	0.4	0.4
C	calendula oil	0.09	0.09	0.09	0.09
C	lemongrass oil	0.045	0.045	0.045	0.045

* Concentration of each surfactant is calculated assuming a total surfactant concentration of 2.5% and a required HLB of approx. 11
**The procentage is fixed according to an existing formulation with similar properties (Iwata and Shimada, 2013)
Some considerations for definitions of process conditions:
A Temperature of 70°C can be used for homogenization. At this temperature all ingredients are melted.
Components of the phase A are compatible/soluble between them. They can be weighted and heated together
Components of the phase B are compatible/soluble between them. Ingredients as polymers and gums, even if soluble in water, are difficult to solubilize. They can be pre-dispersed before solubilization.
It is recommended to introduce components signed with a C at the end of the homogenization and cooling process. This because either they are sensible to heating or they can affect negatively the homogenization process.

4.3. Application of the methods for product design stage in the case study – experimental results

The experimental phase of the case study was done in two parts:

First, formulations with the three surfactant systems corresponding to the solution strategies sets 1 and 3, as shown in Table 4-20, were prepared. Rheological, stability and microstructural properties of these formulations were compared among them, and based on the result, a surfactant system was selected.

Second, with the selected surfactant system, a set of experiments varying the concentration of the cetearyl alcohol (rheological modifier and stabilizer), the speed of homogenization (energy introduced to the formulation) and the surfactant concentration was designed and performed. It was done with the purpose of get to know in which proportions these factors affect the emulsion micro-structure, and how they and the resulting micro-structure influence rheological, texture and stability characteristics of the emulsions (this corresponds to the application of the solution set 2). Finally, all emulsions were compared with product specifications defined in Chapter 3. The emulsion with specifications closest to those specifications of the product was selected as a functional product prototype to be improved in further design stages.

4.3.1. Materials and methods

4.3.1.1. Materials

The ingredients used for the formulations are:

- Deionized water from the laboratory of Chemical Engineering at the Universidad Nacional de Colombia
- Crodamol IPM (Isopropyl myristate) from Croda
- Crodamol GTCC (Caprylic/Capric Triglyceride) from Croda
- Shea butter from Croda
- Crodamol CP (Cetyl palmitate) from Croda
- Cetearyl alcohol from Disan Colombia
- Almond oil from Disproalquímicos Colombia
- Cithrol GMS NE (glyceryl monostearate) from Croda
- Tween 80 (polysorbate 80) from Croda
- Span 60 (sorbitan stearate) from Croda
- Myrj™ 100 (PEG-100 stearate) from Croda
- Sucrose ester (Sucrose palmitate) from Modernist pantry
- Emulgade PL 68/50 (cetearyl glucoside) from BASF
- Geogard 221 (Dehydroacetic Acid and Benzyl Alcohol) from Lonza

- Glycerin from Disproalquímicos Colombia
- Xanthan gum from Disproalquímicos Colombia
- Acetate tocopherol from Roche
- Calendula oil from Xiu Aguee
- Lemongrass oil from Xiu Aguee

The materials used for the preparation and testing of the emulsion are:

- Two thermostatic baths JULABO (for high and low temperature control)
- Ultraturrax T25, disperser S25N-10G.
- Bohlin C-VOR rheometer
- A microscopy Motic B3 professional series
- A pHmeter SI Analytics Lab 860

4.3.1.1. Methods

Emulsion preparation: Emulsions ~100g were prepared by the traditional heating method, where the oily and aqueous phase are heated separately and mixed during high speed homogenization. After the emulsion is formed, it is cooled to ambient temperature while agitating. The preparation process is presented schematically in Figure 4-8 with more detail. Homogenization is done at a temperature of 75°C, an intermediate value between the tipical temperatures of 70 to 80ºC. A homogenization speed varying from 7000 to 14000 rpm is proposed. The first experimental part is done at 7000rpm and the second experimental part is done with the extremes of the proposed interval. Process considerations from Tables 4-18 and 4-19 were used to decide the phase and the form of addition of the ingredients.

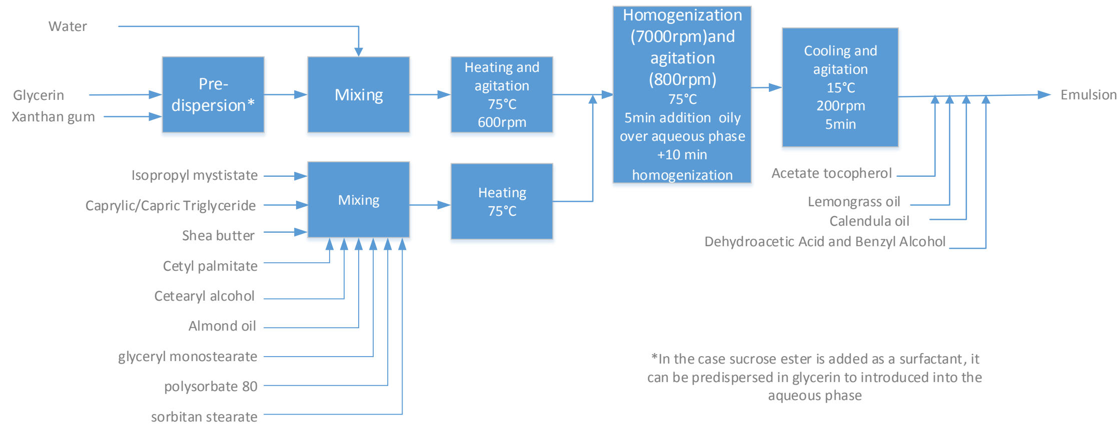

Figure 4-8. Emulsion preparation diagram process for the case study- using polysorbate 80.

Tables 4-21 and 4-22 summarize the conditions of the first and second experimental part respectively.

Table 4-21 Formulations for first experimental part – comparison between different surfactant systems

Product prototype	Surfactant system	Conditions*
P1	Polysorbate 80 +Sorbitan stearate +Glyceryl monostearate	Homogenization speed: 7000rpm Surfactant concentration:2.5% Cetearyl alcohol concentration:4%
P2	Sucrose palmitate +Cetearyl glucoside +Glyceryl monostearate	Homogenization speed: 7000rpm Surfactant concentration:2.5% Cetearyl alcohol concentration:4%
P3	POE 100 stearate +Sorbitan stearate +Glyceryl monostearate	Homogenization speed: 7000rpm Surfactant concentration:2.5% Cetearyl alcohol concentration:4%

Table 4-22 Formulations for the second experimental part – comparison between different micro-structure

Product prototype	Surfactant system	Conditions*
P4	Polysorbate 80 +Sorbitan stearate +Glyceryl monostearate	Homogenization speed: 7000rpm Surfactant concentration:2.5% Cetearyl alcohol concentration:2%
P5	Polysorbate 80 +Sorbitan stearate +Glyceryl monostearate	Homogenization speed: 12000rpm Surfactant concentration:2.5% Cetearyl alcohol concentration:2%
P6	Polysorbate 80 +Sorbitan stearate +Glyceryl monostearate	Homogenization speed: 12000rpm Surfactant concentration:3.5% Cetearyl alcohol concentration:4%
P7	Polysorbate 80 +Sorbitan stearate +Glyceryl monostearate	Homogenization speed: 12000rpm Surfactant concentration:2.5% Cetearyl alcohol concentration:4%

The following properties were measured to the emulsions:

- pH
- Droplet size measured by microscopy: As shown in (Padilla, 2016) and (Sinko and Singh, 2011), droplet size distribution was calculated based on the measurement of 300 to 500 droplets with an optic microscope with the objective of 100X. Emulsions were diluted in a 1:4 proportion and the colorant methylene purple was added in the dilution phase for a better observation. The software Image J was used for image processing.
- Stability tests: Two test were done for screening out instable samples: a temperature cycle test and a centrifugation test. The objective of these tests is to compare the resistance of product prototypes under stress conditions and select those with more resistance.

  Temperature cycle test: As suggested in (Estanqueiro et al., 2014), samples are subject to three heating/cooling cycles, changing their temperature between 40° to 4°C every 24 hours for 6 days. After each 24 h and after the 6 days, samples were visually checked. Centrifugation test: As suggested in (Estanqueiro et al., 2014), samples are centrifuged three times during 30 min at a centrifugation speed of 3000rpm. Any change of emulsions is visually checked.
- In addition to these tests, rheological tests done to the product samples in Chapter 3 are applied to product prototype to compared them with customer requirements.

4.3.2. Results and analysis

4.3.2.1. First part – comparison between different surfactant systems

The pH values of all samples were around 5.1 after the addition of the preservative system. It was decided to maintain this pH without further modification because it corresponds to selected solution strategies.

Droplet size: Table 4-23 presents the results of the droplet size distribution of prototypes P1, P2 and P3. Figure 4-8 presents the corresponding microscopies at 100X. Droplet size distribution diagrams of all of them can be seen in Annex G.

Table 4-23 Statistical results of the droplet size and droplet size distribution for prototypes P1 - main surfactant polysorbate 80, P2 - main surfactant sucrose ester, P3 - main surfactant POE-100 stearate

	P 1 (µm)	P 2 (µm)	P 3 (µm)
Mean	3.6	5.8	4.2
Median	3.2	4.3	2.2
Mode	1.8	2.4	2.0
Standard deviation	1.7	4.0	4.3
Minimum	0.7	0.6	0.8
Maximum	12.7	24.4	23.1

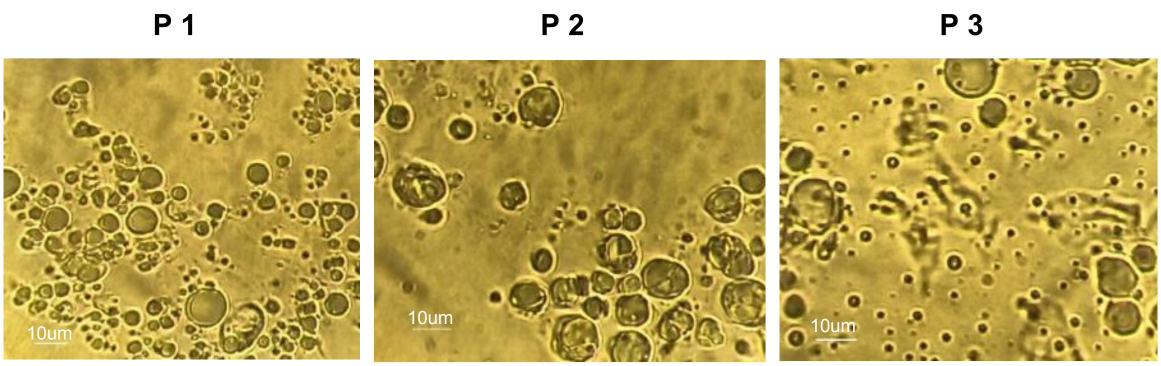

Figure 4-9. Micrographs at 100X of product prototypes P1 – main surfactant polysorbate 80, P2 – main surfactant sucrose ester, P3 – main surfactant POE-100 stearate.

By comparing the means of emulsions in Table 4-23 and the pictures in Figure 4-9, it can be seen that P3 has the smallest droplets of all of the samples but the widest droplet size distribution. P2 has also a wide distribution, and, in the picture it can be seen that some droplets seem to be formed by the fusion of several half-formed droplets.

That behavior can be explained by considering that sucrose palmitate and POE-100 stearate, the main surfactants used in prototypes P2 and P3, respectively, have a relative high molecular weight, and they may be absorbed relative slow on the droplets interface. During homogenization both phenomena breaking and coalescence happen at the same time, and just formed droplets may coalesce rapidly if they are not protected by a strong stearic or ionic repulsion. To reduce coalescence when these ingredients are used in relation to droplet formation, it is recommended to use different homogenization conditions. For example, the use of a higher surfactant concentration, the addition of a coemulsifier that adsorbs more rapidly or the improvement of mixing conditions during homogenization to allow a better transport of surfactants from the bulk liquid to the interphase.

By its part, P4 has an intermediated mean droplet size and the smallest droplet size distribution of the group. The surfactant system seems to adsorb fast on the interface and it forms relative small droplets.

Stability test: In the thermal stability test all emulsions were found stable. It means, any emulsion shows a phase separation after the six temperature cycles. In the centrifugation test, emulsion P2 showed separation of phases. Emulsions before and after the tests are shown in Figure 4-9.

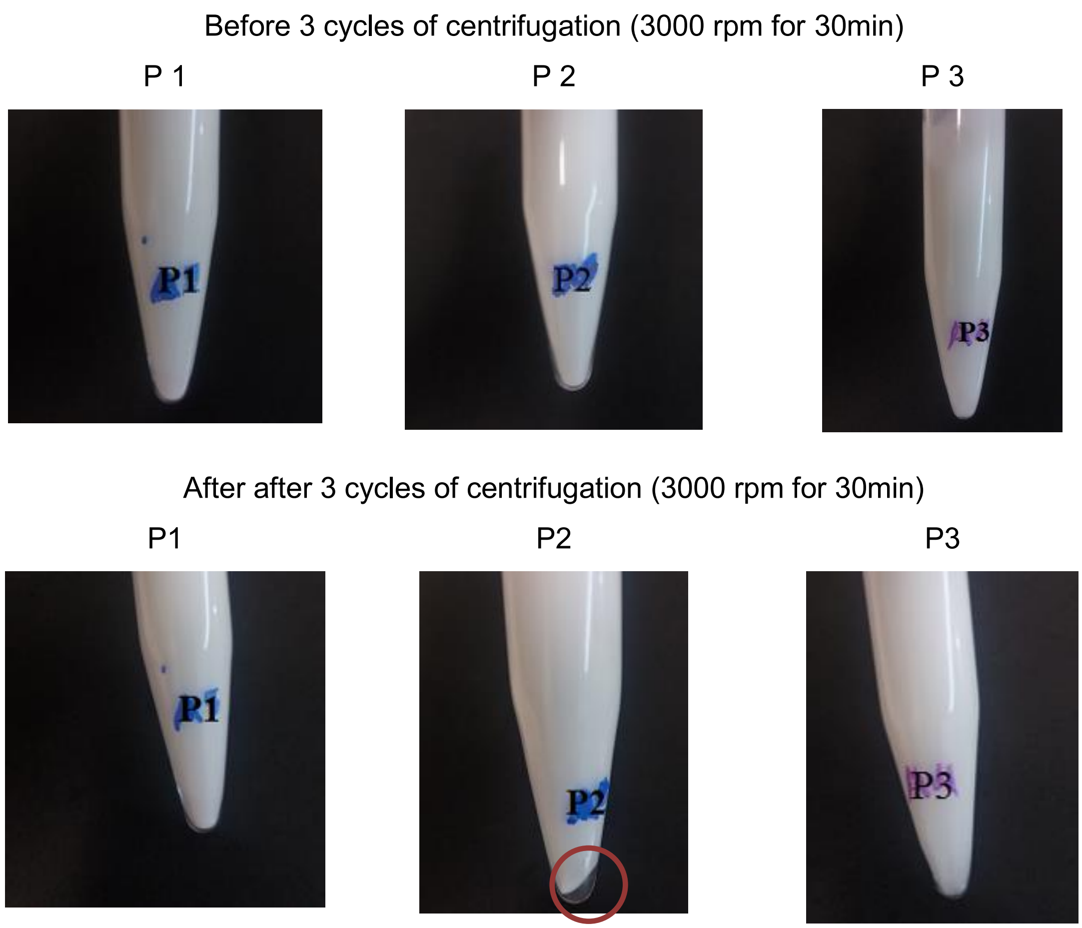

Figure 4-10. Pictures of product prototypes P1, P2 and P3 before and after the centrifugation test. P1 – main surfactant polysorbate 80, P2 – main surfactant sucrose ester, P3 – main surfactant POE-100 stearate.

Behavior of P2 can be explained by considering it has the highest droplet size of the three emulsions. In addition, it has a wide droplet size distribution and low viscosity (as will be shown in the next section). These three factors, according to the first relational matrix (Table 4-3,) increase the risk of gravity separation.

Rheology test: The plot of shear rate and viscosity for emulsions P1, P2 and P3 is shown in Figure 4-11. The measurements were done by triplicate and the standard deviation in most of the measurement points were lower than 10%, it was not plotted in the Figure to have a better visualization. The plot also shows the viscosity of the sample T1 of chapter 3, for which the customer showed to have a high preference.

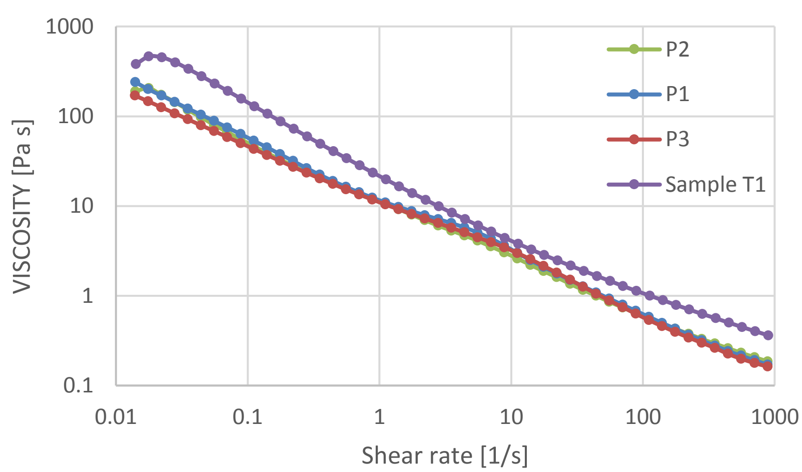

Figure 4-11. Plot viscosity –shear for product prototypes P1, P2, P3, and the sample T1 from Chapter 3

The test shows that prototypes have a relative low viscosity in relation to sample T1 of Chapter 3. P1 and P2 have a viscosity slightly higher than P3. Considering that prototype P1 showed good stability and better rheological characteristics than the others, it is selected as the surfactant to be explored in the second experimental part.

4.3.2.1. Second part – comparison between different surfactant systems

pH: As for the first prototypes, pH of the formulation was around 5.1

Droplet size: Table 4-24 and Figure 4-12 present the statistical results of the droplet size distribution of prototypes P1, P4, P5, P6 and P7. Figure 4-13 presents the corresponding microscopies at 100X. Droplet size distribution diagrams of all of them can be seen in Annex G.

Table 4-24 Statistical results of the droplet size and droplet size distribution for prototypes P1-7000rpm, 2.5 surfactant, 4%cetearyl alcohol, P4 – 7000rpm, 2.5% surfactant, 2% cetearyl alcohol, P5 -12000rpm, 2.5% surfactant, 2%cetearyl alcohol, P6 - 12000rpm, 3.5% surfactant, 4%cetearyl alcohol, P7 12000rpm, 2.5% surfactant, 4%cetearyl alcohol

	P 1 (µm)	P 4 (µm)	P 5 (µm)	P 6 (µm)	P 7 (µm)
Mean	3.6	4.5	3.0	2.5	2.8
Median	3.2	3.7	2.7	2.4	2.6
Mode	1.8	3.9	2.3	2.1	2.6
Std. deviation	1.7	2.5	1.1	0.8	1.2
Minimum	0.7	1.0	1.1	0.9	0.3
Maximum	12.7	18.2	6.9	5.5	7.0

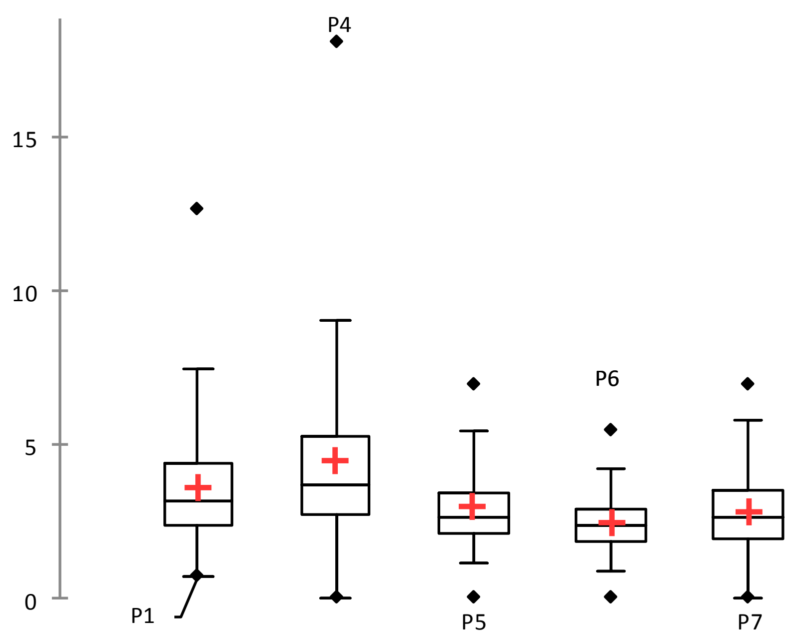

Figure 4-12. Box plot of droplet size distribution for prototypes P1, P4, P5, P6, P7

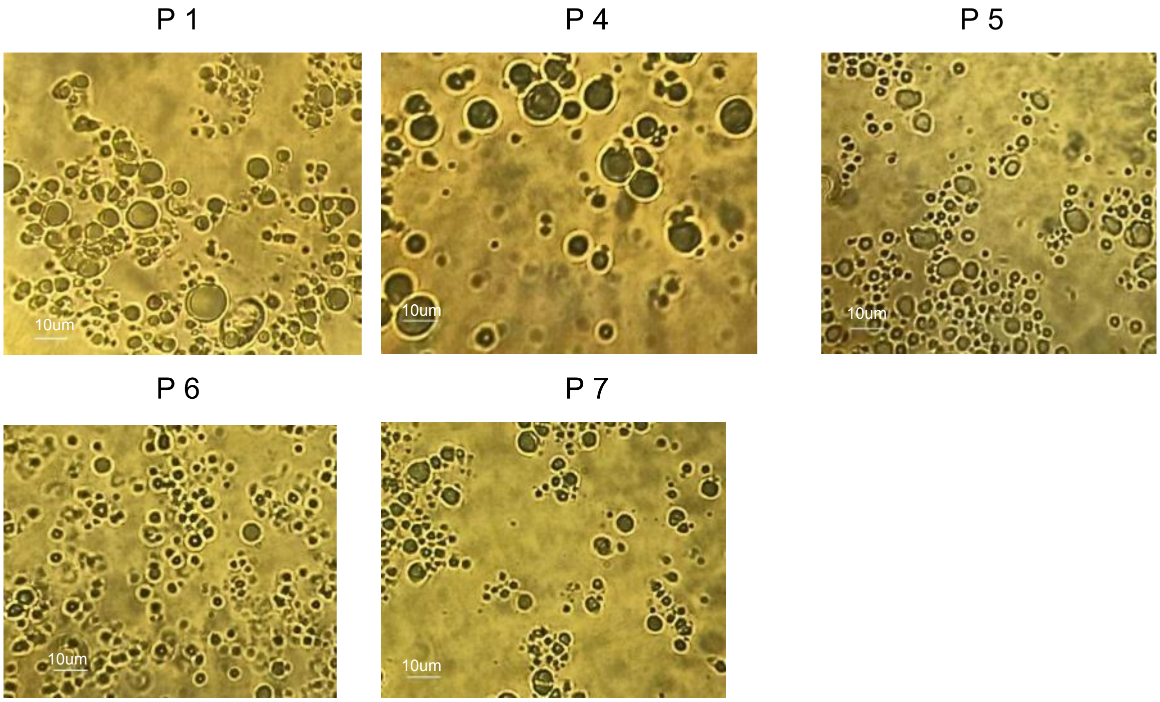

Figure 4-13. Micrographs at 100X of product prototypes P1- 7000rpm, 2.5 surfactant, 4%cetearyl alcohol, P4 – 7000rpm, 2.5% surfactant, 2% cetearyl alcohol, P5 -12000rpm, 2.5% surfactant, 2%cetearyl alcohol, P6 - 12000rpm, 3.5% surfactant, 4%cetearyl alcohol, P7 12000rpm, 2.5% surfactant, 4%cetearyl alcohol

Analyzing Figure 4-12, it can be seen that, as expected, emulsions prepared at higher homogenization speeds have smaller droplet sizes. In addition, as the droplet size decreases, the droplet size distribution also gets narrower, as can be seen in the boxplot in Figure 4-12. This can be explained considering that at higher speeds the disperser increases both the rate of disruption generating smaller droplets and the agitation within the homogenizer, which generates well mixed condition and, in turn, reduces the droplet size distribution. When homogenization speed is kept constant, the increase in concentration of both surfactant and cetearyl alcohol, generates smaller droplet sizes. As explained in the Table 4-2 of solution strategies, in a regimen of high energy, the addition of more surfactant decreases droplet size because there are more surfactant molecules available to cover new formed interfacial area. By its part, cetearyl alcohol works not only as emollient and thickener but also as emulsion stabilizer, because it tends to be closer to the droplet interface, due to its high polarity.

Stability test: All emulsions were resistant the conditions of both, the thermal and centrifugation test without presenting phase separation.

Rheological test: Figure 4-14 shows the viscosity of the prototypes in comparison with the Sample T1 of Chapter 3. It can be seen that viscosity of product prototypes at small shear rates are different, and the one with the smallest droplet size is the more viscous, and the closest to the sample T1. Prototypes are very similar at high shear rates, when they have almost the same viscosity, which is smaller than the viscosity of sample T1. This means that in general all prototypes have a higher shear thinning behavior than T1. By reviewing this problem in the relational matrix 1, it was found that a good solution is the addition of a rheological modifier with a lower shear thinning behavior.

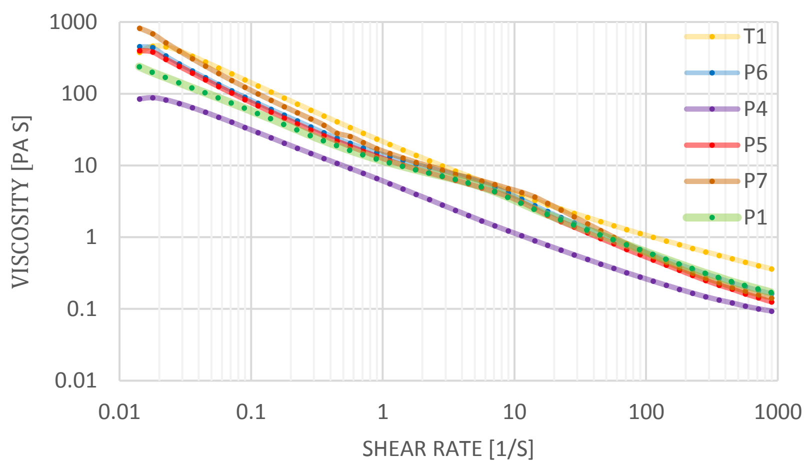

Figure 4-14. Plot viscosity –shear rate for product prototypes P1, P4, P5, P6, P7 and the sample T1 from Chapter 3

The product prototype closest to Sample T1 is P7. It can be further improved in order to create a product that meets all customer requirements.

4.4. Conclusions

In this chapter a method for emulsion design was proposed and applied to the case study. The method has two components: A first relational matrix that enables the classification of product specifications into sub-problems and the connection of the last with sets of solutions strategies and a second relational matrix formed by a series of data bases with information of surfactants, oils, rheological modifiers, preservatives and UV. filters.

The first relational matrix was built based on emulsion science principles and experts knowledge. It can be used for the design of any no concentrated emulsion regardless of the application sector. The second relational matrix is sector specific.

When the methodology was applied to the case study, four sets of possible solution strategies were proposed: one based on a nonionic surfactant system, a second one with the same surfactant system but changing droplet size, a third one using a surfactant that can create a thicker interfacial layer and a fourth one based on ionic/nonionic system. The behavior of prototypes was initially checked based on the scores given by the first relational matrix, and it was found that the fourth option with the ionic/nonionic surfactant system had more warnings than the other solutions, reason why it was screen out before the experimental part.

During the experimental part, first, three surfactant systems were explored: one with sucrose stearate, one with polysorbate 80 and one with POE-100 stearate. It was found that the polysorbate 80 tends to adsorb more quickly on droplets surface under the tested conditions and thus protects the droplets against coalescence and generate smaller droplets than the others.

A second experimental used only the surfactant system with polysorbate 80 and it was tested under two different homogenization speeds. It was found that at the highest homogenization speed more viscous creams were created, mainly due to the reduction of the droplets size.

5. Sustainability analysis

Nowadays, decision-making for product design requires to consider not only product functionalities but also its sustainability dimensions: economic, environmental and social, all of them simultaneously. Each dimension has a specific relative importance, which depends on the product type and its use. The present study proposes a multi-criteria analysis based framework to evaluate different product alternatives under sustainability criteria and guide the selection among them. The framework has three steps: (1) identification and characterization of alternatives, (2) assessment of alternatives through sustainability indicators, and (3) integration of assessments in a global index by a Multi Criteria Decision Analysis (MCDA) method (Figure 5-1).

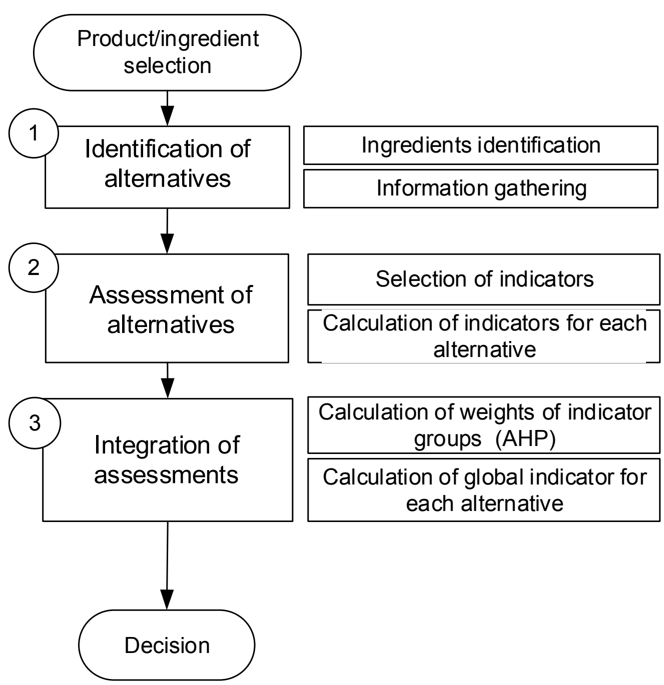

Figure 5-1: Framework for ingredients/products selection considering sustainability criteria

The first chapter section presents the decision framework, the sustainability indicators and the MCDA method - Analytic Hierarchy Process (AHP). The second, applies the decision framework to the case study.

5.1 Framework for the sustainability analysis of products and ingredients

A multi-criteria analysis based framework to evaluate different product alternatives is presented. It comprises the following three steps:

5.1.1. Identification of alternatives:

In this step product ingredients are identified and their behavior in sustainability terms are characterized. For this purpose information about economic, social and environmental properties of the ingredients has to be gathered. Sources for this information are safety data sheet of ingredients, suppliers, governmental and intergovernmental agencies and organizations as the European Chemicals Agency (ECHA), the Organization for Economic Co-operation and Development (OECD), and the Environmental Protection Agency U.S. (EPA), among others. Other information sources are chemical data bases as Pubchem and ECHA dossier of chemicals, and property predictive tools as EPI suite program from EPA. In addition, it is possible to use group contribution methods to calculate some safety and occupational health indices (Ten et al., 2017b).

5.1.2. Assessment of alternatives

In this step, suitable sustainable indicators are selected and used to assess product alternatives. The economic dimension is represented by the product added value calculated with the raw material costs and product price. In this study, environmental and social indicators were defined based on the hazard statements (H statements) of the Globally Harmonized System of Classification and Labelling of Chemicals (GHS), as it was also done in the National Profile of Chemical Substances in Colombia (Suarez Medina and Narváez-Rincón, 2017). In this approach, a number between 0 and 1 is given to each H statement according to its severity and a score combining all H statements of a substance is used for its assessment. This approach was selected because the H statements are available for almost any commercial substace, and especially in the validated information tool of eChemPortal[1] developed by OECD with the participation of different countries and institutions. In addition, their meaning is clear and accepted worldwide.

Figure 5-2 shows the selected indicators and Table 5-1 shows how to calculate their normalized value from H statement as established in (Suarez Medina and Narváez-Rincón, 2017). It is important to note that using all the listed indicators in order to calculate the sustainability of a product is not always necessary. Moreover, some of these can be disregarded or additional ones can be included according to product characteristics, the specific context of the selection problem, information availability and quality.

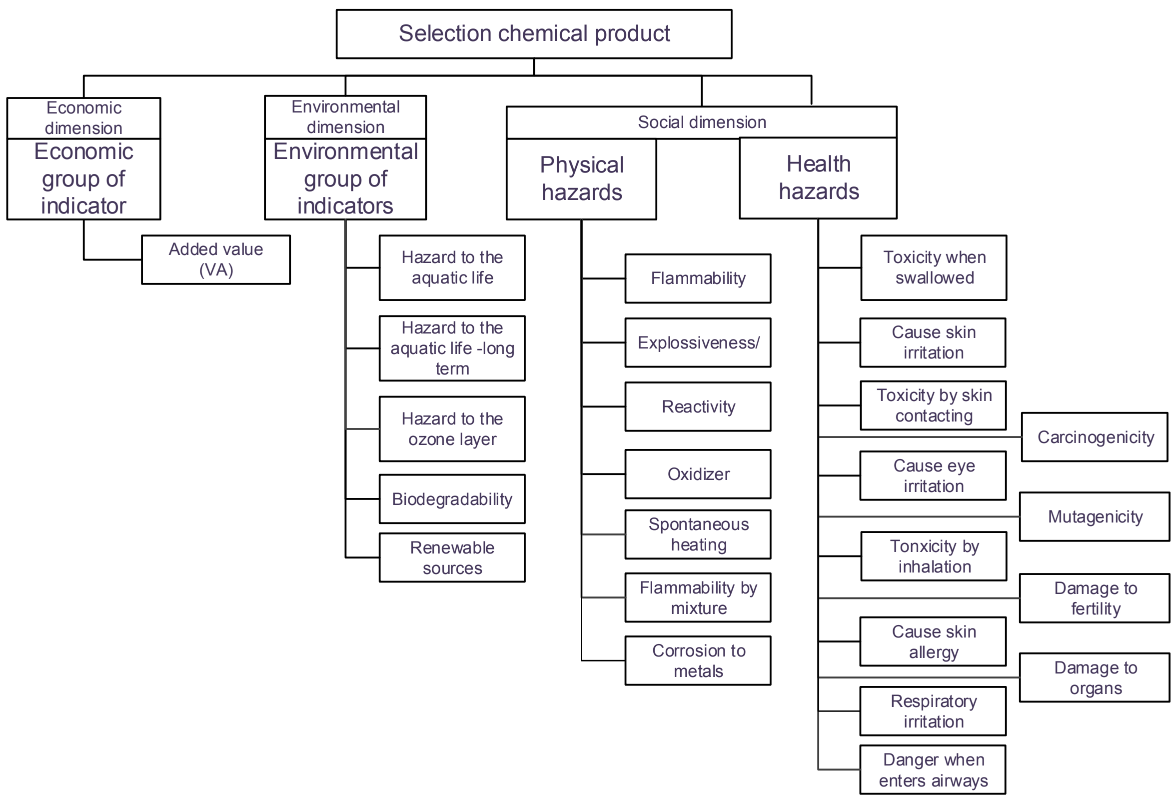

Figure 5-2: Sustainability indicators to assess product alternatives

(i) Economic indicator group

The present approach uses added value as economic indicator. Its normalized value is calculated from the ratio of raw material costs over product prices (Eq. 5.1). The smaller this value, the greater the gain per product.

[1] https://www.echemportal.org/echemportal/substancesearch/page.action?pageID=134

(ii) Environmental indicator group

Five indicators are included to assess the environmental dimension of product alternatives: Hazardous to the aquatic life, defined based on H statements 400 to 402. Hazardous to the aquatic life - long lasting effect defined based on H statements 410 to 413. Hazardous to the ozone layer defined based on H statement 420. Renewable origin is defined by classifying substances into the categories: 1) natural resources only physically modified, 2) enzymatic modified, 3) chemically modified, 4) from both natural and synthetic sources or 5) completely synthetic origin, similarly as proposed by Cosmos-ecocert standards (COSMOS-standard, 2018). In addition, Biodegradability is assessed by classifying substances according to ASTM 5864 in readily, inherent and no biodegradable (Sharma and Biresaw, 2017). A subsrance is readily biodegradable when it has a degradation greater than 60% in 28 days in an ultimately biodegradable test. A substance is inherent biodegradable when it presents a degradation between 20% to 60% in 28 days in an ultimately biodegradable test. A substance is non-biodegradable when it has a lower degradation that the previous one under the same conditions.

(iii) Social indicators –physical hazards

Physical hazards of raw materials are measured with seven indicators, all of them calculated based on H statements. The indicators are: Flammability, defined based on H statements 220 - 226, 228. Explosiveness, defined based on H statements 200 to 205. Reactivity, defined based on H statements 240 to 243. Oxidizer nature that may cause fire or explosion, defined based on H statements 270 to 272. Self-heating substances, defined based on H statements 251, 252. Substances that release flammable gases when mixed with water, defined based on H statements 260, 261. Substances that may be corrosive to metals, defined based on H statement 290.

(iv) Social indicators, health hazards

Health hazards are measured through 13 indicators, all of them calculated based on H statements. The indicators are: Toxicity when swallowed, defined based on H statements 300 to 303. Skin irritation, defined based on H statements 314 to 316. Toxicity by skin contacting, defined based on H statements 310 to 313. Eye irritation, defined based on H statements 318 to 320.Toxicity by inhalation, defined based on H statements 330 to 333. Skin allergy, defined based on H statement 317. Respiratory irritation, defined based on H statement 334. Carcinogenicity, defined based on H statements 350 to 351. Mutagenicity, defined based on H statements 340 to 341. Damage to fertility, defined based on H statements 360 to 362. Damage to organs unique and prolonged exposition, defined based on H statements 370 to 373. Danger when enters airways, defined based on H statements 304 to 305.

Table 5-1 summarizes the indicators and shows how to calculate their normalized value.

Table 5-1: Indicators for sustainability assessment of chemical products. H-statements from (United Nations, 2011b)

Category	Indicator	Explanation	Equation/indicator definition
Economic dimension	Added value	It corresponds to the relation between product prices and raw material costs	$\overline{VA_P} = \frac{\sum_1^C m_c P_c}{\sum_1^P m_p P_p}$ [5-1] $\overline{VA_P}$ is the normalized added value. m is the mass of raw material c or product p P_{rm} is the cost of raw material c and P_p is the product price. If $\overline{VA_P}$ is greater than one, the product is not economically attractive.
Environmental dimension	Hazard to the aquatic life	Defined based on H statements 400-402	H400 - Very toxic to aquatic life: **1** H401 - Toxic to aquatic life: **0.66** H402- Harmful to aquatic life: **0.33** No statement: **0** The value for a product integrated by several compounds is: $\overline{Impact_{p,I}} = \sum_{c=1}^{C} x_c * Impact_{c,I}$ [5-2] ,where C is the total number of compounds in the product. $Impact_{c,I}$ is the impact of compound c associated with impact category I $\overline{Impact_{p,I}}$ is the normalized impact of product p associated with impact category I. x_c is the concentration of the component c in the product. This normalization method is valid for the calculation of all indicators presented in the table except for added value.
	Hazard to the ozone layer	H statement 420	H420 - Harms public health and the environment by destroying ozone in the upper atmosphere: **1** No statement: **0**
	Renewable sources	Raw materials are classified according to their source into into the categories: 1) natural resources only physically modified, 2) enzymatic modified, 3) chemically modified, 4) from both natural and synthetic sources or 5) completely synthetic origin (COSMOS-standard, 2018)	Natural resources only physically modified/enzymatic modified: **0** Natural resources chemically modified: **0.33** From both natural and synthetic sources: **0.66** Completely synthetic origin: **1**
	Hazard to the aquatic life – long lasting effect	Defined based on H statements 410 to 413	H410 - Very toxic to aquatic life with long lasting effects: **1** H411 - Toxic to aquatic life with long lasting effects:**0.75** H412 - Harmful to aquatic life with long lasting effects: **0.5** H413 – May cause long lasting harmful effects to aquatic life: **0.25** No statement: **0**

Category	Indicator	Explanation	Equation/indicator definition
	Biodegradability	According to ASTM 5864, applicable to oils and lubricants. An oil is ready biodegradable if it degrades 60% or more within 28 days. It is inherent biodegradable if it degrades from 30 to 60% in 28 days and it is nonbiodegradable if it not degrades more than 30% in 28 days(Sharma and Biresaw, 2017).	Readily biodegradable: **0** Inherent biodegradable: **0.5** Nonbiodegradable: **1**
Social dimension – physical hazard	Flammability	H statements 220- 226, 228	H-220, 222, 224, 229 Extremely flammable: **1** H -225 very flammable: 0.75 H-221, 223, 226, 228 flammable: **0.5** No statement: **0**
	Explosiveness	H statements 200 to 205	H200 - Unstable explosive: **1** H201 - Explosive; mass explosion hazard: **1** H202 - Explosive; severe projection hazard: **1** H203 - Explosive; fire, blast or projection hazard: **1** H204 - Fire or projection hazard: **0.5** H205 - May mass explode in fire: **1** No statement: **0**
	Reactivity	H statements 240 to 242	H240 - Heating may cause an explosion **1** H241 - Heating may cause a fire or explosion **1** H242 - Heating may cause a fire **0.5** No statement: **0**
	Oxidizer	H statements 270 to 272	H270 - May cause or intensify fire; oxidizer 1 H271 - May cause fire or explosion; strong oxidizer 1 H272 - May intensify fire; oxidizer 0.5 No statement: **0**
	Self-heating substances	H statements 251, 252	H251 - Self-heating; may catch fire: **1** H252 - Self-heating in large quantities; may catch fire:**0.5** No statement: **0**
	Release flammable gases when mixed with water	H statements 260, 261	H260 - In contact with water releases flammable gases which may ignite spontaneously: **1** H261 - In contact with water releases flammable gas:**0.5** No statement: **0**
	Corrosive to metals	H statement 290	H290: May be corrosive to metals
Social dimension – health hazard	Toxicity when swallowed	H statements 300 to 303	H300- Fatal if swallowed:**1** H301-Toxic if swallowed: **0.6** H302- Harmful if swallowed: **0.4** H303-May be harmful if swallowed:**0.2** No statement: **0**
	Skin irritation	H statements 314 to 316	H314- Causes severe skin burns and eye damage:**1** H315- Causes skin irritation:**0.66** H316- Causes mild skin irritation:**0.33** No statement: **0**
	Toxicity by skin contacting	H statements 310 to 313	H310: Fatal in contact with skin:**1** H311: Toxic in contact with skin:**0.6** H312: Harmful in contact with skin:**0.4** H313: May be harmful in contact with skin:**0.2** No statement: **0**
	Eye irritation	H statements 318 to 320	H318: Causes serious eye damage: **1** H319: Causes serious eye irritation:**0.66** H320: Causes eye irritation:**0.33** No statement: **0**
	Toxicity by inhalation	H statements 330 to 333	H330: Fatal if inhaled: 1 H331: Toxic if inhaled:0.6 H332: Harmful if inhaled:0.4 H333: May be harmful if inhaled:0.2 No statement: **0**
	Skin allergy	H statement 317	H317-May cause an allergic skin reaction:1 No statement: **0**

Category	Indicator	Explanation	Equation/indicator definition
	Respiratory irritation	H statement 334, 335, 336	H334: May cause allergy or asthma symptoms or breathing difficulties if inhaled:1 H335: May cause respiratory irritation:1 H336: May cause drowsiness or dizziness:1 No statement: **0**
	Danger when enters airways	H statements 304 to 305	H304: May be fatal if swallowed and enters airways:**1** H305: May be harmful if swallowed and enters airways:**0.5** No statement: **0**
	Carcinogenicity	H statements 350 to 351	H350: May cause cancer:1 H351: Suspected of causing cancer0.5 No statement: **0**
	Mutagenicity	H statements 340 to 341	H340: May cause genetic defects:1 H341: Suspected of causing genetic defects:0.5 No statement: **0**
	Damage to fertility	H statements 360 to 362	H360: May damage fertility or the unborn child:**1** H361: Suspected of damaging fertility or the unborn child:**0.66** H362: May cause harm to breast-fed children:**0.33** No statement: **0**
	Damage to organs	H statements 370 to 373	H370: Causes damage to organs **1** H371: May cause damage to organs **0.5** No statement: **0**
	Damage to organs prolonged exposure		H372: Causes damage to organs through prolonged or repeated exposure **1** H373: May cause damage to organs through prolonged or repeated exposure **0.5** No statement: **0**

5.1.3. Integration of assessment

During this stage, indicators are combined to achieve an integrated sustainability assessment. For this purpose it is suggested to apply the method Analytic Hierarchy Process (AHP) to calculate the weights of indicators groups.

AHP is a method developed by Saaty (1980), that breaks complex problems down into sub-problems and organizes them according to a hierarchical structure. It does not require a prior definition of a preference function, but uses pairwise comparison between criteria and alternatives (Ishizaka and Nemery, 2013). Another advantage of this method is that additional and/or different indicators can be easily included within its structure.

The method comprises four main steps: hierarchical structuring of the problem, assignment of weights, consistency test, and sensibility analysis (Ishizaka and Nemery, 2013):

- Hierarchical structuring of the problem: The method breaks down the problem and organizes its parts hierarchically. The top level is the goal of the decision, the second level comprises the criteria, and the lowest level contains the alternatives. In the product design selection problem, the goal is to select the most sustainable one. The criteria are the sustainability indicator groups shown in Figure 5-1, i.e., environmental indicators, economic indicator, health hazard indicators and physical hazard indicators and the alternatives are the different proposed products.

- Assignment of weights: Weights are calculated for each indicator group using the pairwise comparison given by decision makers and the eigenvalue method. The pairwise comparison is generally made on a ratio scale from 1 to 9, where 1 means equal importance among two indicator groups, and 9 means that one indicator group is much more important than the other.
- Consistency test: To know if the weights are meaningful, that is, that there are not contradictions between the answers during pairwise comparison, a consistency test related to eigenvalue method is performed. A value for the consistency index lower than 10% is normally accepted.
- Sensibility analysis: weights are varied in order to observe the robustness of the solution

Once weights are defined with AHP, it is possible to calculate a Global Sustainability Index (GSI) by adding pondered indicators, as shown in equation 5-3. The larger the GSI, the lower the sustainability of the product. With the results of GSI for each alternative, product designers can rank them, compare them and finally select the most sustainable option.

$$GSI = W_{ec} \cdot I_{ec} + W_e \cdot I_e + F_{hh} \cdot I_{hh} + W_{ph} \cdot I_{ph} \quad [5\text{-}3]$$

,where I correspond to the the average of the indicators that make up each group, W is the weight of groups of indicators calculated with AHP, and the sub-index represents each of the four indicators groups: economic indicator (ec), environmental indicator (e), health hazards indicators (hh), and physical hazards indicators (ph).

5.2. Application of the sustainability assessment to the case study

5.2.1. Identification of alternatives:

As explained in chapter 4, four product alternatives were assessed with the same oily phase and different surfactant systems (Alternatives 1 – 4 in Table 5-2). In this section, a fifth alternative, with a different preservative system, and a sixth alternative, with a different rheological system, are considered for comparative purpose. The alternatives are presented in Table 5-2

Table 5-2: Product alternative for the case study

Ingredients	Alternative 1 (%)	Alternative 2 (%)	Alternative 3 (%)	Alternative 4 (%)	Alternative 5(%)	Alternative 6 (%)
Isopropyl myristate	2	2	2	2	2	2
Caprylic/capric trigliceride	7	7	7	7	7	7
Shea butter	1	1	1	1	1	1
Cetyl palmitate	3	3	3	3	3	3
Cetearyl alcohol	3	3	3	3	3	3
Almond oil	1	1	1	1	1	1
Glyceryl monostearate	0.5	0.5	0.50	2.5	0.5	2.5
Polysorbate 80	1.5	-	-	-	1.5	-
Sorbitan stearate	0.5	0.9	-	-	0.5	-
POE-100 stearate		1.1	-	-		-
Sucrose palmitate	-	-	1.50	-	-	-
Cetearyl glucoside	-	-	0.5	-	-	-
Stearic acid	-	-	-	4	-	4
NaoH (10%)	-	-	-	1.5	-	1.5
Dehydroacetic Acid/ Benzyl Alcohol	0.6	0.6	0.6	0.6	-	0.6
Methyl paraben/ propyl paraben	-	-	-	-	0.3	-
Glycerin	3	3	3	3	3	3
Water	76	76.0	76	76	76	76
Goma xanthan	0.15	0.15	0.15	0.15	0.15	-
Carbomer	-	-	-	-	-	0.15
Acetate tocopherol	0.4	0.4	0.4	0.4	0.4	0.4
Calendula oil	0.09	0.09	0.09	0.09	0.09	0.09
Lemongrass oil	0.045	0.045	0.045	0.045	0.045	0.045

Preparation process:
Heat ingredients 1 to 14 together to 75°C (Phase A)
Heat ingredients 15 to 21 to 75°C (Phase B)
Add Phase A to Phase B (aggregation time =5min) and homogenize (10min)
Cool (cold bath at 15°C) and add 22, 23, 24
pH should be around 5.5, for alternatives 4 and 6 it should be around 7.2

Table 5-3 shows the sustainability characteristics of the compounds presented in Table 5-2, excluding water.

Table 5-3: Price, Origin, H statements, biodegradability and acute toxicity of the compounds of product alternatives for the case study

Ingredients	Price ($USD/kg) (aprox)		Origin		Phrase H		Biodegradability		Acute toxicity LD50 rat (oral mg/kg)	
Isopropyl myristate	16.7	[1]	Natural and synthetic raw material	[2]	H315	[6]	readily biodegradable	[9]	> 5.000	[9]
Caprylic/capric trigliceride	15.8	[1]	Natural raw material chemically processed	[2]	No H statement	[7]	readily biodegradable	[7]	> 2.000	[7]
Shea butter	19.2	[1]	Natural raw material only physically transformed		No H statement	[8]	readily biodegradable	[8]	> 2,600	[8]
cetyl palmitate	12.3	[1]	Natural raw materials chemically processed	[2]	No H statement	[8]	readily biodegradable	[8]	14400	[7]
cetearyl alcohol	11.5 [1]	[1]	Natural raw materials chemically processed	[3]	No H statement	[8]	readily biodegradable	[8]	> 5.000	[9]
almond oil	13.9	[1]	Natural raw material only physically transformed		No H statement	[7]	readily biodegradable	[8]	>5000	[8]
Glyceryl monostearate	9.0	[1]	natural raw materials chemically processed		H315, H319	[6]	readily biodegradable	[8]	> 5000	[8]
polysorbate 80	14.9	[1]	natural and synthetic raw material		H315, H319, H412	[6]	readily biodegradable	[8]	> 60000	[8]
Sorbitan stearate	12.6	[1]	natural raw materials chemically processed		H412	[6]	readily biodegradable	[8]	> 2000	[8]
POE-100 stearate	9.8	[1]	natural and synthetic raw material		H315, H319, H335	[6]	NA		>25000	[16]
Sucrose palmitate	40 (sucrose cocoate)	[1]	natural raw materials chemically processed		No H statement	[9]	readily biodegradable	[14]	> 2000	[8]
Cetearyl glucoside	10.5	[1]	natural raw materials chemically processed		H315, H318	[6]	readily biodegradable	[15]	> 2000	[8]
stearic acid	8.7	[1]	natural raw materials chemically processed		H315, H319, H335	[6]	readily biodegradable	[15]	> 5000	[8]
NaOH (10%)	NA	-	synthetic/mineral origin –ecocert accepted	[4]	H290, H314, H315, H318, H319	[6]	-		325	[8]
Benzyl Alcohol	9.5	[19]	Synthetic –ecocert accepted	[4]	H302, H319, H332	[8]	readily biodegradable	[8]	1230	[13]
Dehydroacetic Acid	9.5	[19]	Synthetic–ecocert accepted	[4]	H315, H318, H372	[8]	readily biodegradable	[8]	2565	[8]
propyl paraben	7	[19]	Synthetic		H315, H319, H335	[6]	readily biodegradable (similar to methylparaben)	-	6000	[6]
Methyl paraben	7	[19]	Synthetic		H315, H319, H335, H412	[8]	readily biodegradable	[8]	2100	[8]
Glycerin	10	[1]	Natural raw material chemically processed		No H statement	[8]	readily biodegradable	[8]	27200	[8]
Water	1.1$USD /m3	[20]	-		-		-		-	
Goma xanthan	35	[1]	Natural raw material chemically processed	[3]	No H statement, (it may form combustible dust concentrations in air)	[10]	readily biodegradable	[10]	> 5000	[10]
Carbomer	21	[1]	synthetic		H402, (it may form combustible dust concentrations in air)	[11]	readily biodegradable	[11]	> 5000	[11]

Ingredients	Price ($USD/kg) (aprox)	Origin	Phrase H	Biodegradability	Acute toxicity LD50 rat (oral mg/kg)
acetate tocopherol	51 [1]	synthetic	H413 [6]	not biodegradable [12]	> 10000 [12]
calendula oil	8.3$USD /mL [18]	Natural raw material only physically transformed	H315, H319, H335 (similar to lemongrass oil) -	readily biodegradable [8]	4640 20 mL/kg (Dermal) [17]
lemongrass oil	1.2$USD /mL [18]	Natural raw material only physically transformed	H315, H319, H335 [12]	Expected to be biodegradable -	> 5000 [12]

References:
[1] (Making cosmetics, 2018), [2] (BASF, 2016), [3] (COSMOS-standard, 2018), [4] (Ecocert Standard, 2012), [5] BASF safery data sheet, [6] Pubchem: (Kim et al., 2016), [7] Croda safery data sheet, [8] (European Chemicals Agency - ECHA, 2018), [9] Evonik safery data sheet, [10] Solvay safery data sheet, [11] Lubrizol safery data sheet, [12] Sigma – Aldrich safery data sheet, [13] Merck safery data sheet, [14] (Baker et al., 2000), [15] (Madsen et al., 2001), [16] (Liebert, 1983), [17] (Andersen et al., 2010), [18] Personal communication Product Engineering of Xiu Aguee, [19] Personal communication supplier of raw materials for cosmetics, [20] Water rates 2018 – Acueducto de Bogotá

5.2.2. Assessment of product alternatives:

Sustainability indicators are calculated based on information presented in Table 5-3. Indicators values are shown in Table 5-4. Non all indicators from Table 5-1 are used because the substances considered in the six formulations do not show all of the negative effects.

Table 5-4: Normalized sustainability indicators of the product alternatives

	Alternative 1	Alternative 2	Alternative 3	Alternative 4	Alternative 5	Alternative 6
Added value**/***	1.49E-01	1.48E-01	1.53E-01	1.51E-01	1.48E-01	1.51E-01
ECONOMIC DIMENSION	**1.49E-01**	**1.48E-01**	**1.53E-01**	**1.51E-01**	**1.48E-01**	**1.51E-01**
Renewable	8.97E-02	8.83E-02	8.47E-02	9.79E-02	8.67E-02	9.90E-02
Biodegradability	4.00E-03	4.00E-03	4.00E-03	4.00E-03	4.00E-03	4.00E-03
Danger to the aquatic life	0	0	0	0	0	4.95E-04
Danger to the aquatic life – long term	1.10E-02	5.50E-03	1.00E-03	1.00E-03	1.25E-02	1.00E-03
ENVIRONMENTAL DIMENSION	**2.62E-02**	**2.45E-02**	**2.24E-02**	**2.57E-02**	**2.58E-02**	**2.61E-02**
Corrosive to metals	0	0	0	1.50E-02	0	1.50E-02
PHYSICAL HAZARD	**0**	**0**	**0**	**1.50E-02**	**0**	**1.50E-02**
Toxicity when swallowed	2.40E-03	2.40E-03	2.40E-03	2.40E-03	0.00E+00	2.40E-03
Toxicity by inhalation	2.40E-03	2.40E-03	2.40E-03	2.40E-03	0.00E+00	2.40E-03

	Alternative 1	Alternative 2	Alternative 3	Alternative 4	Alternative 5	Alternative 6
Skin irritation	2.73E-02	2.46E-02	2.07E-02	7.20E-02	2.93E-02	7.20E-02
Eye irritation	1.81E-02	1.54E-02	1.32E-02	6.28E-02	1.61E-02	6.28E-02
Respiratory irritation	1.35E-03	1.23E-02	1.35E-03	4.14E-02	4.35E-03	4.14E-02
HEALTH HAZARD	**1.03E-02**	**1.14E-02**	**8.00E-03**	**3.62E-02**	**9.94E-03**	**3.62E-02**

**Added value: Product value is set for this calculation at 5USD/50mL. The price correspond to 85% of the price of a product with similar characteristics (Labfarve calendula cream) available in the Colombian market.
***60% of the costs correspond to the essential oils

According to the results in Table 5-4, alternative 3, the one with sucrose ester as surfactant, has the best performance in relation to health hazards and environmental dimension, but it is a little more expensive. Alternative 1, 2 and 5, are equilibrated with good performance in the four groups of indicators, but it is difficult to decide which of them is the best. Alternatives 4 and 6 seem to have the worst performance. To make a selection, MCDA methods are used to identify the most sustainable product alternative

5.2.3. Integration of assessments

The calculation of weights was made considering the criteria of the design team, who compared the groups of indicators by pairs, using the scaling ratio from 1 to 9 of AHP. The pair comparison is shown in Table 5-5.

Table 5-5: Pair comparison between groups of indicators using AHP

	Economic dimension	Environmental dimension	Physical hazard	Health hazard
Economic dimension	1.0	0.25	2.0	0.11
Environmental dimension	4.0	1.0	4.0	0.25
Physical hazard	0.5	0.25	1.0	0.14
Health hazard	9.0	4.0	7.0	1.0

In addition to this comparison, the design team agreed that substances presenting any indication of severe effects to health as carcinogenicity, mutagenicity, damage to fertility and damage to organs are unacceptable and have to be replaced by a sustainable ingredient. This is not the case for any of the alternatives considered in the case study.

Calculation of weights (AHP)

AHP was applied using the free web based software (Goepel, 2017) and the information of Table 5-5. Results are presented in Figure 5-3, where it can be observed that the most important dimension corresponds to social - health hazards indicators, followed by the environmental dimension. The last rated dimensions were the economic dimension and social-physical hazard indicators.

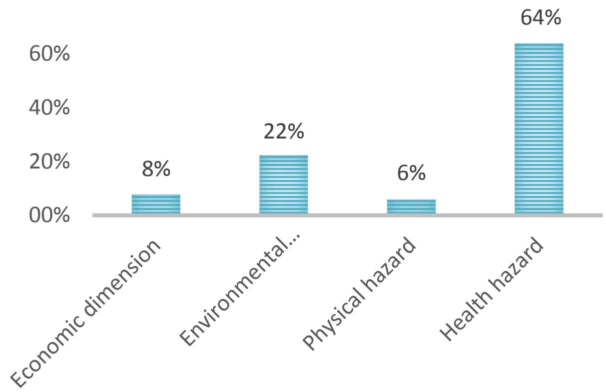

Figure 5-3: Results of weights for groups of indicators using AHP (Consistency index of 5.6%)

Health hazards and environment indicators are the main concern of the members of the design team, because they are aware of their responsibility in relation to consumer health and environment and also because of the increasing demand from consumers for cleaner and safer products and processes. Any damage to consumer and/or formulator health in short or long terms have to be avoided. Physical hazards are not that important in this case, because almost any of the substances considered, except from sodium hydroxide, have this kind of hazard.

The economic indicator, added value, has a relative low importance. This can be explained, considering that for the design team the dimensions are interrelated. A product will be more successful and will generate more gain if people can trust that it does not cause any damage. In addition, in the cosmetic sector, more than the price, the trust of the consumer seems to be a determinant factor.

Calculation of global sustainability index

Weights from AHP and indicators of Table 5-4 are used in equation 5-3 to calculate the global sustainable index (GSI) for each alternative and rank them. Results are shown in Table 5-6.

Table 5-6: Global Sustainable index (GSI) of alternatives of the study case

	Caracteristic	GSI	Rank
Alternative 3	Surfactant system: Sucrose ester Preservative: Dehydroacetic Acid and Benzyl Alcohol Rheological modifier: xanthan gum	0.022	1
Alternative 5	Surfactant system: Polysorbate/ sorbitan stearate Preservative system: Methyl/propyl paraben Rheological modifier: xanthan gum	0.024	2
Alternative 1	Surfactant system: Polysorbate/ sorbitan stearate Preservative: Dehydroacetic Acid and Benzyl Alcohol Rheological modifier: xanthan gum	0.024	2
Alternative 2	Surfactant system: POE-100 stearate and span Preservative: Dehydroacetic Acid and Benzyl Alcohol Rheological modifier: xantham gum	0.024	2
Alternative 4	Surfactant system: Sodium stearate Preservative: Dehydroacetic Acid and Benzyl Alcohol Rheological modifier: xantham gum	0.042	3
Alternative 6	Surfactant system: Sodium stearate Preservative: Dehydroacetic Acid and Benzyl Alcohol Rheological modifier: carbomer	0.042	3

According to Table 5-6, alternative 3 is the most sustainable of the options. The surfactant and rheological modifier of this alternative are both bio-based, which favors its positive results. Alternatives 5, 1 and 2 are closed between each other. The alternatives 5 and 1 have the same surfactant system but different preservatives, however, they obtain a similar score. Alternatives 4 and 6 have the highest global sustainability score. They were punished with a high score because in their preparation sodium hydroxide is used and it is highly irritant to skin and eyes even in dilution at 10%. In addition, acid stearic is used in relative high concentrations and it is reported to be irritant for eyes and skin. Other surfactants are milder or are used in lower concentrations, which made them less irritant and better for leave-on cosmetic products.

Experimentally, alternative 3 did not show good stability or rheological behavior in the proven process conditions as shown in Chaper 4. However, due to its high sustainability it would be interesting to try this surfactant under different conditions.

Alternative 1 is not as sustainable as alternative 3, but it is a little less expensive and it showed a good performance in stability and rheological parameters established based on customer needs.

5.3. Conclusions

The selection stage proposed the use of sustainability indicators to assess product alternatives and multi-criteria analysis methods to integrate them. The indicators were calculated based on the H statements of the Globally Harmonized System of Classification and Labelling of Chemicals (GHS), because their meaning is accepted worldwide and H statements are available in almost any data base. The set of indicators can be completed with sector specific ones when required. The multi-criteria analysis method AHP was used to integrate the assessment because of its high flexibility when analyzing very complex problems.

This approach was applied to 6 prototypes based on those proposed in Chapter 4. It was found that the most sustainable of the options is the one containing sucrose esters as emulsifier, because it is biobased, followed nearly by the option prepared with sorbitan ester and polysorbate. The worst ranking alternative was the one using stearic acid.

Ingredients used in formulations are relatively safe. Those with more warnings are the preservatives.

6. Conclusions and recommendations

6.1. Conclusions

The main objective of this work was to propose a methodological approach for chemical product design considering both customer needs and sustainability criteria. The methodological approach developed and tested has three stages: needs stage, design stage and selection stage.

The stage of needs proposes to use a method for need analysis: Kano model and a method for needs translation into product specifications: Quality Function Deployment (QFD). The first use a questionnaire to investigate the nature of customer needs in relation to their satisfaction. It classifies needs in those that are constraints (must-be), those that can be optimized to increase customer satisfaction (one-dimensional) and those that are differentiation market factors (attractive needs). QFD combines information from experts and users in order to translate needs into product specifications with their respective target values. Experts were interviewed in technical terms about the meaning of standards and well established cosmetic test used for product design and their relation with a predefined set of customer needs. Customers were interviewed using characterized product samples, which are not finished product prototypes but representations of design ideas to achieve a communication based not only in words, but in factual objects with which the customers can interact. Product sample can be instrumentally characterized and those characteristics can be statistically associated to customer expressed opinion about the sample. With this approach it is possible to analyze and translate needs based on statistically robust methods.

The design stage proposes the use of two relation matrix which are used to connect first product specifications to a set of solution strategies and second, identified solution strategies with product components. These matrices constitute a multivariate approach in which it is possible to consider the effect of multiple solution strategies in relation to multiple problems at the same time.

The first relational matrix was built based on emulsion science principles and expert knowledge. It is not sector specific and it can be used for the design of any emulsion. The second relational matrix, which is the database of ingredients is specific for the cosmetic sector. Data bases for other sectors can be created in a similar form than the presented here for cosmetic ingredients: first, it is necessary to identify those properties that are relevant for each type of ingredient in the sector of interest, second a list of ingredients of this sector is selected. Lists of ingredients classified by application sector can be found in web pages of suppliers or in search engines as Ulprospector (www.ulprospector.com). Third, ingredients properties are searched or calculated. Information about properties can be consulted in suppliers' web pages, technical encyclopedias, data bases, or they can be calculated using methods such as group contribution.

The selection stage proposed the use of sustainability indicators to assess product alternatives and multi-criteria analysis methods to integrate them. The indicators were calculated based on the H statements of the Globally Harmonized System of Classification and Labelling of Chemicals (GHS), because their meaning is accepted worldwide and H statements are available in almost any data base. The set of indicators can be completed with sector specific ones when required. The multi-criteria analysis method AHP was used to integrate the assessment because of its high flexibility when analyzing very complex problems. Other methods as MACBETH and PROMETHEE can be used to explore other characteristics and interrelations between indicators and indicators groups.

In relation to the hypothesis of this study, it was possible to address systematically the design of emulsion type chemical products by the implementation of a multivariate approach. Such an approach comprises the three stages previously presented and it was applied to a design study case successfully.

Additionally, this study explored some aspects of innovation by giving tools to designers that enable them to introduced novelty at least in to parts of the design process. In the needs stage, when concepts representing sensations by customers are created. And in the design stage, when designers introduce data of new ingredients and used them to develop a product. Although, the workflow was presented in a certain order, designer can use just a part of it, or they can reorganize the design stages according to their specific problem structure. For example, the approach can be used backwards when designers have to change an ingredient and want to search for the needs related to those ingredients to prepare a redesign. Additionally, design can begin with a sustainability analysis when the objective of the designers is the creation of more sustainable products. Moreover, the first relational matrix and the data base presented here can be enriched with more ingredients and phenomena, every time a designer introduces a new design scenario that needs to address new information.

6.2. Recommendations

The subject of chemical product design is very extensive and because of its relative recent emergence, a lot of work is required to take it to a mature state in relation to other disciplines in chemical engineering as chemical process design. Here, some recommendations in relation to the specific topics discussed in this study are suggested for deeper exploration.

In relation to the stage of need analysis:

The proposed methodology focuses on customer needs for chemical product design, but it is possible to have a bigger perspective by considering the needs of other stakeholders such as local raw material producers, government, workers and owners of the company, among others. In such, an approach it is necessary to take into account both the positive and negative consequence that the design of a new product/the redesign of an existing product can bring to all stakeholders in order to make the best possible design decisions.

The use of product samples was already recognized as a powerful communication tool with customers, and its use is recommended not only for needs translation but also for need analysis with Kano model, where it may lead to more accurate conclusions.

In this work, customer needs were integrated into the design by a classical approach, in which the customers were directly interviewed about their needs. This strategy can be complemented by using other information sources: for example, interviewing lead users or information searching in cosmetic blogs and influencer channels among many others. This considering the role that the internet and internet social networks have in current people life and customer choices.

In this work, some aspects of the tactile sensations and olfactory sensations were explored. However, the subject is huge and requires more research looking to the creation of models to enable an accurate customer needs translation.

In relation to the stage of product design:

It is possible to complement the approach of the first relational matrix, which connects sub-problems with solutions strategies, by searching also the interrelations between product strategies. This can be done by consulting experts and filling the roof of the first relational matrix, in a similar way it is done with the House of Quality of the QDF approach.

The first and the second relational matrices can be complemented by considering synergies between their elements. That, in the case when it is possible to know that more than one solution strategies or more than one ingredient together can bring extra benefits in relation to the independent solutions.

The two relational matrices here proposed can be extended in three directions. It is possible to add more components and more phenomena to them and adapt them to other productive sectors different than cosmetics. Moreover, it is also possible to adapt them with more details and a greater degree of accuracy to specific design problems. The last case may be interesting for companies working in specific sectors and/or with a specific group of products. For them, and in the case there are enough data available, it may be possible to define interrelation between elements not with a categorical variable but with a continuous function depending.

Information about ingredients is normally presented in the form of databases or predictive equations, but there is a lack of graphical tools that enable a quick analysis of the possible solutions. Thus, it is necessary to propose forms to visualize the solution space in an holistic space allowing the designer to have a map of possibilities and take better informed decisions. A different representation of the information may lead to new decisions and new product creations.

In relation to the stage sustainability:

It is possible to complement the economic dimension by considering not only the costs of raw material as the main decisive factor, but the capacity of product to create value. This is particular important in the cosmetic case, where people are willing to buy certain products based on specific features that represent value to them, and do not care specially about product price. An indicator representing the potential of growth of the market when new and valuable features are introduced into a product is still to be developed.

New sustainability indicators can be defined by considering the specific regulation of the cosmetic sector. For example, by introducing indicators that represent if a product is green certified, organic certified, bio certified, among others.

It is possible to use multi-criteria analysis methods to explore the interrelations between indicators and sustainability dimension in order to make better informed design decisions. An example of such a methods is DEMATEL

In this work weights to the different sustainability dimensions were defined by the design team. It is also possible to interview experts from the cosmetic sector to get to know the sustainability perspective that professionals have within this sector.

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A. Annex: List of some standard test and instrumental measurements used in the cosmetic industry

Table A1: Some standard test of the cosmetic sector

	Specification	Definition and example of target values	Units	Measurement and/or approximation	Reference
Safety and Regulation	Physical/chemical stability	Physico-chemical stability corresponds to the time that emulsion keeps its properties almost constant in such a way that user cannot perceive any change. Common times of stability correspond to 6 months, 1 year and 2 years	Months, years	For stability, it is possible to perform preliminary stability tests, accelerated stability test and natural stability test (ONUDI, 2018): Preliminary stability test: emulsion behavior is examined under determinate stress conditions to observe if emulsion is resistant. Example of conditions are centrifugation, temperature cycles, changes in temperature, light exposition, among others. This test does not give the time emulsion remains stable, but of if they resist to certain stress conditions. This test does not probe that the product remains stable during a period, but can be used to rapidly assess emulsion resistant and take design decisions (ONUDI, 2018). Accelerated stability test: emulsions are examined under temperatures higher than the environmental temperature (over 30°C) during a period of 3 to 6 months. This test does not give exactly the shelf product life but shows emulsion behavior in relation to packaging, active ingredients and when positive it is a good indication of long term stability (ONUDI, 2018) Natural stability test: Emulsion is examined in standard conditions during the expected shelf life. This test provide the real stability time ONUDI, 2018).	(ONUDI, 2018)
	Toxicology	The major concerns of safety are related to toxicology profile of ingredients and possible effects of the final product in relation to skin irritation and sensitization. For more of the cases, when products with similar ingredients have been prepared, or when product functions do not included percutaneous absorption, it is enough to review safety information of ingredients(COLIPA, 2004). Attention should be given to regulation. An example is the European Cosmetics Directive, which contains a list of prohibited Ingredients (Annex II), restricted ingredients (Annex III), and other ingredients Annex IV to VII that are used for specific uses and conditions.	Allowed ingredients are used. Additional information is given by ingredients provider in terms of acute toxicity, invitro irritation, invitro ski sensitization, genetic toxicology, among others. These test can be also done to finished products when necessary.	In most of the cases it is only necessary to review toxicology information of ingredients used in the formulation. Information can be found in data bases: Toxline, Medline, and in safety data sheets given by ingredients providers (COLIPA, 2004).	(COLIPA, 2004)
	Microbiological quality	-	For the test of direct colony count: Not more than 10^3 cfu/g or ml (cfu= colony formatting units) (COLIPA, 1997).	There are commonly two type of test that can be used for testing microbiological quality: the challenge test and direct count of viable aerobic mesophyllic miscroorganims. In the first, product is inoculate with different microorganism and then, it is tested to know if it can resist microorganism growth at various periods. This is done to prove preservatives efficacy, for example in cases a new preservative is used. The second measures the number of bacteria and yields that are in the finished product (COLIPA, 1997).	Additional information can be found in (Huang et al., 2017) (COLIPA, 1997)

	Dermal tolerance and non-irritability	This test is related to product safety. For more of the cases, if it is know that the ingredients used do not generate irritation and if the product application has a low risk, it may not be necessary to perform a dermal tolerance test.	Use of probed ingredients that do not generate irritation	In case a literature search does not give results, dermal irritation can be measured by an invitro test or by invivo test with volonteers	(COLIPA, 2004)
Sensorial evaluation	It is a descriptive technique used to evaluate sensations of an individual or a group of individual in relation to a stimulus, in this case a product (Pensé-Lhéritier, 2016). For a trained panel, it is suggested to have at least 10 evaluators, while for an untrained panel, it is recommended to have at least 20(Pensé-Lhéritier, 2016). All test conditions, including the space of test, product presentation and survey protocol are carefully planned to avoid data variability. done people. evaluatrFor an untrained paPeople is asked about the sensation an specific For a trained panel, 10 indivi. It can be used to evaluate the effectiveness of a cosmetic product		Units depend on the evaluation scale.	Examples of product characteristics that can be measured under this method are: Product appearance and odor, which makes reference to quality of aspect and fragrance of the product. Product stringiness, which is the degree that a product stretches when it is located between two fingers that are compressed and separate successively(Gilbert et al., 2013). Oil in skin: sensation of oiliness/ grease on skin Spreadability: Facility of the product to move when a force is applied (Gilbert).	(Pensé-Lhéritier, 2016)
Performance evaluation	Skin appearance – clinical test	A clinical test enable to measure the product effect with the help of an expert, for example a dermatologist (Pensé-Lhéritier, 2016).	Units depend on the evaluation scale. An examples is: skin dryness measure as: a. Absent b. Light c. moderate d. severe e. extreme	This test can be done before and after product application	(Pensé-Lhéritier, 2016)
	Skin appearance 8h after application	-	Skin dryness is desired to be absent	This test can be done before and 8 h after product application, to explore the long term effect of the product	-
	Allergenic test	Clinical test can be used to explore allergies.	Allergies are expected to be absent	-	-
	TEWL (assessment of the Transepidermal Waterloss)	This test measures the transfer of water from skin to the outside. Its value is expressed as quantity of water evaporated per area.	NA	NA	(Pensé-Lhéritier, 2016)
	TEWL 8h after application	-	NA	NA	(Pensé-Lhéritier, 2016)
	Corneometer	This test is done based on the electric conductivity of skin, which increases as hydration increases. Instead of measuring conductivity, normally the capacitance is the measured variable.	When corneometer is used, hydration is measured in hydration index (HI), which goes from 0 to 120 for very dry skin to very hidrated skin (Pensé-Lhéritier, 2016). When product is tested in the face, the measure scale is: HI <	This measurement can be done with different	(Pensé-Lhéritier, 2016)

			50, then skin is very dry; from 50-60 it is dry, over 60, it is normal When the product s tested in the hand, arm or leg, the measure scale is: HI < 35, then skin is very dry; from 35-50 it is dry, over 50, it is normal (Pensé-Lhéritier, 2016).		
	Corneometer 8h after application	-	-	-	-
Instrumental tests	Rheological profile	-	-	-	-
	Instrumental measurement - oil on skin	-	-	-	-
	Texturometer - Spreadability	-	-	-	-
	Texturometer - extrusion test	-	-	-	-
	Texturometer - penetration test	-	-	-	-

Additional tests

Safety	Human toxicity potential by inhalation or dermal exposure (HTPE)	-	-	-	-
-	Toxicity	-	-	-	-
	Non-evidence of hormonal activity	-	-	-	-
	Ingredients percentage must-be less than the limit approved by FDA (FDA protocol from CFR - Code of Federal Regulations Title 21- Chapter I subchapter D part 352 (FDA, 2016))	-	-	-	-

Functional ities	Sun protection measured as SPF protection.	According to FDA, a product with a SPF less than 15 can be labeled as "helps prevent sunburn" but an alert message explaining that it does not help to prevent skin cancer has to be added. According to the European commission this product is labeled as "low protection" A product with a SPF equal and superior than 15 with a broad-spectrum can be labeled as it helps prevent sun burn and decreases the risk of skin cancer. In Europe products with a SPF between 15 and 30 are labeled as "medium protection". In Europe products with a SPF between 30 and 50 and broad-spectrum are labeled as "high protection" and products with 50 or more as "very high protection".	SPF units (UVA and UVB to be labelled as broad spectrum)	SPF is measured in an in vivo test, where a group of subjects with fair skin is exposed in a determined skin area (at least 1 cm2) to a specific dosage of UV radiation. The respond variable is Minimal erythema dose (MED), i.e., the quantity of energy use to produce a skin reaction (redness), which is measured in two conditions with and without protection (blank). SPF of the product is the ratio of MED of the protected skin over the MED of the unprotected skin section. Detail procedure is given in the FDA protocol from CFR - Code of Federal Regulations Title 21 (FDA, 2016). To give a broad protection, the product has to protect against UVA and UVB. There are guidelines for in vitro measurement of UVA PF as those given by COLIPA (COLIPA, 2007) and the FDA. As approximation method during design, it is possible to simulate the SPF of a mixture of U.V. filters. A free simulator made by BASF is available (BASF, n.d.)	1) Labeling and Effectiveness Testing: Sunscreen Drug Products for Over-The-Counter Human Use — Small Entity Compliance Guide (FDA, 2012b) 2) Press release - Consumers: Be sun-smart this summer(European Commision, 2009). 3) FDA protocol from CFR - Code of Federal Regulations Title 21 (FDA, 2016)

B. First customer survey: Profile of customers and their expectations about the moisturizing cream

B1 Survey to the customers to ask them about of their expectations

The English translation with the main questions is shown in this section

Questions:

1. Email address
2. How old are you?
    a. Less than 20 years
    b. From 20 to 29 years
    c. From 30 to 39 years
    d. From 40 to 49 years
    e. From 50 to 59 years
    f. More than 60 years
3. Gender
    a. Male
    b. Female
4. What is your occupation
5. Where do you normally purchase cosmetic and / or personal care products? (It is possible to select more than one option)
    a. Supermarket
    b. Pharmacy
    c. Naturist store
    d. Beauty salon
    e. Consultant - sale by catalog
    f. Store specialized in cosmetics and perfumery
    g. Internet
    h. Other:
6. How often do you apply a facial moisturizer?
    a. 2 times a day or more
    b. Once a day
    c. 2 to 5 times per week
    d. 1 time a week
    e. Sporadically
    f. Never
7. From the following list, which criteria do you consider most important when selecting a cosmetic and / or personal care product? (It is possible to select more than one option)
    a. Price
    b. Brand
    c. Packing
    d. Adaptation to your skin type
    e. Presence of certain ingredients
    f. Absence of certain ingredients
    g. Odor
    h. Proven efficiency

   i. Other:

8. What do you expect from a facial moisturizer? (In terms of functionality, appearance,aroma, nature, sensations, personality. Express it all!)

B2 Analysis of answer of customers to the first survey

In this section, the profile of the respondents of the first survey is presented. In total the survey was answered by 213 people, with the following distribution according to age and gender:

1. **Respondents of the first survey by age and gender**

Table B-1 Respondents of the first survey - age and gender

Age group	Gender	Number of respondents
Less than 20 years	Man	2
	Woman	10
20 to 29 years	Man	33
	Woman	81
30 to 39 years	Man	13
	Woman	45
40 to 49 years	Man	2
	Woman	10
50 to 59 years	Man	2
	Woman	8
60 years or more	Man	0
	Woman	7

2. **Information of preferences of all respondents and the group of interest: women of age between 20 to 29**

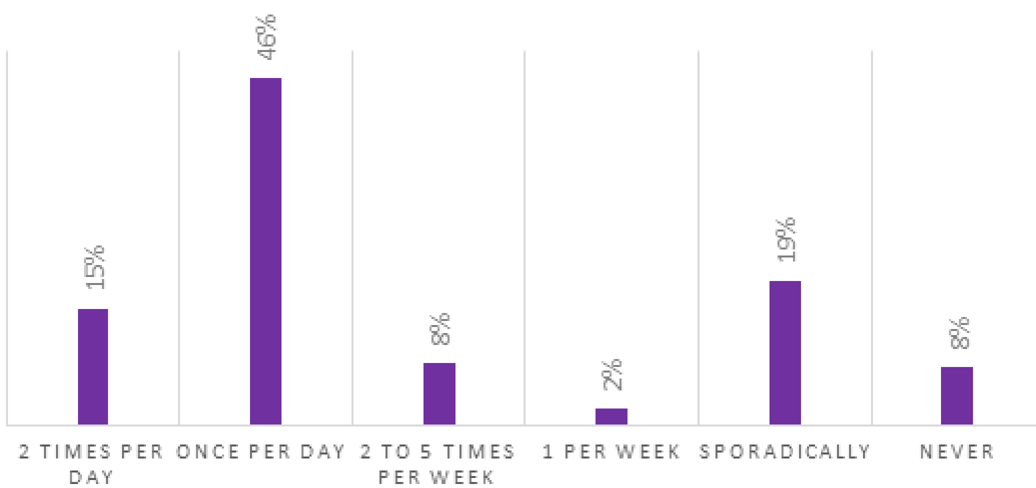

Figure B-1 Frequency of application of a moisturizing cream for all respondents

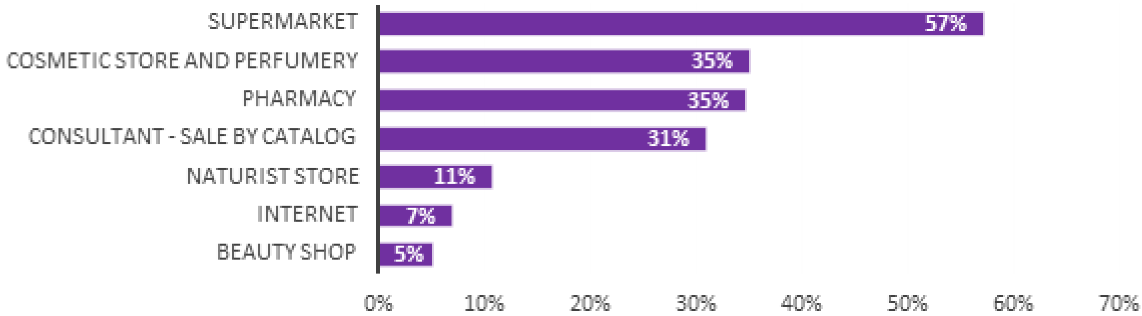

Figure B-2 Places of purchase of cosmetics according to all respondents

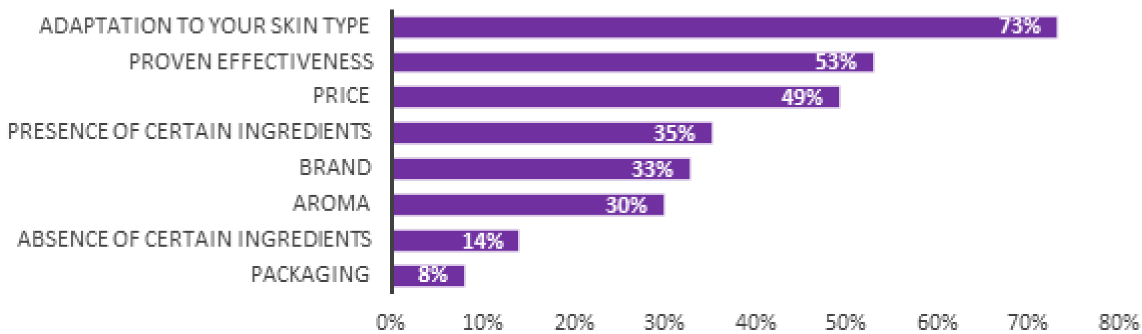

Figure B-3 Main criteria for the selection of a cosmetic product for all respondents

3. Information of preferences comparing two groups: women of age between 20 to 29 (target customers) and women of age between 30 to 39 (current customers)

Table B-2 Frequency of application of a moisturizing cream women of age between 20 to 29 (target customers) and women of age between 30 to 39 (current customers)

	Frequency of application					
	2 times per day	Once a day	2 to 5 times per week	Once per week	Sporadically	Never
Woman of 20 to 29 years	16%	56%	7%	1%	19%	1%
Woman of 30 to 39 years	24%	49%	9%	2%	11%	4%

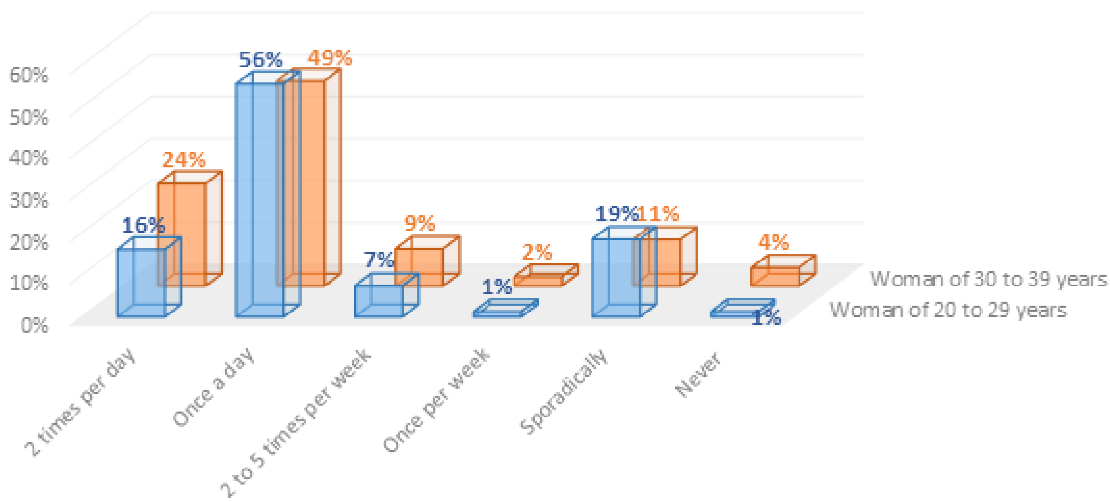

Figure B-4 Frequency of application of a moisturizing cream for women of age between 20 to 29 and women of age between 30 to 39

Table B-3 Place of purchase of cosmetic products of women of age between 20 to 29 (target customers) and women of age between 30 to 39 (current customers)

	Place of purchase						
	Supermarket	Pharmacy	Naturist store	Beauty salon	Sale by catalog	Store specialized in cosmetics	Internet
Woman of 20 to 29 years	62%	40%	12%	7%	36%	37%	7%
Woman of 30 to 39 years	33%	29%	7%	2%	40%	51%	7%

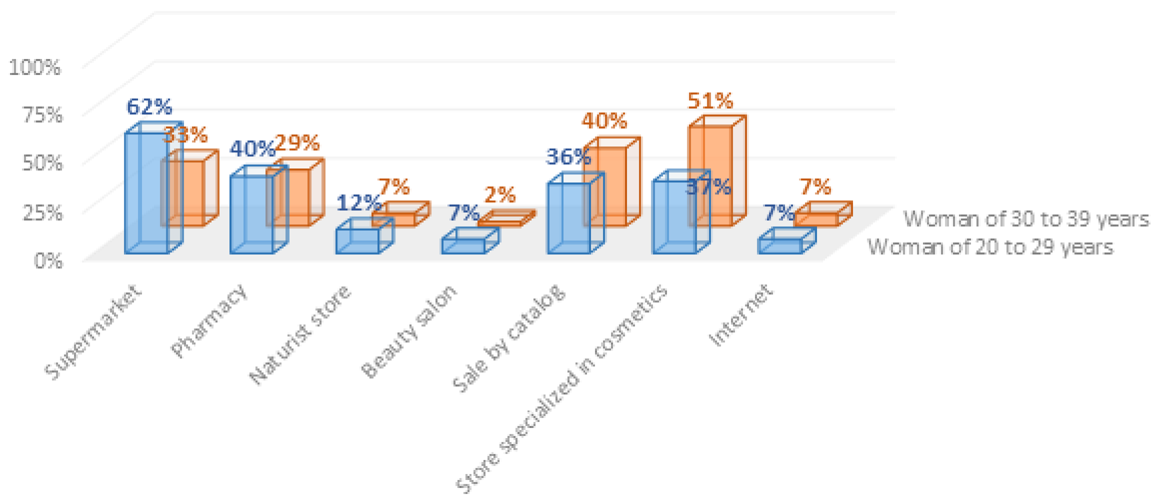

Figure B-5 Places of purchase of cosmetics according to women of age between 20 to 29 and women of age between 30 to 39

Table B-4 Criteria for selection of cosmetic products of women of age between 20 to 29 (target customers) and women of age between 30 to 39 (current customers)

	Criteria to elect a cosmetic							
	Price	Brand	Packaging	Adaptation to skin type	Presence of certain ingredients	Absence of certain ingredients	Aroma	Proven effectiveness
Woman of 20 to 29 years	51%	40%	9%	69%	46%	16%	26%	52%
Woman of 30 to 39 years	44%	31%	9%	82%	33%	7%	33%	49%

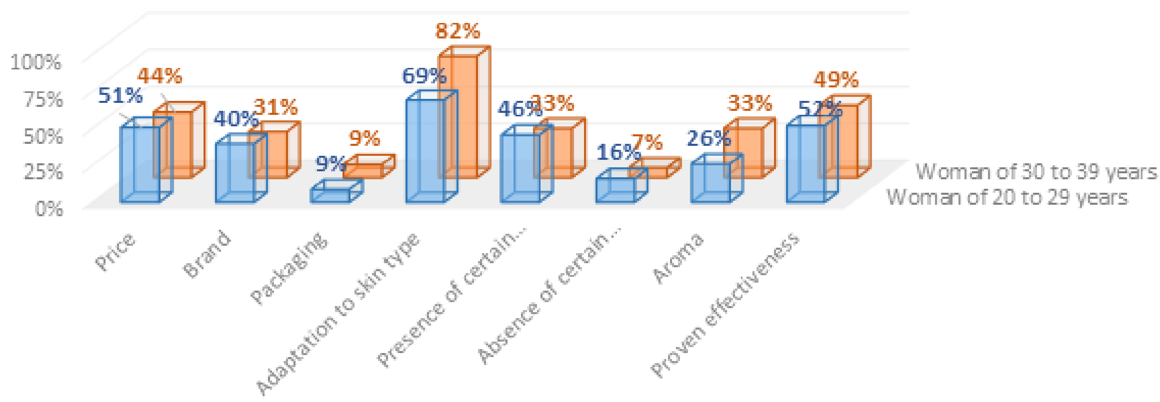

Figure B-6 Main criteria for the selection of a cosmetic product for women of age between 20 to 29 and women of age between 30 to 39

C. Annex: Survey to experts to translate needs into product specifications

Relationship between customer needs and product target specifications

The objective of this survey is to find the degree of interrelation between customer needs and technical specifications for the design of a facial moisturizing cream. Each question ask you how well a technical specification (of the type sensorial evaluation, clinical tests, safe and regulation, instrumental tests) represents and measures a list of customer needs.

You can answer in a scale between 1 to 9, where

1 means a weak relation between the technical specification and the need,
3 a moderate relationship,
5 a medium relationship,
7 a strong relationship and
9 a very strong relationship

The survey has 25 questions and takes around 15 min to be completed. Thank you very much for your time and support!

*Obligatorio

1. **Dirección de correo electrónico** *

____

2. **Please select your work experience in the cosmetic sector** *
Selecciona todos los que correspondan.
   - [ ] less than 2 years
   - [ ] from 2 to 5 years
   - [ ] from 5 to 10 years
   - [ ] more than 10 years

Safety and regulation

3. **1. How strong is the relationship between the PHYSICAL/CHEMICAL STABILITY OF THE COSMETIC PRODUCT* and the following customer needs** *
* Article 3 EC 1223/2009 Period-after-opening and Date of minimum durability (indicated if <30 months)
Marca solo un óvalo por fila.

	1	3	5	7	9	N/A
The product has a pleasant appearance	◯	◯	◯	◯	◯	◯
It has a pleasant aroma	◯	◯	◯	◯	◯	◯
It is safe and reliable	◯	◯	◯	◯	◯	◯
It is natural	◯	◯	◯	◯	◯	◯

4. **2. How strong is the relationship between the PHYSICOCHEMICAL, TOXICOLOGICAL, AND ECOTOXICOLOGICAL PROFILE OF THE SUBSTANCES and the following customer needs** *
Marca solo un óvalo por fila.

	1	3	5	7	9	N/A
The product has a pleasant appearance	◯	◯	◯	◯	◯	◯
It has a pleasant aroma	◯	◯	◯	◯	◯	◯
It is safe and reliable	◯	◯	◯	◯	◯	◯
It is natural	◯	◯	◯	◯	◯	◯

5. **3. How strong is the relationship between the MICROBIOLOGICAL QUALITY* and the following customer needs** *
* Challenge test: Microbiological stability, following Cosmetics Europe guidelines (CTFA and COSMETICS EUROPE, 2004) and ISO 21148 - General instructions for microbiological examination
Marca solo un óvalo por fila.

	1	3	5	7	9	N/A
The product has a pleasant appearance	◯	◯	◯	◯	◯	◯
It has a pleasant aroma	◯	◯	◯	◯	◯	◯
It is safe and reliable	◯	◯	◯	◯	◯	◯
It is natural	◯	◯	◯	◯	◯	◯

6. **4. How strong is the relationship between the USE OF ALLOWED SUBSTANCES* and the following customer needs?** *
* Negative list (Annex II), Restrictive positive list (Annex III) and Positive list with special precautions (Annex IV to VI)
Marca solo un óvalo por fila.

	1	3	5	7	9	N/A
The product is safe and reliable	◯	◯	◯	◯	◯	◯
It is natural	◯	◯	◯	◯	◯	◯
It has a pleasant aroma	◯	◯	◯	◯	◯	◯
It has a pleasant appearance	◯	◯	◯	◯	◯	◯

7. **5. How strong is the relationship between the DERMAL TOLERANCE AND NON-IRRITABILITY and the following customer needs?** *
Marca solo un óvalo por fila.

	1	3	5	7	9	N/A
The product is safe and reliable	◯	◯	◯	◯	◯	◯
It is natural	◯	◯	◯	◯	◯	◯

8. **Comments**
Please complete if you have any comment or suggestion

Sensorial evaluation*

*Sensory panel tests description at Pensé-Lhéritier, A.-M. Evaluation des produits cosmétiques: L'objectivation - Chapter 10 Mesure sensorielle . Lavoisier Tec & Doc, Paris 2016

9. **6. How strong is the relationship between a SENSORY PANEL TEST FOR STICKINESS and the following customer needs?** *

Marca solo un óvalo por fila.

	1	3	5	7	9	N/A
The product is easy to dose and spread						
It does not leave an oily texture						
It does not feel sticky						
It has a soft/light texture						

10. **7. How strong is the relationship between a SENSORY PANEL TEST FOR PRODUCT APPEARANCE and the following customer needs?**

Marca solo un óvalo por fila.

	1	2	5	7	9	N/A
The product is easy to dose and spread						
It has a pleasant appearance						
It does not leave an oily texture						
It does not feel sticky						
It has a soft/light texture						
It is natural						

11. **8. How strong is the relationship between a SENSORY PANEL TEST FOR STRINGINESS and the following customer needs?** *

Marca solo un óvalo por fila.

	1	3	5	7	9	N/A
The product is easy to dose and spread						
It does not leave an oily texture						
It does not feel sticky						
It has a soft/light texture						

12. **9. How strong is the relationship between a SENSORY PANEL TEST FOR PRODUCT ODOR and the following customer needs?** *

Marca solo un óvalo por fila.

	1	3	5	7	9	N/A
The product has a pleasant aroma						
It has a soft/light texture						
It is natural						

13. **10. How strong is the relationship between a SENSORY PANEL TEST FOR OIL ON SKIN and the following customer needs?** *
Marca solo un óvalo por fila.

	1	3	5	7	9	N/A
The product does not leave an oily texture						
It does not feel sticky						
It has a soft/light texture						

14. **11. How strong is the relationship between a SENSORY PANEL TEST FOR SPREADABILITY and the following customer needs?** *
Marca solo un óvalo por fila.

	1	3	5	7	9	N/A
The product is easy to dose and spread						
It does not leave an oily texture						
It does not feel sticky						
It has a soft/light texture						

15. **Comments**
Please complete if you have any comment or suggestion

Performance evaluation - clinical tests

*Sensory panel tests description at Pensé-Lhéritier, A.-M. Evaluation des produits cosmétiques: L'objectivation - Chapitre 10 Mesure sensorielle . Lavoisier Tec & Doc, Paris 2016

16. **12. How strong is the relationship between a CLINICAL TEST FOR SKIN APPEARANCE BEFORE AND AFTER PRODUCT APPLICATION and the following customer needs?** *
Marca solo un óvalo por fila.

	1	3	5	7	9	N/A
The product provides an inmediant moisturizing effect						
It is affordable						
It is safe and reliable						

17. **13. How strong is the relationship between a CLINICAL TEST FOR SKIN APPEARANCE BEFORE AND 8H AFTER PRODUCT APPLICATION and the following customer needs?** *
Marca solo un óvalo por fila.

	1	3	5	7	9	N/A
The product provides a prolonged moisturizing effect						
It is affordable						
It is safe and reliable						

18. **14. How strong is the relationship between a CLINICAL TEST FOR ALLERGENES and the following customer needs?** *

Marca solo un óvalo por fila.

	1	3	5	7	9	N/A
It is affordable						
It is safe and reliable						
It is natural						

19. **15. How strong is the relationship between a CLINICAL TEST - TEWL* BEFORE AND IMMEDIATELY AFTER APPLICATION and the following customer needs? (Use of Tewameter®)** *

* TEWL = Transepidermal Water Loss

Marca solo un óvalo por fila.

	1	3	5	7	9	N/A
The product provides an inmediant moisturizing effect						
It is affordable						
It is safe and reliable						

20. **16. How strong is the relationship between a CLINICAL TEST - TEWL BEFORE AND 8H AFTER APPLICATION and the following customer needs? (Use of Tewameter®)** *

* TEWL = Transepidermal Water Loss

Marca solo un óvalo por fila.

	1	3	5	7	9	N/A
The product provides a prolonged moisturizing effect						
It is affordable						
It is safe and reliable						

21. **17. How strong is the relationship between a CLINICAL TEST - SKIN CONDUCTIVITY BEFORE AND AFTER APPLICATION and the following customer needs? (Use of Corneometer®)** *

Marca solo un óvalo por fila.

	1	3	5	7	9	N/A
The product provides an inmediant moisturizing effect						
It is affordable						
It is safe and reliable						

22. **18. How strong is the relationship between a CLINICAL TEST - SKIN CONDUCTIVITY BEFORE AND 8H AFTER APPLICATION and the following customer needs? (Use of Corneometer®)** *

Marca solo un óvalo por fila.

	1	3	5	7	9	N/A
The product provides a prolonged moisturizing effect						
It is affordable						
It is safe and reliable						

23. **Comments**

Please complete if you have any comment or suggestion

Instrumental tests

24. **19. How strong is the relationship between THE RHEOLOGICAL PROFILE and the following customer needs?** *

Marca solo un óvalo por fila.

	1	3	5	7	9	N/A
It is easy to dose and spread						
It is affordable						
It does not leave an oily texture						
It does not feel sticky						
It has a soft/light texture						

25. **20. How strong is the relationship between THE INSTRUMENTAL MEASUREMENT OF OIL ON SKIN AFTER PRODUCT APPLICATION and the following customer needs?** *

Marca solo un óvalo por fila.

	1	3	5	7	9	N/A
It is affordable						
It does not leave an oily texture						
It has a soft/light texture						

26. **21. How strong is the relationship between THE SPREADABILITY TEST IN TEXTUROMETER and the following customer needs?** *

Marca solo un óvalo por fila.

	1	3	5	7	9	N/A
It is easy to dose and spread						
It is affordable						
It does not feel sticky						
It has a soft/light texture						

27. **22. How strong is the relationship between EXTRUSION TEST IN TEXTUROMETER and the following customer needs?** *

Marca solo un óvalo por fila.

	1	3	5	7	9	N/A
It is easy to dose and spread						
It is affordable						
It does not feel sticky						
It has a soft/light texture						

28. **23. How strong is the relationship between PENETRATION TEST IN TEXTUROMETER and the following customer needs?** *
Marca solo un óvalo por fila.

	1	3	5	7	9	N/A
It is easy to dose and spread						
It is affordable						
It does not feel sticky						
It has a soft/light texture						

29. **24. How strong is the relationship between PRODUCT pH and the following customer needs?** *
Marca solo un óvalo por fila.

	1	3	5	7	9	N/A
It provides an inmediant moisturizing effect						
It provides a prolonged moisturizing effect						
It is safe and reliable						
It is natural						

30. **Comments**
Please complete if you have any comment or suggestion

Price

31. **25. How strong is the relationship between a PRODUCT PRICE and the following customer needs?** *
Marca solo un óvalo por fila.

	1	3	5	7	9	N/A
The product provides an inmediant moisturizing effect						
It provides a prolonged moisturizing effect						
It is easy to dose and spread						
It has a pleasant appearance						
It has a pleasant aroma						
It is affordable						
It does not leave an oily texture						
It does not feel sticky						
It has a soft/light texture						
It is natural						

32. **Comments**
Please complete if you have any comment or suggestion

Thank you very much for your time and support.

33. **Do you want a copy of the survey analysis to be sent to your email address?** *
Marca solo un óvalo.
- Yes
- No

Con la tecnología de
Google Forms

Analysis of the information given by experts to translate need into product requirements

Here answers given by customers are analyzed. Table C-1 shows the representativeness of each product specification according to each expert, which was calculated as the average value of the representativeness of the specification in relation to assessed needs.

Table C-1. Representativeness of specifications

Safety and regulation					Sensorial evaluation						Clinical tests							Instrumental tests						Price
SR - PC Stability	SR - Toxicity	SR - Mbiology	SR - allowsubs	SR - irritation	SP - stickiness	SP - appearance	SP - stringiness	SP - fragance	SP - oiliness	SP - spreadability	CT - appearance	CT - appearance8	CT - allergenic	CT - TEWL	CT - TEWL8	CT-corneometer	CT-corneometer8	IT - Rheo	IT - oiliness	IT - spreadbility	IT - extrusion	IT - penetration	IT - pH	Price
4.00	5.00	5.50	5.50	4.00	4.00	5.00	4.00	6.33	5.00	7.00	5.00	8.33	5.00	5.00	3.67	4.33	4.33	5.80	5.00	5.00	6.00	6.50	6.00	5.40
5.50	5.00	8.00	5.00	9.00	5.00	6.75		7.00	6.33	7.00	9.00	9.00	5.00	9.00	9.00	5.00	9.00	6.33	6.00	7.00	6.00	5.00		7.00
8.00	8.50	8.00	6.00	8.00	7.50	6.67	7.50	6.33	7.67	6.00	6.33	6.33	5.00	6.33	6.33	6.33	6.33	6.60	5.00	6.00	6.00	6.00	8.00	4.20
4.50	3.50	5.00	4.50	5.00	5.00	4.50	3.00	2.33	5.00	4.50	3.67	3.67	2.33	2.33	4.33	4.33	4.33	2.20	3.00	2.50	2.50	2.50	3.00	4.20
7.00	5.00	5.50	9.00	5.00	6.50	6.33	6.50	3.67	5.00	5.00	6.33	6.33	3.67	6.33	6.33	6.33	6.33	4.60	5.00	5.50		4.00	7.00	3.22
8.00	6.00	8.00	5.50	9.00	8.00	5.80	7.50	5.00	9.00	9.00	5.67	5.67	7.00	5.67	5.67	6.33	6.33	6.60	7.00	7.50	6.00	6.50	4.50	6.60
7.00	6.50	5.00	5.50	5.00	6.50	5.67	5.50	3.67	7.67	6.00	5.67	7.00	4.33	5.00	6.33	5.00	5.00	6.20	2.33	3.50	3.00	2.00	5.00	7.60
9.00	4.33	4.50	6.00	5.00	6.00	5.67	6.50	5.00	8.33	9.00	5.00	5.00	6.00	9.00	9.00	9.00	9.00	6.00	9.00	7.00	6.33	6.33	5.00	5.67
8.00	7.00	8.00	6.00	9.00	8.00	6.83	8.00	5.67	6.33	8.00	6.33	8.33	8.33	8.33	8.33	5.00	5.00	7.40	7.00	8.50	8.50	7.50	7.50	8.60
7.67	9.00	9.00	9.00	9.00	5.50	7.40	5.00	9.00	6.00	6.33	7.00	6.00	7.00	7.00	7.00	7.00	7.00	7.00	4.00	7.00	5.00	2.33	5.00	7.60
7.00	7.50	8.00	6.50	8.00	8.50	7.33	6.50	6.33	8.33	6.50	5.00	5.67	3.67	6.33	5.00	4.33	4.33	5.80	6.33	5.50	6.00	5.00	4.50	6.80
7.00	6.00	6.00	4.50	7.00	6.50	5.00	6.50	7.00	8.33	7.00	6.33	6.33	7.00	4.33	6.33	5.00	6.33	5.80	7.67	6.00	6.50	6.00	4.50	6.80
6.50	5.50	4.00	5.50	7.00	7.00	3.50		5.67	7.00	6.50	4.33	4.33	5.67	5.00	5.00	3.67	3.67	5.80	5.67	5.50		5.67	5.00	5.40
9.00	9.00	7.00	3.50	9.00	7.50	4.60	7.00	6.33	9.00	7.00	6.33	6.33	4.33	3.67	3.67	3.67	3.67	4.60	6.33	5.00	3.00	3.00	4.50	7.60
6.50	6.50	9.00	4.00	7.00	9.00	9.00	9.00	3.67	7.67	7.50	9.00	9.00	7.00	9.00	9.00	9.00	9.00	9.00	7.00	9.00		7.00	9.00	7.20
6.00	3.00	8.00	5.00	9.00	5.00	6.67	7.00	6.33	7.00	8.50	6.33	6.33	9.00	9.00	6.33	6.33	5.00	7.00	3.00	5.50	3.67	1.00	7.00	7.40
7.00	7.00	9.00	9.00	9.00	5.00	8.20	6.50	8.00	7.00	7.00	7.67	7.67	9.00	7.00	7.00	5.00	5.00	3.80	5.67	6.50	6.50	5.00	6.33	3.60
3.50	5.50	4.50	3.67	7.00	8.00	7.17	5.50	6.33	6.33	5.50	5.67	5.00	5.00	4.33	4.33	3.67	3.67	4.60	3.67	4.50	4.50	5.00	4.00	7.40
8.00	8.00	5.00	7.50	9.00	8.00	8.33	5.00	7.00	9.00	9.00	7.00	4.33	5.00	7.00	8.33	5.00	5.00	8.20	5.00	5.00	5.00	5.00	6.50	5.00
9.00	8.00	8.00	9.00	9.00	9.00	7.00	6.00	7.00	9.00	7.50	6.33	8.33	6.33	7.67	7.67	7.67	7.67	8.33	5.00	7.50	7.50	7.50	9.00	9.00

The representativeness of each group of specifications is calculated as the average of its components (which are presented in Table C-1)

Table C-2. Representativeness of groups of specifications

Expert	Level of expertise	Safety	Sensorial t.	Clinical t.	Instrumental t.	Price
1.00	1.00	4.80	5.22	5.10	5.72	5.40
2.00	1.00	6.50	6.42	7.86	6.07	7.00
3.00	4.00	7.70	6.94	6.14	6.27	4.20
4.00	8.00	4.50	4.06	3.57	2.62	4.20
5.00	8.00	6.30	5.50	5.95	5.22	3.22
6.00	4.00	7.30	7.38	6.05	6.35	6.60
7.00	4.00	5.80	5.83	5.48	3.67	7.60
8.00	2.00	5.77	6.75	7.43	6.61	5.67
9.00	8.00	7.60	7.14	7.10	7.73	8.60
10.00	2.00	8.73	6.54	6.86	5.06	7.60
11.00	8.00	7.40	7.25	4.90	5.52	6.80
12.00	4.00	6.10	6.72	5.95	6.08	6.80
13.00	1.00	5.70	5.93	4.52	5.53	5.40
14.00	2.00	7.50	6.91	4.52	4.41	7.60
15.00	8.00	6.60	7.64	8.71	8.20	7.20
16.00	8.00	6.20	6.75	6.90	4.53	7.40
17.00	2.00	8.20	6.95	6.90	5.63	3.60
18.00	1.00	4.83	6.47	4.52	4.38	7.40
19.00	8.00	7.50	7.72	5.95	5.78	5.00
20.00	4.00	8.60	7.58	7.38	7.47	9.00

Using the data in Table C-2 a PCA analysis is performed. Results are presented in Table C-3, C-4 and Figure C1. In addition PCA analysis to the sub-groups within the groups of specifications are also performed. This PCA analysis are shown in Figures C2 to C5

Table C-3 Results of the PCA for groups of specifications - Principal components correlation summary

PC	Eigenvalue	% variance
1	3.00	49.9
2	1.04	17.4
3	0.80	13.4
4	0.67	11.1
5	0.32	5.29
6	0.17	2.87

Table C-4. Results of the PCA for groups of specifications - Principal components correlation of specifications with principal components

	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6
Level of expertise	0.069855	0.88986	0.43764	0.097027	0.010646	0.047064
Safety	0.43481	0.047215	-0.049182	-0.74227	0.34172	0.37222
Sensorial t.	0.51748	-0.011534	0.078674	-0.25417	-0.49422	-0.64578
Clinical t.	0.46972	0.062248	-0.27872	0.43242	0.63982	-0.31852
Instrumental t.	0.48659	0.043608	-0.29849	0.37485	-0.46537	0.56138
Price	0.28437	-0.44723	0.79566	0.21798	0.11368	0.16

Graphic results of PCA

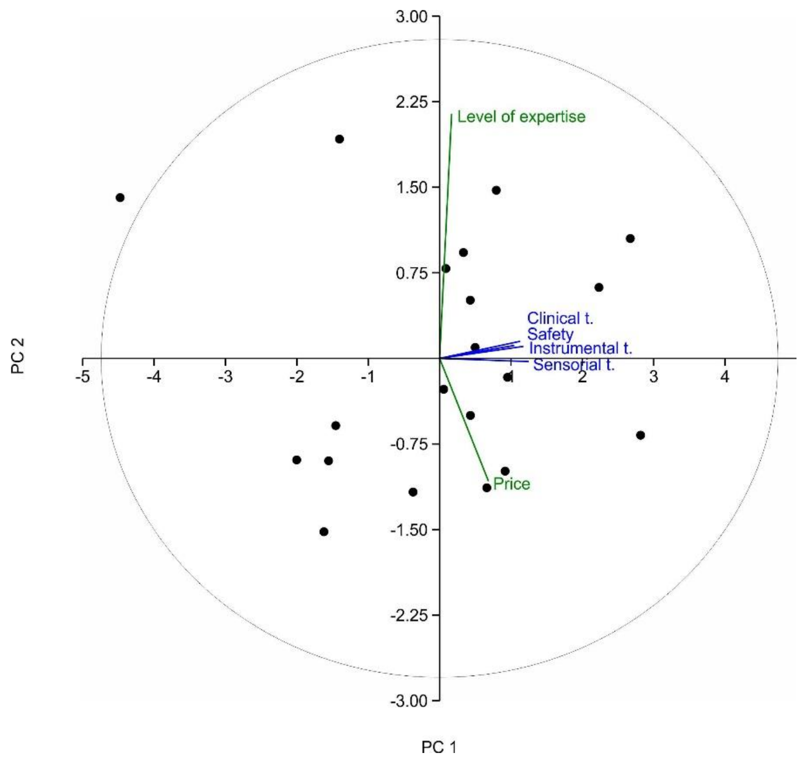

Figure C1- PCA by groups of specifications

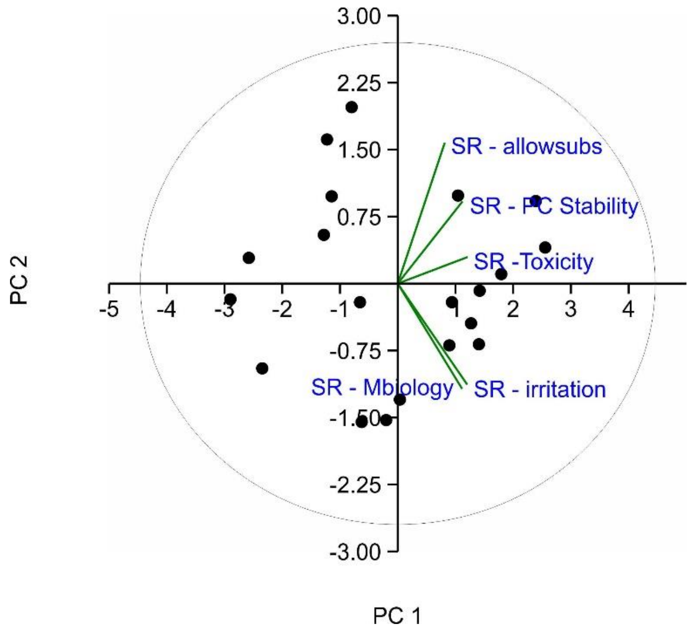

Figure C2 PCA of specifications grouped in Safety and Regulation

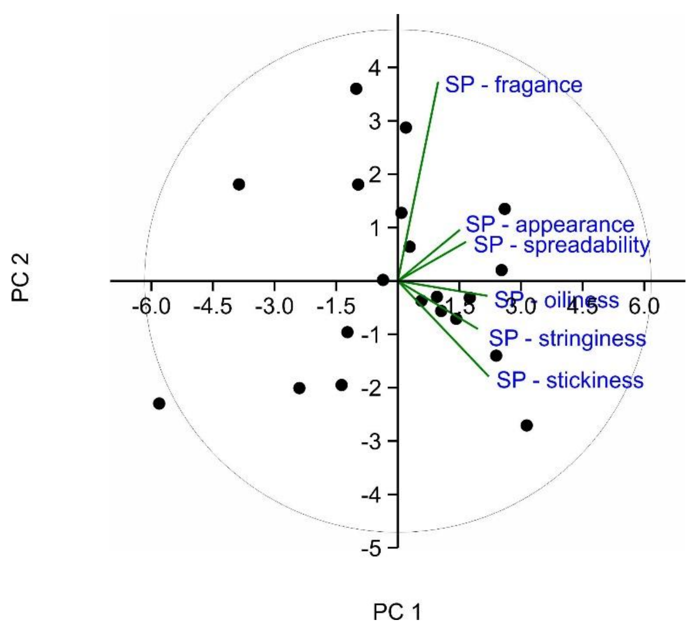

Figure C3 PCA of specifications grouped in Sensorial evaluation

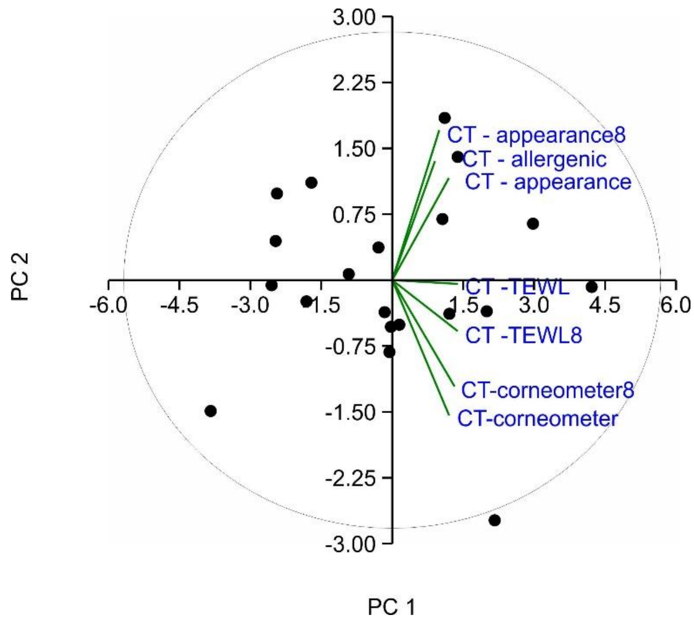

Figure C4 PCA of specifications grouped in Performance evaluation

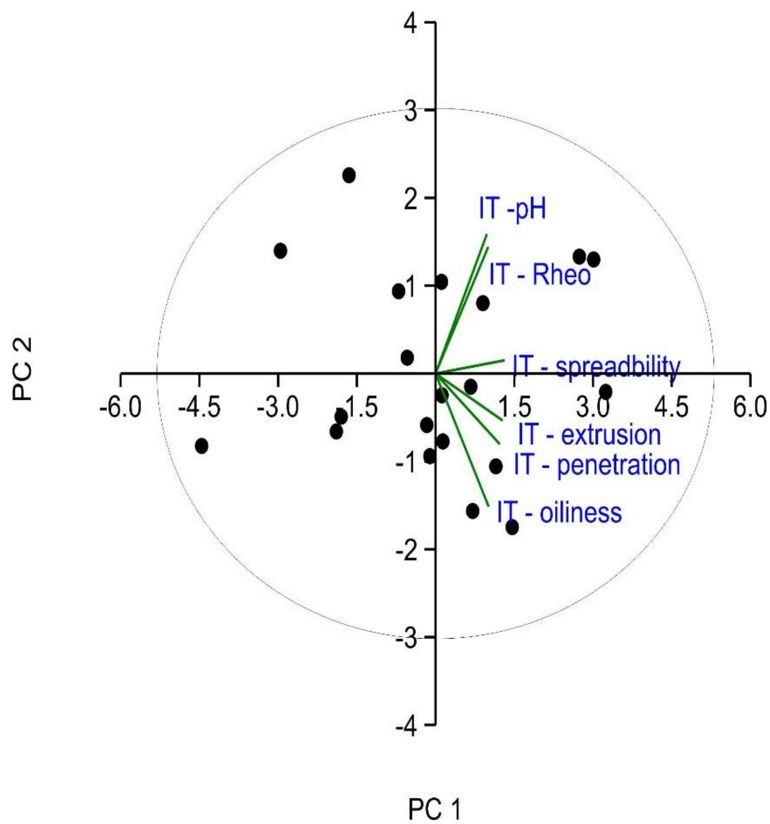

Figure C5: PCA of specifications grouped in Instrumental test

D. Customer interview with product samples

User preferences in relation to product samples

The design team formed by the Engineer Juliana Serna and the company Xiu Aague is working in the creation of a new cosmetic product: a facial moisturizer using the powerful action of the calendula. In this opportunity we want to ask you to answer the following questionnaire in order to know what their preferences are and what sensations generate some characteristics that we want include in our product.

This project is carried out within the framework of the doctoral thesis of the Engineer Juliana Serna that is being developed in co-supervision at the National University of Colombia and the Université de Lorraine in France.

Additionally, the project has the collaboration of Xiu Aague, a cosmetic company Colombian, dedicated to the production of essential oils and hydrosols of high quality and 100% natural

Texture test

You have 6 samples of creams to evaluate according to their texture and appearance.

To fill the questionnaire take into account the following instructions:

1) Before touching each sample, observe it.

2) Take a little of the sample, apply it on a clean section of your hand or arm and rub it gently

3) Wait 5 minutes and answer the following questions.

By observing the cream, you think that it is

Very light
Light
Between light and thick
Thick
Very thick

By applying the cream you think that it is

Very easy to spread (very fluid)
easy to spread (fluid)
between easy and slow to spread
spreads slowly (thick during the application)
spreads very slowly (very thick during application)

The cream leaves a feeling

Very fresh
Fresh
Between fresh and not fresh
Not fresh
Nothing fresh

The cream leaves a feeling

Of much vitality
Of vitality
Between vitality and not vitality
Of Not vitality
Of Nothing vitality

The cream absorbs

very fast
fast
intermediate between fast and slow
slow
very slow

The cream feels

Very oily
Oily
Intermediate between oily and not oily
Not oily
Nothing oily

Aroma test

You will evaluate 6 samples according to their aroma. Smell each sample and answer the questions

The sample has an aroma:

very soft
soft
between soft and intense
intense
very intense

The aroma of the sample gives a sensation

Very fresh
Fresh

Between fresh and not fresh
Not fresh
Nothing fresh

The aroma of the sample gives a sensation

Of much vitality
Of vitality
Between vitality and not vitality
Of Not vitality
Of Nothing vitality

Thank you for your collaboration!

E. Statistical test for customer assessment and instrumental measurements

Statistical tests for consumer assessment and instrumental measurements samples

1. Statistics of customer assessment

Light texture [1] -thick texture [0]

Descriptive statistic						
	N	Min	Max	Percentiles		
				25	50 (Median)	75
Sample1	55	0	1	0.75	0.75	0.75
Sample2	57	0	1	0.25	0.5	0.75
Sample3	56	0	1	0.25	0.375	0.5
Sample4	57	0	1	0.25	0.5	0.625
Sample5	58	0	1	0.25	0.25	0.5
Sample6	58	0	1	0	0.25	0.5

There was a statistically significant difference in perceived sensation of lightness in the tested samples, $\chi^2(2) = 75.036$, p = 0.000

Friedman test	
N	51
Chi-cuadrado	75.036
gl	5
Sig. asintótica	9.14466E-15

The post-hoc of the samples is done with Wilcoxon signed-rank tests with a Bonferroni correction, resulting a significant level at p <0.0033. Table report the comparison between samples. The pairs with stadistical difference are colored in gray.

		Post-hoc test - Wilcoxon signed-rank tests				
		Sample1	Sample2	Sample3	Sample4	Sample5
Sample2	Z	**3.24E-05**				
	Sig.	**-4,156[b]**				
Sample3	Z	**1.30E-08**	**7.73E-04**			
	Sig.	**-5,686[b]**	**-3,362[b]**			
Sample4	Z	**7.15E-08**	2.51E-01	2.61E-02		
	Sig.	**-5,387[b]**	-1,147[b]	-2,225[c]		
Sample5	Z	**1.60E-08**	**1.53E-04**	7.10E-01	**1.67E-03**	
	Sig.	**-5,651[b]**	**-3,787[b]**	-,372[b]	**-3,143[b]**	
Sample6	Z	**3.05E-08**	**4.95E-05**	1.07E-01	**7.50E-04**	1.28E-01
	Sig.	**-5,539[b]**	**-4,058[b]**	-1,613[b]	**-3,371[b]**	-1,522[b]

at p<0.05 (with Bonferroni correction, it corresponds to a significant level at p <0.0033)

a. Wilcoxon Signed Rank test

b. Based on positive ranks

The grey shadow show the pairs with a significant difference at p<0.05

Spreads easily (1) - Spreads slowly (0)

Descriptive statistic						
	N	Min	Max	Percentiles		
				25	50 (Median)	75
Sample1	58	0.25	1	0.75	0.75	1
Sample2	58	0	1	0.5	0.75	0.8125
Sample3	58	0	0.75	0.25	0.25	0.5625
Sample4	58	0	1	0.25	0.5	0.75
Sample5	58	0	1	0.25	0.5	0.75
Sample6	58	0	1	0.1875	0.5	0.75

There was a statistically significant difference in perceived spreadability in the tested samples, $\chi2(2) = 88.351$, $p = 0.000$

Friedman test	
N	58
Chi-cuadrado	88.351
gl	5
Sig. asintótica	1.4913E-17

The post-hoc of the samples is done with Wilcoxon signed-rank tests with a Bonferroni correction, resulting a significant level at p <0.0033. Table report the comparison between samples. The pairs with stadistical difference are colored in gray.

	Post-hoc test - Wilcoxon signed-rank tests					
		Sample1	Sample2	Sample3	Sample4	Sample5
Sample2	Z	-2,305[b]				
	Sig.	0.02119079				
Sample3	Z	-6,194[b]	-5,389[b]			
	Sig.	5.8696E-10	7.10282E-08			
Sample4	Z	-4,491[b]	-2,941[b]	-3,596[c]		
	Sig.	7.0865E-06	0.003273426	0.000323605		
Sample5	Z	-4,949[b]	-3,865[b]	-1,270[c]	-2,650[b]	
	Sig.	7.4506E-07	0.000111288	0.203917204	0.008060732	
Sample6	Z	-4,797[b]	-3,865[b]	-1,492[c]	-1,383[b]	-,491[c]
	Sig.	1.6113E-06	0.00011106	0.135747439	0.166532454	0.623585511

at p<0.05 (with Bonferroni correction, it corresponds to a significant level at p <0.0033)
a. Wilcoxon Signed Rank test
b. Based on positive ranks
c. Based on negative ranks
The grey shadow show the pairs with a significant difference at p<0.05

Fresh (1)- not fresh at all(0)

Descriptive statistic						
	N	Min	Max	Percentiles		
				25	50 (Median)	75
Sample1	55	0.00	1.00	0.5000	0.7500	0.7500
Sample2	55	0.00	1.00	0.5000	0.7500	0.7500
Sample3	55	0.00	1.00	0.2500	0.5000	0.7500
Sample4	55	0.00	1.00	0.5000	0.7500	0.7500
Sample5	55	0.00	1.00	0.2500	0.5000	0.7500
Sample6	55	0.00	1.00	0.2500	0.7500	0.7500

There was a statistically significant difference in perceived fresh feeling in the tested samples, $\chi2(2) = 30.71$, $p = 0.000$

Friedman test	
N	55
Chi-cuadrado	30.711
gl	5
Sig. asintótica	0.000

The post-hoc of the samples is done with Wilcoxon signed-rank tests with a Bonferroni correction, resulting a significant level at p <0.0033. Table report the comparison between samples. The pairs with stadistical difference are colored in gray.

		Post-hoc test - Wilcoxon signed-rank tests				
		Sample1	Sample2	Sample3	Sample4	Sample5
Sample2	Z	-,299b				
	Sig.	0.765				
Sample3	Z	-3,387b	-3,627b			
	Sig.	0.001	0.000			
Sample4	Z	-2,279b	-1,952b	-2,030c		
	Sig.	0.023	0.051	0.042		
Sample5	Z	-3,038b	-3,276b	-,414c	-1,554b	
	Sig.	0.002	0.001	0.679	0.120	
Sample6	Z	-1,860b	-1,569b	-1,853c	-,163c	-1,694c
	Sig.	0.063	0.117	0.064	0.870	0.090

at p<0.05 (with Bonferroni correction, it corresponds to a significant level at p <0.0033)
a. Wilcoxon Signed Rank test
b. Based on positive ranks
c. Based on negative ranks
The grey shadow show the pairs with a significant difference at p<0.05

Feeling of vitality (1) - not feeling at all (0)

Descriptive statistic						
	N	Min	Max	Percentiles		
				25	50 (Median)	75
Sample1	53	0.25	1.00	0.5000	0.7500	0.7500
Sample2	53	0.25	1.00	0.5000	0.7500	0.7500
Sample3	53	0.25	1.00	0.5000	0.5000	0.7500
Sample4	53	0.25	1.00	0.5000	0.5000	0.7500
Sample5	53	0.00	1.00	0.5000	0.5000	0.7500
Sample6	53	0.00	1.00	0.5000	0.5000	0.7500

There was a statistically significant difference in perceived feeling of vitality in the tested samples, $\chi2(2) = 15.71$, $p = 0.008$

Friedman test	
N	53
Chi-cuadrado	15.706
gl	5
Sig. asintótica	0.008

The post-hoc of the samples is done with Wilcoxon signed-rank tests with a Bonferroni correction, resulting a significant level at p <0.0033. Table report the comparison between samples. The pairs with stadistical difference are colored in gray.

		Post-hoc test - Wilcoxon signed-rank tests				
		Sample1	Sample2	Sample3	Sample4	Sample5
Sample2	Z	-,742[b]				
	Sig.	0.458				
Sample3	Z	-2,110[c]	-2,722[c]			
	Sig.	0.035	0.006			
Sample4	Z	-,541[c]	-1,409[c]	-1,876[b]		
	Sig.	0.589	0.159	0.061		
Sample5	Z	-1,759[c]	-2,824[c]	-,464[b]	-1,776[c]	
	Sig.	0.079	0.005	0.643	0.076	
Sample6	Z	-1,638[c]	-2,450[c]	-,429[b]	-2,057[c]	-,296[b]
	Sig.	0.101	0.014	0.668	0.040	0.768

at p<0.05 (with Bonferroni correction, it corresponds to a significant level at p <0.0033)
a. Wilcoxon Signed Rank test

b. Based on positive ranks
c. Based on negative ranks
The grey shadow show the pairs with a significant difference at p<0.05

Rapid absorption (1) - slow absorption (0)

Descriptive statistic						
	N	Min	Max	Percentiles		
				25	50 (Median)	75
Sample1	55	0.00	1.00	0.2500	0.5000	0.7500
Sample2	55	0.00	1.00	0.5000	0.7500	0.7500
Sample3	55	0.00	1.00	0.2500	0.2500	0.5000
Sample4	55	0.00	1.00	0.2500	0.5000	0.7500
Sample5	55	0.00	1.00	0.2500	0.5000	0.5000
Sample6	55	0.00	1.00	0.2500	0.5000	0.7500

There was a statistically significant difference in perceived feeling of absorption in the tested samples, $\chi2(2) = 17.7$, $p = 0.003$

Friedman test	
N	55
Chi-cuadrado	17.666
gl	5
Sig. asintótica	0.003

The post-hoc of the samples is done with Wilcoxon signed-rank tests with a Bonferroni correction, resulting a significant level at p <0.0033. Table report the comparison between samples. The pairs with stadistical difference are colored in gray.

		Post-hoc test - Wilcoxon signed-rank tests				
		Sample1	Sample2	Sample3	Sample4	Sample5
Sample2	Z	$-1,348^{b}$				
	Sig.	0.178				
Sample3	Z	$-2,597^{c}$	$-3,910^{c}$			
	Sig.	0.009	0.000			
Sample4	Z	$-,082^{b}$	$-1,597^{c}$	$-3,049^{b}$		
	Sig.	0.934	0.110	0.002		
Sample5	Z	$-1,448^{c}$	$-2,861^{c}$	$-1,842^{b}$	$-1,916^{c}$	
	Sig.	0.148	0.004	0.065	0.055	
Sample6	Z	$-,238^{c}$	$-1,466^{c}$	$-2,555^{b}$	$-,215^{c}$	$-1,469^{b}$
	Sig.	0.812	0.143	0.011	0.830	0.142

at p<0.05 (with Bonferroni correction, it corresponds to a significant level at p <0.0033)
a. Wilcoxon Signed Rank test
b. Based on positive ranks
c. Based on negative ranks

The grey shadow show the pairs with a significant difference at $p<0.05$

Oiliness (1)

Descriptive statistic						
	N	Min	Max	Percentiles		
				25	50 (Median)	75
Sample1	56	0.5313	0.34398	0.00	1.00	0.2500
Sample2	56	0.5179	0.30472	0.00	1.00	0.2500
Sample3	56	0.5714	0.29663	0.00	1.00	0.3125
Sample4	56	0.5982	0.27666	0.00	1.00	0.5000
Sample5	56	0.5982	0.24624	0.00	1.00	0.5000
Sample6	56	0.4821	0.34986	0.00	1.00	0.2500

There was not a statistically significant difference in perceived oiliness in tested samples, $\chi 2(2) = 8.556$, $p = 0.128$

Friedman test	
N	56
Chi-cuadrado	8.556
gl	5
Sig. asintótica	0.128

Intense aroma (1) - soft aroma (0)

Descriptive statistic						
	N	Min	Max	Percentiles		
				25	50 (Median)	75
Sample1	58	0.00	1.00	0.5000	0.7500	1.0000
Sample2	58	0.00	1.00	0.5000	0.6250	0.7500
Sample3	58	0.00	1.00	0.2500	0.3750	0.5625
Sample4	58	0.00	1.00	0.5000	0.7500	0.7500
Sample5	58	0.00	1.00	0.2500	0.5000	0.7500
Sample6	58	0.00	1.00	0.2500	0.5000	0.7500

There was a statistically significant difference in perceived aroma intensity in the tested samples, $\chi 2(2) = 49.51$, $p = 0.000$

Friedman test	
N	58
Chi-cuadrado	49.508
gl	5
Sig. asintótica	0.000

The post-hoc of the samples is done with Wilcoxon signed-rank tests with a Bonferroni correction, resulting a significant level at $p < 0.0033$. Table report the comparison between samples. The pairs with stadistical difference are colored in gray.

		Post-hoc test - Wilcoxon signed-rank tests				
		Sample1	Sample2	Sample3	Sample4	Sample5
Sample2	Z	-3,256b				
	Sig.	0.001				
Sample3	Z	-5,518b	-4,332b			
	Sig.	0.000	0.000			
Sample4	Z	-1,349b	-1,536c	-4,550c		
	Sig.	0.177	0.124	0.000		
Sample5	Z	-3,355b	-,737b	-2,895c	-2,455b	
	Sig.	0.001	0.461	0.004	0.014	
Sample6	Z	-3,561b	-1,396b	-1,661c	-3,992b	-1,052b
	Sig.	0.000	0.163	0.097	0.000	0.293

at p<0.05 (with Bonferroni correction, it corresponds to a significant level at p <0.0033)
a. Wilcoxon Signed Rank test
b. Based on positive ranks

c. Based on negative ranks
The grey shadow show the pairs with a significant difference at p<0.05

Fresh aroma (1)

Descriptive statistic						
	N	Min	Max	Percentiles		
				25	50 (Median)	75
Sample1	58	0.00	1.00	0.2500	0.5000	0.7500
Sample2	58	0.00	1.00	0.2500	0.5000	0.7500
Sample3	58	0.00	1.00	0.2500	0.5000	0.7500
Sample4	58	0.00	1.00	0.7500	0.7500	1.0000
Sample5	58	0.00	1.00	0.2500	0.5000	0.7500
Sample6	58	0.00	1.00	0.7500	0.7500	1.0000

There was a statistically significant difference in perceived fresh aroma in the tested samples, $\chi 2(2) = 90.11$, $p = 0.000$

Friedman test	
N	58
Chi-cuadrado	90.110
gl	5
Sig. asintótica	0.000

The post-hoc of the samples is done with Wilcoxon signed-rank tests with a Bonferroni correction, resulting a significant level at p <0.0033. Table report the comparison between samples. The pairs with stadistical difference are colored in gray.

	Post-hoc test - Wilcoxon signed-rank tests					
		Sample1	Sample2	Sample3	Sample4	Sample5
Sample2	Z	-,759b				
	Sig.	0.448				
Sample3	Z	-1,132b	-,613b			
	Sig.	0.258	0.540			
Sample4	Z	-4,772b	-5,310b	-4,960b		
	Sig.	0.000	0.000	0.000		
Sample5	Z	-1,596b	-,765b	-,865b	-4,470c	
	Sig.	0.110	0.444	0.387	0.000	
Sample6	Z	-4,622b	-4,941b	-4,648b	-,429c	-4,852b
	Sig.	0.000	0.000	0.000	0.668	0.000

at p<0.05 (with Bonferroni correction, it corresponds to a significant level at p <0.0033)

a. Wilcoxon Signed Rank test
b. Based on positive ranks
c. Based on negative ranks
The grey shadow show the pairs with a significant difference at p<0.05

Feeling of vitality (1)

Descriptive statistic						
	N	Min	Max	Percentiles		
				25	50 (Median)	75
Sample1	58	0.00	1.00	0.2500	0.5000	0.7500
Sample2	58	0.00	1.00	0.2500	0.5000	0.5625
Sample3	58	0.00	0.75	0.2500	0.5000	0.7500
Sample4	58	0.00	1.00	0.5000	0.7500	1.0000
Sample5	58	0.00	1.00	0.5000	0.5000	0.7500
Sample6	58	0.00	1.00	0.5000	0.7500	0.7500

There was a statistically significant difference in perceived feeling of vitality in the tested samples, $\chi2(2) = 90.11$, $p = 0.000$

Friedman test	
N	58
Chi-cuadrado	81.270
gl	5
Sig. asintótica	0.000

The post-hoc of the samples is done with Wilcoxon signed-rank tests with a Bonferroni correction, resulting a significant level at p <0.0033. Table report the comparison between samples. The pairs with statistical difference are colored in gray.

		Post-hoc test - Wilcoxon signed-rank tests				
		Sample1	Sample2	Sample3	Sample4	Sample5
Sample2	Z	-,426b				
	Sig.	0.670				
Sample3	Z	-1,708c	-2,490c			
	Sig.	0.088	0.013			
Sample4	Z	-4,785c	-4,676c	-4,273c		
	Sig.	0.000	0.000	0.000		
Sample5	Z	-2,445c	-2,486c	-,987c	-3,857b	
	Sig.	0.014	0.013	0.324	0.000	
Sample6	Z	-4,669c	-4,767c	-4,400c	-,159b	-4,066c
	Sig.	0.000	0.000	0.000	0.874	0.000

at p<0.05 (with Bonferroni correction, it corresponds to a significant level at p <0.0033)
a. Wilcoxon Signed Rank test
b. Based on positive ranks

c. Based on negative ranks
The grey shadow show the pairs with a significant difference at p<0.05

2. Statistics of instrumental assessments

Instrumental assessment of samples T1-T6

Sample	Penetration_work*		Maximal_force*		Spreadability	
	mean [mJ]	Error	mean [mJ]	Error	mean [mm]	Std
T1	0.5	+ 0.1 - 0.1 [a]	7.7	+ 0.6 - 0.6 [a]	72.4	± 1.3 [a]
T2	1.1	+ 0.2 - 0.2 [b]	13.1	+ 1.1 - 1.0 [b]	59.8	± 0.8 [b]
T3	1.4	+ 0.0 - 0.0 [b]	13.2	+ 0.3 - 0.3 [b]	85.3	± 4.1 [b]
T4	2.2	+ 0.0 - 0.0 [c]	24.2	+ 0.3 - 0.3 [c]	62.7	± 1.9 [c]
T5	3.7	+ 0.1 - 0.1 [d]	38.5	+ 0.9 - 0.9 [d]	56.3	± 1.7 [d]
T6	5.7	+ 0.7 - 0.7 [e]	64.5	+ 8.2 - 7.3 [e]	56.3	± 2.0 [e]

Sample	η (0.1)*		η (1)		η (11)		η (113)		η (356)		η (895)*	
	mean [Pas]	Error	mean [Pas]	Std	mean [Pas]	Std	mean [Pas]	Std	mean [Pas]	Std	mean[Pas]	Error
T1	128.7	+ 1.9 - 1.9 [a]	19.7	± 0.1 [a]	3.8	± 0.0 [a]	1.00	± 0.01 [a]	0.56	± 0.00 [a]	0.36	+ 0.00 - 0.00 [a]
T2	214.5	+ 30.1 - 28.1 [a]	68.9	± 8.9 [b]	10.8	± 0.6 [b]	2.74	± 0.15 [b,c]	1.30	± 0.02 [b]	0.72	+ 0.02 - 0.02 [b]
T3	180.2	+ 11.8 - 11.4 [a]	30.8	± 2.7 [a]	7.2	± 0.3 [c]	1.64	± 0.08 [d]	0.68	± 0.03 [a]	0.32	+ 0.01 - 0.01 [a]
T4	868.5	+ 239.0 - 210.0 [b]	129.7	± 2.8 [c]	16.8	± 0.9 [d]	2.89	± 0.26 [b,c]	1.38	± 0.12 [b]	0.75	+ 0.07 - 0.07 [b]
T5	570.3	+ 45.6 - 43.9 [b]	97.3	± 11.3 [d]	17.8	± 0.4 [d]	2.35	± 0.04 [c]	1.01	± 0.02 [c]	0.56	+ 0.01 - 0.01 [c]
T6	626.3	+ 159.5 - 141.4 [b]	134.0	± 1.4 [c]	35.1	± 1.6 [e]	3.40	± 0.24 [e]	1.24	± 0.09 [b]	0.57	+ 0.02 - 0.02 [c]

Sample	σ (0.1)*		σ (1)		σ (11)		σ (113)		σ (356)		σ (895)[Pa]*	
	mean [Pa]	Error	mean [Pa]		mean [Pa]		mean [Pa]		mean [Pa]		mean	Error
T1	14.3	+ 0.2 - 0.2 [a]	21.9	± 0.1 [a]	42.2	± 0.4 [a]	111.57	± 0.86 [a]	197.40	± 1.25 [a]	320.49	+ 3.36 - 3.34 [a]
T2	23.9	+ 3.4 - 3.1 [a]	76.7	± 9.9 [b]	120.8	± 6.2 [b]	305.17	± 16.78 [b,d]	457.40	± 7.02 [b]	640.91	+ 15.04 - 14.87 [b]
T3	20.1	+ 1.3 - 1.3 [a]	34.3	± 3.0 [a]	80.6	± 3.3 [c]	182.50	± 9.10 [c]	237.97	± 12.01 [a]	284.70	+ 10.50 - 10.31 [a]
T4	96.8	+ 26.7 - 23.4 [b]	144.5	± 3.2 [c]	187.1	± 9.8 [d]	321.83	± 28.92 [b]	485.33	± 43.79 [b]	662.52	+ 60.49 - 57.84 [b]
T5	63.3	+ 4.9 - 4.7 [c]	108.4	± 12.6 [d]	198.1	± 4.2 [d]	261.57	± 4.80 [d]	356.80	± 6.42 [c]	496.01	+ 8.10 - 8.04 [c]
T6	66.2	+ 9.9 - 9.2 [c]	149.3	± 1.6 [c]	391.4	± 17.5 [e]	378.20	± 26.39 [e]	437.10	± 30.49 [b]	501.63	+ 20.21 - 19.81 [c]

Sample	Elastic modulus(G')**		Viscous modulus (G'')**		Critial strain (γcr)**	
	Mean	Error (+/-)	Mean	Error (+/-)	Mean	Error (+/-)
T1	192.5	9.2	45.9	1.7	4.7	0.2
T2	627.7	4.1	97.2	1.4	1.9	0.0
T3	5259.5	609	4692	555	25.9	0.4
T4	2617.5	102	412.0	75	62.1	0.2
T5	6789.0	116	1843	10	60.4	1.5
T6	10770.0	60	2902	12	100.8	0.5

* Anova were applied to square root transformed data
** Samples were measured by duplicate

Penetration work

Data were square-root transformed to meet a normal distribution. The results are presented below:

Descriptive statistics

```
  Sample count  mean      sd
  <ord>  <int> <dbl>   <dbl>
1 1         3 0.731 0.0496
2 2         3 1.05  0.0912
3 3         3 1.20  0.00637
4 4         3 1.50  0.0107
5 5         3 1.92  0.0319
6 6         3 2.38  0.142
```

Anova results

```
           Df Sum Sq Mean Sq F value   Pr(>F)
Sample       5  5.505  1.1010     206 3.37e-11 ***
Residuals   12  0.064  0.0053
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

Result: There is a statistically significant difference between samples as determined by one-way ANOVA (F = 206, p = 3.37e-11)

Assumptions

1. Normality

```
        Shapiro-Wilk normality test

data:  aov_residuals
W = 0.9205, p-value = 0.1319
```

Result: The hypothesis of normallity is acepted because p>0.05

2. Homogeneity of Variance

```
Levene's Test for Homogeneity of Variance (center = median)
      Df F value Pr(>F)
group  5  1.1017 0.4089
12
```

Result: The hypothesis of homogeneity of variance is accepted because p > 0.05

Tukey multiple comparisons of means

```
    95% family-wise confidence level
$`Sample`
         diff         lwr       upr     p adj
2-1 0.3147055  0.11422777 0.5151832 0.0020915
3-1 0.4657530  0.26527533 0.6662307 0.0000555
4-1 0.7662959  0.56581823 0.9667737 0.0000003
5-1 1.1840922  0.98361453 1.3845700 0.0000000
6-1 1.6532045  1.45272684 1.8536823 0.0000000
3-2 0.1510476 -0.04943016 0.3515253 0.1895345
4-2 0.4515905  0.25111275 0.6520682 0.0000756
5-2 0.8693868  0.66890905 1.0698645 0.0000001
6-2 1.3384991  1.13802136 1.5389768 0.0000000
4-3 0.3005429  0.10006520 0.5010206 0.0030553
5-3 0.7183392  0.51786150 0.9188169 0.0000006
6-3 1.1874515  0.98697380 1.3879292 0.0000000
```

```
5-4 0.4177963  0.21731859 0.6182740 0.0001619
6-4 0.8869086  0.68643090 1.0873863 0.0000001
6-5 0.4691123  0.26863460 0.6695900 0.0000517
```

Result: For the pairs where p-value is less than the significance level 0.05, it is possible to concluded that there are significant differences

Maximal force

Data were log transformed to meet a normal distribution. The results are presented below:

Descriptive statistics

```
  Sample count  mean      sd
  <ord>  <int> <dbl>   <dbl>
1 1         3 0.884 0.0335
2 2         3 1.12  0.0350
3 3         3 1.12  0.00946
4 4         3 1.38  0.00517
5 5         3 1.59  0.00983
6 6         3 1.81  0.0518
```

Anova results

```
            Df Sum Sq Mean Sq F value  Pr(>F)
Sample       5 1.7558  0.3512   401.6 6.4e-13 ***
Residuals   12 0.0105  0.0009
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
```

Result: There is a statistically significant difference between samples as determined by one-way ANOVA (F = 401.6, p = 6.3e-13)

Assumptions

1. Normality

```
        Shapiro-Wilk normality test

data:  aov_residuals
W = 0.94913, p-value = 0.4116
```

Result: The hypothesis of normallity is acepted because p>0.05

2. Homogeneity of Variance

```
Levene's Test for Homogeneity of Variance (center = median)
      Df F value Pr(>F)
group  5   0.586 0.7109
12
```

Result: The hypothesis of homogeneity of variance is accepted because p > 0.05

```
Tukey multiple comparisons of means
    95% family-wise confidence level

$`Sample`
            diff         lwr        upr    p adj
2-1 0.2347883453  0.15368934 0.31588735 5.70e-06
3-1 0.2356474860  0.15454848 0.31674649 5.50e-06
4-1 0.4994368513  0.41833785 0.58053585 0.00e+00
5-1 0.7016274893  0.62052849 0.78272649 0.00e+00
6-1 0.9259335023  0.84483450 1.00703250 0.00e+00
3-2 0.0008591407 -0.08023986 0.08195814 1.00e+00
4-2 0.2646485060  0.18354950 0.34574751 1.60e-06
5-2 0.4668391440  0.38574014 0.54793815 0.00e+00
6-2 0.6911451570  0.61004616 0.77224416 0.00e+00
4-3 0.2637893653  0.18269036 0.34488837 1.60e-06
5-3 0.4659800033  0.38488100 0.54707901 0.00e+00
6-3 0.6902860163  0.60918701 0.77138502 0.00e+00
```

```
5-4 0.2021906380  0.12109164 0.28328964 2.71e-05
6-4 0.4264966510  0.34539765 0.50759565 0.00e+00
6-5 0.2243060130  0.14320701 0.30540501 9.20e-06
```

Result: For the pairs where p-value is less than the significance level 0.05, it is possible to concluded that there are significant differences

Spreadability

Descriptive statistics

```
  Sample count  mean    sd
  <ord>  <int> <dbl> <dbl>
1 1         4  72.4 1.28
2 2         4  59.8 0.849
3 3         4  85.3 4.06
4 4         3  62.7 1.94
5 5         4  56.2 1.72
6 6         4  56.4 2.05
```

Anova results

```
            Df Sum Sq Mean Sq F value   Pr(>F)
Sample       5 2591.2   518.2     103 4.27e-12 ***
Residuals   17   85.6     5.0
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
```

Result: There is a statistically significant difference between samples as determined by one-way ANOVA (F = 103, p = 4.27e-12)

Assumptions

1. Normality

```
        Shapiro-Wilk normality test

data:  aov_residuals
W = 0.93835, p-value = 0.1656
```

Result: The hypothesis of normallity is acepted because p>0.05

2. Homogeneity of Variance

```
Levene's Test for Homogeneity of Variance (center = median)
      Df F value Pr(>F)
group  5  1.2112 0.3459
17
```

Result: The hypothesis of homogeneity of variance is accepted because p > 0.05

```
Tukey multiple comparisons of means
    95% family-wise confidence level

$`Sample`
            diff         lwr        upr    p adj
2-1 0.2347883453  0.15368934 0.31588735 5.70e-06
3-1 0.2356474860  0.15454848 0.31674649 5.50e-06
4-1 0.4994368513  0.41833785 0.58053585 0.00e+00
5-1 0.7016274893  0.62052849 0.78272649 0.00e+00
6-1 0.9259335023  0.84483450 1.00703250 0.00e+00
3-2 0.0008591407 -0.08023986 0.08195814 1.00e+00
4-2 0.2646485060  0.18354950 0.34574751 1.60e-06
5-2 0.4668391440  0.38574014 0.54793815 0.00e+00
6-2 0.6911451570  0.61004616 0.77224416 0.00e+00
4-3 0.2637893653  0.18269036 0.34488837 1.60e-06
5-3 0.4659800033  0.38488100 0.54707901 0.00e+00
6-3 0.6902860163  0.60918701 0.77138502 0.00e+00
```

```
5-4 0.2021906380  0.12109164 0.28328964 2.71e-05
6-4 0.4264966510  0.34539765 0.50759565 0.00e+00
6-5 0.2243060130  0.14320701 0.30540501 9.20e-06
```

Result: For the pairs where p-value is less than the significance level 0.05, it is possible to concluded that there are significant differences

σ (0.11)

Data were square-root transformed to meet a normal distribution. The results are presented below:

Descriptive statistics

```
  Sample count  mean     sd
  <ord>  <int> <dbl>  <dbl>
1 1         3  3.79 0.0270
2 2         3  4.89 0.332
3 3         3  4.48 0.145
4 4         3  9.84 1.27
5 5         3  7.95 0.303
6 6         3  8.14 0.587
```

Anova results

```
            Df Sum Sq Mean Sq F value   Pr(>F)
Sample       5  89.95  17.990   49.35 1.37e-07 ***
Residuals   12   4.37   0.365
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

Result: There is a statistically significant difference between samples as determined by one-way ANOVA (F = 49.35, p =1.37e-07)

Assumptions

1. Normality

```
        Shapiro-Wilk normality test

data:  aov_residuals
W = 0.91098, p-value = 0.08952
```

Result: The hypothesis of normallity is acepted because p>0.05

2. Homogeneity of Variance

```
Levene's Test for Homogeneity of Variance (center = median)
      Df F value Pr(>F)
group  5   1.296 0.3285
12
```

Result: The hypothesis of homogeneity of variance is accepted because p > 0.05

```
Tukey multiple comparisons of means
    95% family-wise confidence level

$`Sample`
          diff        lwr         upr     p adj
2-1  1.1016736 -0.5541654  2.75751269 0.2906468
3-1  0.6949859 -0.9608531  2.35082496 0.7213432
4-1  6.0526501  4.3968111  7.70848919 0.0000004
5-1  4.1680532  2.5122142  5.82389229 0.0000246
6-1  4.3516382  2.6957992  6.00747727 0.0000157
3-2 -0.4066877 -2.0625268  1.24915132 0.9570289
4-2  4.9509765  3.2951374  6.60681555 0.0000040
5-2  3.0663796  1.4105406  4.72221866 0.0004914
6-2  3.2499646  1.5941255  4.90580363 0.0002865
4-3  5.3576642  3.7018252  7.01350328 0.0000017
5-3  3.4730673  1.8172283  5.12890639 0.0001521
6-3  3.6566523  2.0008133  5.31249136 0.0000920
```

```
5-4 -1.8845969 -3.5404359 -0.22875784 0.0228666
6-4 -1.7010119 -3.3568510 -0.04517287 0.0428736
6-5  0.1835850 -1.4722541  1.83942403 0.9988055
```

Result: For the pairs where p-value is less than the significance level 0.05, it is possible to concluded that there are significant differences

σ (1.1)

Descriptive statistics

```
  Sample count  mean     sd
  <ord>  <int> <dbl>  <dbl>
1 1         3  21.9  0.136
2 2         3  76.7  9.93
3 3         3  34.3  2.95
4 4         3 144.   3.18
5 5         3 108.  12.6
6 6         3 149.   1.56
```

Anova results

```
            Df Sum Sq Mean Sq F value   Pr(>F)
Sample       5  44213    8843     191 5.27e-11 ***
Residuals   12    556      46
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

Result: There is a statistically significant difference between samples as determined by one-way ANOVA (F = 191, p =5.27e-11)

Assumptions

1. Normality

```
        Shapiro-Wilk normality test
data:  aov_residuals
W = 0.94485, p-value = 0.35
```

Result: The hypothesis of normallity is acepted because p>0.05

2. Homogeneity of Variance

Levene's Test for Homogeneity of Variance (center = median)

```
      Df F value Pr(>F)
group  5  0.7299 0.6146
12
```

Result: The hypothesis of homogeneity of variance is accepted because p > 0.05

Tukey multiple comparisons of means
95% family-wise confidence level

```
$`Sample`
         diff        lwr       upr     p adj
2-1  54.83667  36.176761  73.49657 0.0000048
3-1  12.39000  -6.269905  31.04991 0.2924467
4-1 122.59667 103.936761 141.25657 0.0000000
5-1  86.49667  67.836761 105.15657 0.0000000
6-1 127.39667 108.736761 146.05657 0.0000000
3-2 -42.44667 -61.106572 -23.78676 0.0000686
4-2  67.76000  49.100095  86.41991 0.0000005
5-2  31.66000  13.000095  50.31991 0.0010758
6-2  72.56000  53.900095  91.21991 0.0000002
4-3 110.20667  91.546761 128.86657 0.0000000
5-3  74.10667  55.446761  92.76657 0.0000002
6-3 115.00667  96.346761 133.66657 0.0000000
5-4 -36.10000 -54.759905 -17.44009 0.0003280
```

```
6-4   4.80000 -13.859905  23.45991 0.9482467
6-5  40.90000  22.240095  59.55991 0.0000990
```

Result: For the pairs where p-value is less than the significance level 0.05 , it is possible to concluded that there are significant differences

σ (11)

Descriptive statistics

```
  Sample count  mean     sd
  <ord>  <int> <dbl>  <dbl>
1 1          3  42.2  0.359
2 2          3 121.   6.15
3 3          3  80.6  3.27
4 4          3 187.   9.81
5 5          3 198.   4.22
6 6          3 391.  17.5
```

Anova results

```
            Df Sum Sq Mean Sq F value   Pr(>F)
Sample       5 230559   46112   591.8 6.33e-14 ***
Residuals   12    935      78
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
```

Result: There is a statistically significant difference between samples as determined by one-way ANOVA (F = 591.8, p =6.33e-14)

Assumptions

1. Normality

```
        Shapiro-Wilk normality test

data:  aov_residuals
W = 0.92497, p-value = 0.1583
```

Result: The hypothesis of normallity is acepted because p>0.05

2. Homogeneity of Variance

```
Levene's Test for Homogeneity of Variance (center = median)
      Df F value Pr(>F)
group  5  0.6078 0.6959
12
```

Result: The hypothesis of homogeneity of variance is accepted because p > 0.05

```
Tukey multiple comparisons of means
    95% family-wise confidence level

$`Sample`
         diff       lwr       upr     p adj
2-1  78.60333  54.39542 102.81125 0.0000016
3-1  38.44667  14.23875  62.65458 0.0018968
4-1 144.93667 120.72875 169.14458 0.0000000
5-1 155.87000 131.66209 180.07791 0.0000000
6-1 349.23667 325.02875 373.44458 0.0000000
3-2 -40.15667 -64.36458 -15.94875 0.0013089
4-2  66.33333  42.12542  90.54125 0.0000102
5-2  77.26667  53.05875 101.47458 0.0000020
6-2 270.63333 246.42542 294.84125 0.0000000
4-3 106.49000  82.28209 130.69791 0.0000001
5-3 117.42333  93.21542 141.63125 0.0000000
6-3 310.79000 286.58209 334.99791 0.0000000
```

```
5-4  10.93333 -13.27458  35.14125 0.6610479
6-4 204.30000 180.09209 228.50791 0.0000000
6-5 193.36667 169.15875 217.57458 0.0000000
```

Result: For the pairs where p-value is less than the significance level 0.05 , it is possible to concluded that there are significant differences

σ (356)

Descriptive statistics

```
  Sample count  mean    sd
  <ord>  <int> <dbl> <dbl>
1 1         3  197.  1.25
2 2         3  457.  7.02
3 3         3  238. 12.0
4 4         3  485. 43.8
5 5         3  357.  6.42
6 6         3  437. 30.5
```

Anova results

```
            Df Sum Sq Mean Sq F value   Pr(>F)
Sample       5 217370   43474   84.61 6.23e-09 ***
Residuals   12   6166     514
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

Result: There is a statistically significant difference between samples as determined by one-way ANOVA (F = 84.61, p =6.23e-9)

Assumptions

1. Normality

```
        Shapiro-Wilk normality test

data:  aov_residuals
W = 0.90001, p-value = 0.05748
```

Result: The hypothesis of normallity is acepted because p>0.05

2. Homogeneity of Variance

```
Levene's Test for Homogeneity of Variance (center = median)
      Df F value Pr(>F)
group  5  0.7158 0.6236
12
```

Result: The hypothesis of homogeneity of variance is accepted because p > 0.05

```
Tukey multiple comparisons of means
    95% family-wise confidence level

$`Sample`
          diff        lwr        upr     p adj
2-1  260.00000  197.83146  322.16854 0.0000001
3-1   40.56667  -21.60188  102.73521 0.3082234
4-1  287.93333  225.76479  350.10188 0.0000000
5-1  159.40000   97.23146  221.56854 0.0000203
6-1  239.70000  177.53146  301.86854 0.0000002
3-2 -219.43333 -281.60188 -157.26479 0.0000007
4-2   27.93333  -34.23521   90.10188 0.6655062
5-2 -100.60000 -162.76854  -38.43146 0.0016190
6-2  -20.30000  -82.46854   41.86854 0.8735838
4-3  247.36667  185.19812  309.53521 0.0000002
5-3  118.83333   56.66479  181.00188 0.0003669
6-3  199.13333  136.96479  261.30188 0.0000019
```

```
5-4 -128.53333 -190.70188  -66.36479 0.0001747
6-4  -48.23333 -110.40188   13.93521 0.1690680
6-5   80.30000   18.13146  142.46854 0.0096003
```

Result: For the pairs where p-value is less than the significance level 0.05 , it is possible to concluded that there are significant differences

σ (895)

Data were square-root transformed to meet a normal distribution. The results are presented below:

Descriptive statistics

```
  Sample count  mean     sd
  <ord>  <int> <dbl>  <dbl>
1 1          3  17.9 0.0936
2 2          3  25.3 0.295
3 3          3  16.9 0.308
4 4          3  25.7 1.15
5 5          3  22.3 0.181
6 6          3  22.4 0.447
```

Anova results

```
            Df Sum Sq Mean Sq F value   Pr(>F)
Sample       5 203.74   40.75   140.2 3.27e-10 ***
Residuals   12   3.49    0.29
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
```

Result: There is a statistically significant difference between samples as determined by one-way ANOVA (F = 140.2, p =3.27e-10)

Assumptions

1. Normality

```
        Shapiro-Wilk normality test
data:  aov_residuals
W = 0.90909, p-value = 0.0829
```

Result: The hypothesis of normallity is acepted because p>0.05

2. Homogeneity of Variance

```
Levene's Test for Homogeneity of Variance (center = median)
      Df F value Pr(>F)
group  5  1.0209 0.4477
12
```

Result: The hypothesis of homogeneity of variance is accepted because p > 0.05

```
Tukey multiple comparisons of means
    95% family-wise confidence level

$`Sample`
          diff        lwr        upr     p adj
2-1  7.4138199  5.935068  8.8925713 0.0000000
3-1 -1.0291968 -2.507948  0.4495547 0.2515625
4-1  7.8371017  6.358350  9.3158531 0.0000000
5-1  4.3689640  2.890213  5.8477155 0.0000046
6-1  4.4948274  3.016076  5.9735789 0.0000034
3-2 -8.4430167 -9.921768 -6.9642652 0.0000000
4-2  0.4232818 -1.055470  1.9020333 0.9216533
5-2 -3.0448559 -4.523607 -1.5661044 0.0001817
6-2 -2.9189925 -4.397744 -1.4402410 0.0002715
4-3  8.8662985  7.387547 10.3450500 0.0000000
5-3  5.3981608  3.919409  6.8769123 0.0000005
6-3  5.5240242  4.045273  7.0027757 0.0000003
```

```
5-4 -3.4681377 -4.946889 -1.9893862 0.0000505
6-4 -3.3422742 -4.821026 -1.8635228 0.0000731
6-5  0.1258634 -1.352888  1.6046149 0.9996672
```

Result: For the pairs where p-value is less than the significance level 0.05 , it is possible to concluded that there are significant differences

σ (0.11)

Data were square-root transformed to meet a normal distribution. The results are presented below:

Descriptive statistics

```
  Sample count  mean     sd
  <ord>  <int> <dbl>  <dbl>
1 1          3  11.3 0.0834
2 2          3  14.6 0.994
3 3          3  13.4 0.433
4 4          3  29.5 3.81
5 5          3  23.9 0.937
6 6          3  25.0 3.01
```

Anova results

```
            Df Sum Sq Mean Sq F value  Pr(>F)
Sample       5  828.0  165.59   38.81 5.3e-07 ***
Residuals   12   51.2    4.27
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
```

Result: There is a statistically significant difference between samples as determined by one-way ANOVA (F = 38.81, p =5.3e-07)

Assumptions

1. Normality

```
        Shapiro-Wilk normality test

data:  aov_residuals
W = 0.92808, p-value = 0.1796
```

Result: The hypothesis of normallity is acepted because p>0.05

2. Homogeneity of Variance

```
Levene's Test for Homogeneity of Variance (center = median)
      Df F value Pr(>F)
group  5  1.0188 0.4487
12
```

Result: The hypothesis of homogeneity of variance is accepted because p > 0.05

```
Tukey multiple comparisons of means
    95% family-wise confidence level

$`Sample`
         diff        lwr        upr     p adj
2-1  3.300208  -2.364988  8.96540518 0.4170774
3-1  2.079539  -3.585658  7.74473559 0.8132629
4-1 18.125003  12.459806 23.79019960 0.0000019
5-1 12.534701   6.869504 18.19989755 0.0000903
6-1 13.679600   8.014404 19.34479717 0.0000376
3-2 -1.220670  -6.885866  4.44452721 0.9750762
4-2 14.824794   9.159598 20.48999123 0.0000165
5-2  9.234492   3.569296 14.89968918 0.0015213
6-2 10.379392   4.714195 16.04458879 0.0005419
4-3 16.045464  10.380267 21.71066082 0.0000072
5-3 10.455162   4.789965 16.12035877 0.0005071
6-3 11.600062   5.934865 17.26525839 0.0001917
```

```
5-4 -5.590302 -11.255499  0.07489475 0.0538554
6-4 -4.445402 -10.110599  1.21979437 0.1615336
6-5  1.144900  -4.520297  6.81009642 0.9810750
```

σ (1.1)

Descriptive statistics

```
  Sample count  mean     sd
  <ord>  <int> <dbl>  <dbl>
1 1         3  19.7  0.121
2 2         3  68.9  8.92
3 3         3  30.8  2.65
4 4         3 130.   2.83
5 5         3  97.3 11.3
6 6         3 134    1.39
```

Anova results

```
            Df Sum Sq Mean Sq F value   Pr(>F)
Sample       5  35609    7122   191.6 5.18e-11 ***
Residuals   12    446      37
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
```

Result: There is a statistically significant difference between samples as determined by one-way ANOVA (F = 191.6, p =5.18e-11)

Assumptions

1. Normality

```
        Shapiro-Wilk normality test

data:  aov_residuals
W = 0.94487, p-value = 0.3503
```

Result: The hypothesis of normallity is acepted because p>0.05

2. Homogeneity of Variance

```
Levene's Test for Homogeneity of Variance (center = median)
      Df F value Pr(>F)
group  5   0.731 0.6139
      12
```

Result: The hypothesis of homogeneity of variance is accepted because p > 0.05

```
Tukey multiple comparisons of means
    95% family-wise confidence level

$`Sample`
         diff        lwr       upr     p adj
2-1  49.213333  32.491715  65.93495 0.0000048
3-1  11.123333  -5.598285  27.84495 0.2908078
4-1 110.006667  93.285049 126.72828 0.0000000
5-1  77.653333  60.931715  94.37495 0.0000000
6-1 114.340000  97.618382 131.06162 0.0000000
3-2 -38.090000 -54.811618 -21.36838 0.0000676
4-2  60.793333  44.071715  77.51495 0.0000005
5-2  28.440000  11.718382  45.16162 0.0010532
6-2  65.126667  48.405049  81.84828 0.0000002
4-3  98.883333  82.161715 115.60495 0.0000000
5-3  66.530000  49.808382  83.25162 0.0000002
6-3 103.216667  86.495049 119.93828 0.0000000
```

```
5-4 -32.353333 -49.074951 -15.63172 0.0003277
6-4   4.333333 -12.388285  21.05495 0.9467031
6-5  36.686667  19.965049  53.40828 0.0000981
```

Result: For the pairs where p-value is less than the significance level 0.05 , it is possible to concluded that there are significant differences

σ (11)

Descriptive statistics

```
  Sample count  mean     sd
  <ord>  <int> <dbl>  <dbl>
1 1          3  3.79 0.0324
2 2          3 10.8  0.557
3 3          3  7.24 0.293
4 4          3 16.8  0.881
5 5          3 17.8  0.370
6 6          3 35.1  1.57
```

Anova results

```
           Df Sum Sq Mean Sq F value   Pr(>F)
Sample       5 1858.2   371.6   590.7 6.41e-14 ***
Residuals   12    7.6     0.6
---
Signif. codes:  0 ‘***’ 0.001 ‘**’ 0.01 ‘*’ 0.05 ‘.’ 0.1 ‘ ’ 1
```

Result: There is a statistically significant difference between samples as determined by one-way ANOVA (F = 590.7, p =6.41e-14)

Assumptions

1. Normality

```
        Shapiro-Wilk normality test

data:  aov_residuals
W = 0.92448, p-value = 0.1552
```

Result: The hypothesis of normallity is acepted because p>0.05

2. Homogeneity of Variance

```
Levene's Test for Homogeneity of Variance (center = median)
      Df F value Pr(>F)
group  5  0.6124 0.6927
      12
```

Result: The hypothesis of homogeneity of variance is accepted because p > 0.05

```
Tukey multiple comparisons of means
   95% family-wise confidence level

$`Sample`
          diff       lwr       upr     p adj
2-1  7.0556667  4.880257  9.231076 0.0000017
3-1  3.4513333  1.275924  5.626743 0.0019136
4-1 13.0090000 10.833591 15.184409 0.0000000
5-1 13.9923333 11.816924 16.167743 0.0000000
6-1 31.3523333 29.176924 33.527743 0.0000000
3-2 -3.6043333 -5.779743 -1.428924 0.0013224
4-2  5.9533333  3.777924  8.128743 0.0000103
5-2  6.9366667  4.761257  9.112076 0.0000020
6-2 24.2966667 22.121257 26.472076 0.0000000
4-3  9.5576667  7.382257 11.733076 0.0000001
5-3 10.5410000  8.365591 12.716409 0.0000000
6-3 27.9010000 25.725591 30.076409 0.0000000
```

```
5-4  0.9833333 -1.192076  3.158743 0.6603204
6-4 18.3433333 16.167924 20.518743 0.0000000
6-5 17.3600000 15.184591 19.535409 0.0000000
```

Result: For the pairs where p-value is less than the significance level 0.05 , it is possible to concluded that there are significant differences

σ (113)

Descriptive statistics

```
  Sample count  mean     sd
  <ord>  <int> <dbl>  <dbl>
1 1          3  1.00 0.00770
2 2          3  2.74 0.151
3 3          3  1.64 0.0816
4 4          3  2.89 0.259
5 5          3  2.35 0.0433
6 6          3  3.40 0.237
```

Anova results

```
            Df Sum Sq Mean Sq F value   Pr(>F)
Sample       5 11.581  2.3162   89.89 4.38e-09 ***
Residuals   12  0.309  0.0258
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

Result: There is a statistically significant difference between samples as determined by one-way ANOVA (F = 89.89, p =4.38e-9)

Assumptions

1. Normality

```
        Shapiro-Wilk normality test

data:  aov_residuals
W = 0.91889, p-value = 0.1236
```

Result: The hypothesis of normallity is acepted because p>0.05

2. Homogeneity of Variance

```
Levene's Test for Homogeneity of Variance (center = median)
      Df F value Pr(>F)
group  5   0.732 0.6132
12
```

Result: The hypothesis of homogeneity of variance is accepted because p > 0.05

```
Tukey multiple comparisons of means
    95% family-wise confidence level

$`Sample`
          diff        lwr         upr     p adj
2-1  1.7384333  1.2982129  2.17865374 0.0000002
3-1  0.6367667  0.1965463  1.07698707 0.0040685
4-1  1.8881000  1.4478796  2.32832040 0.0000001
5-1  1.3467667  0.9065463  1.78698707 0.0000031
6-1  2.3941000  1.9538796  2.83432040 0.0000000
3-2 -1.1016667 -1.5418871 -0.66144626 0.0000261
4-2  0.1496667 -0.2905537  0.58988707 0.8548006
5-2 -0.3916667 -0.8318871  0.04855374 0.0922717
6-2  0.6556667  0.2154463  1.09588707 0.0032206
4-3  1.2513333  0.8111129  1.69155374 0.0000069
5-3  0.7100000  0.2697796  1.15022040 0.0016653
6-3  1.7573333  1.3171129  2.19755374 0.0000002
```

```
5-4 -0.5413333 -0.9815537 -0.10111293 0.0136105
6-4  0.5060000  0.0657796  0.94622040 0.0214489
6-5  1.0473333  0.6071129  1.48755374 0.0000437
```

Result: For the pairs where p-value is less than the significance level 0.05 , it is possible to concluded that there are significant differences

σ (356)

```
Descriptive statistics
  Sample count  mean      sd
  <ord>  <int> <dbl>   <dbl>
1 1         3 0.560 0.00356
2 2         3 1.30  0.0201
3 3         3 0.676 0.0341
4 4         3 1.38  0.125
5 5         3 1.01  0.0181
6 6         3 1.24  0.0885

Anova results
          Df Sum Sq Mean Sq F value  Pr(>F)
Sample       5 1.7497  0.3499   83.12 6.9e-09 ***
Residuals   12 0.0505  0.0042
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
```

Result: There is a statistically significant difference between samples as determined by one-way ANOVA (F = 83.12, p =6.9e-9)

Assumptions

1. Normality

```
        Shapiro-Wilk normality test

data:  aov_residuals
W = 0.89932, p-value = 0.05592
```

Result: The hypothesis of normallity is acepted because p>0.05

2. Homogeneity of Variance

```
Levene's Test for Homogeneity of Variance (center = median)
      Df F value Pr(>F)
group  5  0.7466 0.6038
12
```

Result: The hypothesis of homogeneity of variance is accepted because p > 0.05

```
Tukey multiple comparisons of means
   95% family-wise confidence level

$`Sample`
           diff         lwr         upr     p adj
2-1  0.73816667  0.56022176  0.91611157 0.0000001
3-1  0.11513333 -0.06281157  0.29307824 0.3160192
4-1  0.81750000  0.63955509  0.99544491 0.0000000
5-1  0.45243333  0.27448843  0.63037824 0.0000222
6-1  0.67850000  0.50055509  0.85644491 0.0000003
3-2 -0.62303333 -0.80097824 -0.44508843 0.0000007
4-2  0.07933333 -0.09861157  0.25727824 0.6721707
5-2 -0.28573333 -0.46367824 -0.10778843 0.0017287
6-2 -0.05966667 -0.23761157  0.11827824 0.8614709
4-3  0.70236667  0.52442176  0.88031157 0.0000002
5-3  0.33730000  0.15935509  0.51524491 0.0003965
6-3  0.56336667  0.38542176  0.74131157 0.0000022
```

5-4 -0.36506667 -0.54301157 -0.18712176 0.0001882
6-4 -0.13900000 -0.31694491 0.03894491 0.1645205
6-5 0.22606667 0.04812176 0.40401157 0.0108163

Result: For the pairs where p-value is less than the significance level 0.05 , it is possible to concluded that there are significant differences
σ (895)
Data were square-root transformed to meet a normal distribution. The results are presented below:

Descriptive statistics
Sample count mean sd
<ord> <int> <dbl> <dbl>
1 1 3 0.602 0.00316
2 2 3 0.851 0.00997
3 3 3 0.567 0.0104
4 4 3 0.865 0.0386
5 5 3 0.748 0.00609
6 6 3 0.753 0.0151

Anova results
Df Sum Sq Mean Sq F value Pr(>F)
Sample 5 0.23005 0.04601 140.1 3.28e-10 ***
Residuals 12 0.00394 0.00033

Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1
Result: There is a statistically significant difference between samples as determined by one-way ANOVA (F = 140.1, p =3.28e-10)

Assumptions
1. Normality

Shapiro-Wilk normality test

data: aov_residuals
W = 0.90953, p-value = 0.0844
Result: The hypothesis of normallity is acepted because p>0.05

2. Homogeneity of Variance

Levene's Test for Homogeneity of Variance (center = median)
Df F value Pr(>F)
group 5 1.0171 0.4496
12
Result: The hypothesis of homogeneity of variance is accepted because p > 0.05
Tukey multiple comparisons of means
95% family-wise confidence level

$`Sample`
diff lwr upr p adj
2-1 0.24914160 0.19943780 0.29884540 0.0000000
3-1 -0.03459809 -0.08430189 0.01510571 0.2514481
4-1 0.26332810 0.21362430 0.31303190 0.0000000
5-1 0.14677833 0.09707453 0.19648214 0.0000046
6-1 0.15102458 0.10132078 0.20072838 0.0000034
3-2 -0.28373968 -0.33344348 -0.23403588 0.0000000
4-2 0.01418651 -0.03551729 0.06389031 0.9224999
5-2 -0.10236326 -0.15206706 -0.05265946 0.0001814
6-2 -0.09811702 -0.14782082 -0.04841322 0.0002714
4-3 0.29792619 0.24822239 0.34762999 0.0000000
5-3 0.18137642 0.13167262 0.23108022 0.0000005
6-3 0.18562266 0.13591886 0.23532646 0.0000004

5-4 -0.11654977 -0.16625357 -0.06684597 0.0000506
6-4 -0.11230353 -0.16200733 -0.06259973 0.0000733
6-5 0.00424624 -0.04545756 0.05395004 0.9996612

Result: For the pairs where p-value is less than the significance level 0.05 , it is possible to concluded that there are significant differences

F. Data base of ingredients – tables

Table F-I: Continuation of Table 4-7 – Emollients data base

INCI	Chemistry	Polarity		Viscosity (mPa*s) (25°C)		Spreading		Surface tension at 25 °C (mN/m)		Emollience		Afterfeel		Price ($/Kg)	
Dibutyl Adipate	Ester	high	(2)	6*	(2)	high	(2)	NA	-		-	NA	-	NA	-
Dicaprylyl Carbonate	Ester	medium	(2)	7*	(2)	high	(2)	NA	-		-	low oily sensation	(2)	NA	-
Dicaprylyl Ether	Ether	low	(2)	4*	(2)	high	(2)	NA	-		-	low oily sensation	(2)	NA	-
Diethylhexyl Carbonate	Ester	medium	(7)	5	(11)	high	(7)	28	(11)	light	(7)	low oily sensation	(7)	NA	-
Diisopropyl Dimer Dilinoleate	Ester	medium	(3)	81.7	(3)	low	(3)	NA	-	medium	(3)	smooth	(3)	NA	-
Diisostearyl Dimer Dilinoleate	Ester	medium	(3)	270.6	(3)	low	(3)	NA	-	medium	(3)	smooth	(3)	NA	-
Dimethicone	Silicone	low	(-)	350	(11)	low	(-)	20	-11	Rich	(7)	smooth	(7)	30-70	(1)
Di-PPG-2 Myreth-10 Adipate	Ester	high	(3)	149.4	(3)	low	(3)	NA	-	Rich	(3)	smooth	(3)	NA	-
Di-PPG-3 Myristyl Ether Adipate	Ester	high	(3)	81	(5)	low	(3)	NA	-	Rich	(3)	smooth	(3)	NA	-
Ethylhexyl Cocoate (and) Cocos Nucifera Oil	Ester	medium	(2)	9*	(2)	high	(2)	NA	-		-	NA	-	NA	-
Ethylhexyl Palmitate	Ester	medium	(2, 7)	11.2	(2, 7)	medium	(2)	29	(7)	light	(4, 7)	low oily sensation	(4, 7)	14	(1)
Ethylhexyl Stearate	Ester	medium	(2, 7)	12.8	(2, 5, 7)	medium	(11)	30	(11)	medium to light	(7)	low oily sensation	(7)	NA	-
Glyceryl Isostearate	Ester	high	(3)	476.5	(3)	low	(3)	NA	-	Rich	(3)	NA	-	NA	-
Hexyl Laurate	Ester	medium	(2)	6*	(2)	high	(2)	NA	-	light	(2)	NA	-	NA	-
Hexyldecanol	Fatty alcohol	medium	(2)	45*	(2)	medium	(2)	NA	-		-	NA	-	NA	-
Hexyldecanol (and) Hexyldecyl Laurate	Fatty alcohol	medium	(2)	30*	(2)	medium	(2)	NA	-		-	NA	-	NA	-

INCI	Chemistry	Polarity		Viscosity (mPa*s) (25°C)		Spreading		Surface tension at 25 °C (mN/m)		Emollience		Afterfeel		Price ($/Kg)	
Hexyldecyl Stearate	Ester	medium	(2)	31.5*	(2)	low	(2)	NA	-		-	NA	-	NA	-
Hydrogenated Polyisobutene	Hydrocarbon	low	(2)	5*	(2)	high	(2)	NA	-		-	NA	-	NA	-
Isoamyl Cocoate	Ester	medium	(7)	5.6	(7)	medium	(7)	28	(11)	light	(7)	low oily sensation	(7)	NA	-
Isohexadecane	Hydrocarbon	low	(3)	3.1	(3)	NA	(3)	NA	-	light	(3)	low oily sensation	(3)	22	(1)
Isopropyl Isostearate	Ester	medium	(3)	7.7	(3)	NA	(3)	NA	-	light	(3)	low oily sensation	(3)	NA	-
Isopropyl Myristate	Ester	medium	(2, 7)	5.6	(2, 5, 7)	high	(11)	28	(11)	light	(4, 7)	low oily sensation	(7)	17	(1)
Isopropyl Palmitate	Ester	medium	(2, 7)	6.4	(2, 7)	high	(2)	29	(11)	light	(4, 7)	smooth	(7)	17	(1)
Isostearyl Isostearate	Ester	medium	(3)	34.9	(3)	low	(3)	NA	-	medium	(3)	smooth	(3)	NA	-
Isotridecyl Isononanoate	Ester	low	()	9.1*	(2)	medium to high	(2)	26.7	-	light	()	low oily sensation	()	NA	-
Mineral oil	Hydrocarbon	low	()	15	NA	medium	NA	NA	-	medium to rich	()	NA	()	NA	-
Myristyl Myristate	Ester	medium	(2)	6**	(2, 11)	NA	-	NA	-	Rich	(3)	low oily sensation	(3)	18	(1)
Octyldodecanol	Fatty alcohol	high	(2)	47.5	(7)	low	(2)	28	(7)	medium to light	(7)	low oily sensation	(7)	23	(1)
Oleyl Erucate	Ester	medium to high	(2, 7)	45	(2, 11, 7)	low	(2)	32	(11)	Rich	(2, 7)	smooth	(2, 7)	NA	-
Olus Oil	Vegetable oil	medium	(2)	85	(2)	low	(2)	NA	-	Rich	(2)	smooth	(2)	NA	-
Passiflora Incarnata Seed Oil	Vegetable oil	medium	(2)	33	(2)	low	(2)	NA	-	Rich	(2)	smooth	(2)	NA	-
PCA Dimethicone	Silicone	low	(3)	620	(3)	low	(3)	NA	-	light	(3)	NA	-	NA	-
Pentaerythrityl Isostearate/Caprate	Ester	high	(3)	767.2	(3)	low	(3)	NA	-	Rich	(3)	NA	-	NA	-

INCI	Chemistry	Polarity		Viscosity (mPa*s) (25°C)		Spreading		Surface tension at 25 °C (mN/m)		Emollience		Afterfeel		Price ($/Kg)	
/Caprylate/Adipate															
Pentaerythrityl Tetraisostearate	Ester	high	(3)	305	(3, 5)	low	(6)	NA	-	Rich	(3)	smooth	(3)	NA	-
Phenoxyethyl Caprylate	Ester	high	(11)	10	(11, 7)	low	(12)	32	(11)	light	(7)	low oily sensation	(7)	NA	-
Polyglyceryl-2 Isostearate	Ester	high	(3)	1352	(3)	low	(3)	NA	-	Rich	(3)	NA	-	NA	-
Polyglyceryl-2 Triisostearate	Ester	high	(3)	240	(3)	low	(3)	NA	-	Rich	(3)	NA	-	NA	-
Polyglyceryl-3 Diisostearate	Ester	high	(3)	1779	(3)	low	(3)	NA	-	Rich	(3)	NA	-	NA	-
Polyglyceryl-3 Polyricinoleate	Ester	high	(3)	2288.5	(3)	low	(3)	NA	-	Rich	(3)	NA	-	NA	-
PPG-11 Stearyl Ether	ether	high	(7)	76	(7)	low	(12)	30	(11)	medium	(1)	NA	-	NA	-
PPG-14 Butyl Ether	ether	high	(7)	99	(7)	medium to low	(7)	31	(11)	Rich	(7)	smooth	(7)	NA	-
PPG-15 Stearyl Ether	ether	high	(3, 7)	56.2	(3)	low	(3)	30	(11)	Rich	(7)	smooth	(3)	NA	-
PPG-3 Benzyl Ether Ethylhexanoate	ether	high	(3)	11.1	(3)	low	(3)	32	-	light	(3)	NA	-	NA	-
PPG-3 Benzyl Ether Myristate	ether	high	(3)	100	(3, 5)	low	(6)	NA	-	medium	(3)	smooth	(3)	NA	-
PPG-3 Myristyl Ether	ether	high	(7)	25.1	(7)	low	(7)	30	(11)	medium to light	(7)	low oily sensation	(7)	NA	-
PPG-5-Ceteth-20	ether	high	(3)	163.6	(3)	low	(3)	NA	-	Rich	(3)	NA	-	NA	-
Propylene Glycol Dicaprylate/ Dicaprate	Ester	medium to low	(2)	10.5*	(2)	medium to high	(2)	NA	-	light	NA	low oily sensation	NA	NA	-
Propylene Glycol Isostearate	Ester	high	(3)	42.3	(3)	medium	(2)	NA	-	medium	(3)	smooth	(3)	NA	-
Propylheptyl Caprylate	Ester	medium	(2)	5*	(2)	high	(2)	NA	-		-	NA	-	NA	-

INCI	Chemistry	Polarity		Viscosity (mPa*s) (25°C)		Spreading		Surface tension at 25 °C (mN/m)		Emollience		Afterfeel		Price ($/Kg)	
Sucrose Polysoyate	Ester	high	(3)	320.3	(3)	low	(3)	NA	-	Rich	(3)	smooth	(3)	NA	-
Triethylhexanoin	Ester	medium	(3)	22.8	(3)	low	(3)	NA	-	medium	(3)	smooth	(3)	NA	-
Triisononanoin	Ester	medium	(3)	46.8	(3)	low	(3)	NA	-	medium	(3)	smooth	(3)	NA	-
Triisostearin	Triglyceride	high	(3)	114	(3)	low	(3)	31	(7)	medium to rich	(3, 7)	smooth	(3, 7)	NA	-
Trimethylolpropane Triisostearate	Ester	medium	(3)	137	(3)	low	(3)	NA	-	medium	(3)	NA	-	NA	-
Undecane (and) Tridecane	Hydrocarbon	low	(2)	1*	(2)	high	(2)	NA	-	light	(2)	NA	-	NA	-

Notes: *Viscosity at 20°C, ** Viscosity at 40°C

References: (1) Making cosmetics - ingredient supplier, (2) BASF. BASF emollients - choosing the right emollient. BASF Personal Care andNutrition GmbH. 2016, (3) Croda. Emollients Your Essential Selection Guide. Seventh Edition. 2013, (4) Technical information -Crodamol TM (spanish). Croda. NA. NA, (5) Croda. Pigment Wetting Guid DS-120R-1. Croda February 25, 1999, (6) Croda. Emollient Skin Spreading Factor DS-128. Croda. January 6, 1998, (7) M. Mentel*, S. Wiechers, A. Howe, P Biehl, J. Meyer. Senses- A Scientific Tool for the Selection of The Right Emailient. SOFW-Journal, 2014, (11) Croda datasheet, (12) Evonik datasheet

Table F-2: Continuation of Table 4-8 –Surfactant data base

General information						**Properties**						Texture				
Classification 1	**Classification 2**	**Type**	**INCI name**	**Price ($/Kg)**		**HLB**		**Usage concen-tration**		**CMC (M) - 25°C**		**Cream**	**Lotion**	**Spray**	**Gel**	
Anionic	Acylamino acid salts	O/W	Sodium Stearoyl Glutamate	NA	-	23	(3)	0.25 –2	(3)	NA	-	Yes	Yes	Yes	Yes	(3)
nonionic	POE Alkyl ethers	O/W	Ceteareth-25	15.7	(9)	~16	(1)	2 – 4	(2)	NA	-	Yes	-	-	NA	(2)
Nonionic	POE Alkyl ethers	O/W	Ceteareth-30	NA	-	17	(3)	2 – 4	(3)	NA	-	NA	NA	NA	NA	-
nonionic	POE Alkyl ethers	O/W	Ceteth-10	NA	-	12.9	(7)	NA	-	2.00E-06	(5)	NA	NA	NA	NA	-
nonionic	POE Alkyl ethers	NA	Ceteth-2	NA	-	5.3	(7)	NA	-	6.70E-08	(5)	NA	NA	NA	NA	-
nonionic	POE Alkyl ethers	NA	Ceteth-20	NA	-	15.7	(5)	NA	-	7.00E-06	(5)	NA	NA	NA	NA	-
nonionic	POE Alkyl ethers	O/W	Isoceteth-20	NA	-	~16	(1)	1.0 - 20.0	(8)	NA	-	Yes	Yes	NA	NA	(8)
nonionic	POE Alkyl ethers	O/W	Laureth-23	NA	-	16.9	(8)	emulsions: 1.0 - 6.0	(8)	0.00006	(5)	Yes	Yes	NA	NA	(8)
nonionic	POE Alkyl ethers	NA	Laureth-4	NA	-	9.7	(7)	NA	-	0.000064/ 0.000004	(6)	NA	NA	NA	NA	-
Nonionic	POE Alkyl ethers	NA	Oleth-10	NA	-	12.4	(7)	NA	-	9.40E-04	(5)	NA	NA	NA	NA	-
Nonionic	POE Alkyl ethers	NA	Oleth-2	NA	-	4.9	(7)	NA	-	2.48E-02	(5)	NA	NA	NA	NA	-
Nonionic	POE Alkyl ethers	NA	Oleth-20	NA	-	15.3	(7)	NA	-	2.65E-04	(5)	NA	NA	NA	NA	-
Nonionic	POE Alkyl ethers	NA	Oleth-3	NA	-	6.6	(7)	NA	-	NA	-	NA	NA	NA	NA	-
Nonionic	POE Alkyl ethers	NA	Oleth-5	NA	-	8.8	(7)	NA	-	NA	-	NA	NA	NA	NA	-
nonionic	POE Alkyl ethers	NA	Steareth-10	NA	-	12.4	(7)	NA	-	3.00E-06	(5)	NA	NA	NA	NA	-
nonionic	POE Alkyl ethers	NA	Steareth-100	NA	-	18.8	(7)	NA	-	2.00E-05	(5)	NA	NA	NA	NA	-

General information						**Properties**						Texture				
Classification 1	**Classification 2**	**Type**	**INCI name**	**Price ($/Kg)**		**HLB**		**Usage concen-tration**		**CMC (M) - 25°C**		**Cream**	**Lotion**	**Spray**	**Gel**	
nonionic	POE Alkyl ethers	O/W and W/O	Steareth-2	NA	-	4.9	(1)	emulsions: 1.0 - 6.0	(8)	2.50E-07	(5)	Yes	Yes	Yes	NA	(8)
nonionic	POE Alkyl ethers	O/W	Steareth-20	NA	-	15.3	(1)	emulsions: 1.0 - 6.0	(8)	5.70E-06	(5)	Yes	Yes	Yes	NA	(8)
nonionic	POE Alkyl ethers	O/W	Steareth-21	NA	-	15.5	(1)	emulsions: 1.0 - 6.0	(8)	3.90E-06	(5)	Yes	Yes	Yes	NA	(8)
nonionic	Polyglycerol ester	W/o Emulsifiers	Diisostearoyl Polyglyceryl-3 Dimer Dilinoleate	NA	-	~5	(1)	NA	-	NA	-	Yes	Yes	-	NA	(2)
nonionic	Polyglycerol ester	W/O; SWOP	Polyglyceryl-2 Dipolyhydroxystearate	NA	-	5	(3)	3 –5	(3)	NA	-	Yes	Yes	Yes	-	(3)
nonionic	Polyglycerol ester	O/W	Polyglyceryl-3 Dicitrate/Stearate	NA	-	~11	(1)	NA	-	NA	-	NA	NA	NA	NA	-
nonionic	Polyglycerol ester	W/O	Polyglyceryl-3 Diisostearate	NA	-	4	(3)	1 – 4	(3)	NA	-	NA	NA	NA	NA	(3)
nonionic	Polyglycerol ester	O/W	Polyglyceryl-3 Distearate	NA	-	9	(3)	2 –5	(3)	NA	-	Yes	Yes	Yes	-	(3)
nonionic	Polyglycerol ester	O/W	Polyglyceryl-3 Methylglucose Distearate	NA	-	~12	(1)	2.0 – 3.0	(2)	NA	-	Yes	Yes	-	NA	(2)
nonionic	Polyglycerol ester	W/o Emulsifiers	Polyglyceryl-3 Oleate	27.4	(9)	~5	(1)	NA	-	NA	-	NA	NA	NA	NA	-
nonionic	Polyglycerol ester	W/o Emulsifiers	Polyglyceryl-4 Diisostearate/ Polyhydroxystearate/ Sebacate	NA	-	~5	(1)	NA	-	NA	-	Yes	Yes	-	NA	(2)
nonionic	Polyglycerol ester	W/o Emulsifiers	Polyglyceryl-4 Isostearate	NA	-	~5	(1)	NA	-	NA	-	Yes	-	-	NA	(2)
nonionic	Polyglycerol ester	O/W	Polyglyceryl-4 Laurate	NA	-	~11	(1)	NA	-	NA	-	NA	NA	NA	NA	(2)
nonionic	POE glycerides	O/W	PEG-100 Stearate	19.0	(9)	~19	(1)	2.0 - 3.0	(8)	NA	-	Yes	Yes	NA	NA	(8)
nonionic	POE glycerides	NA	PEG-50 stearate	NA	-	17.9	(5)	NA	-	NA	-	NA	NA	NA	NA	()
nonionic	POE glycerides	NA	PEG-20 Almond Glycerides	NA	-	high	(7)	NA	-	NA	-	NA	NA	NA	NA	(7)

General information						**Properties**						Texture				
Classification 1	**Classification 2**	**Type**	**INCI name**	**Price ($/Kg)**		**HLB**		**Usage concentration**		**CMC (M) - 25°C**		**Cream**	**Lotion**	**Spray**	**Gel**	
nonionic	POE glycerides	NA	PEG-20 Sorbitan Monolaurate	15.3	(9)	16.7	(7)	NA	-	0.0000804/ 0.00005	((21°C)6 , 5)	NA	NA	NA	NA	-
nonionic	POE glycerides	NA	PEG-20 sorbitan monooleate	14.9	(9)	15	(7)	NA	-	1.00E-05	(5)	NA	NA	NA	NA	-
nonionic	POE glycerides	NA	PEG-20 sorbitan monopalmitate	NA	-	15.6	(7)	NA	-	2.30E-05	(5)	NA	NA	NA	NA	-
nonionic	POE glycerides	NA	PEG-20 sorbitan monostearate	15.4	(9)	14.9	(7)	NA	-	2.10E-05	(5)	NA	NA	NA	NA	-
nonionic	POE glycerides	NA	PEG-20 sorbitan tristearate	NA	-	10.5	(7)	NA	-	1.80E-07	(5)	NA	NA	NA	NA	-
nonionic	POE glycerides	NA	PEG-20 sorbitan trioleate	NA	-	11	(5)	NA	-	2.90E-07	(5)	NA	NA	NA	NA	-
nonionic	POE glycerides	NA	PEG-4 Sorbitan Monolaurate	NA	-	13.3	(7)	NA	-	NA	-	NA	NA	NA	NA	-
nonionic	POE glycerides	NA	PEG-4 sorbitan monostearate	NA	-	9.6	(7)	NA	-	NA	-	NA	NA	NA	NA	-
nonionic	POE glycerides	O/W	PEG-40 Stearate	NA	-	~17	(1)	2.0 - 3.0	(8)	NA	-	Yes	Yes	NA	NA	(8)
nonionic	POE glycerides	NA	PEG-8 Stearate	NA	-	11.1	(7)	NA	-	3.73E-04	(5)	NA	NA	NA	NA	(7)
nonionic	POE glycerides	NA	PEG-80 Sorbitan Laurate	NA	-	19.1	(7)	NA	-	NA	-	NA	NA	NA	NA	-
nonionic	POE sorbitans	O/W	Polysorbate 60	NA	-	~15	(1)	NA	-	NA	-	NA	NA	NA	NA	-
nonionic	POE sorbitans	O/W	Polysorbate 80	NA	-	~15	(1)	NA	-	NA	-	NA	NA	NA	NA	-
nonionic	**silicone derivatives**	W/o Emulsifiers	Bis-(Glyceryl/Lauryl) Glyceryl Lauryl Dimethicone; Caprylic/Capric Triglyceride	NA	-	~4	(1)	NA	-	NA	-	NA	NA	NA	NA	-
nonionic	**silicone derivatives**	W/o Emulsifiers	Bis-PEG/PPG-14/14 Dimethicone; Dimethicone	NA	-	~5	(1)	NA	-	NA	-	Yes	Yes	-	NA	(2)
nonionic	**silicone derivatives**	O/W	Bis-PEG/PPG-16/16 PEG/PPG-16/16 Dimethicone;	NA	-	~10	(1)	1.5 – 3.0	(2)	NA	-	Yes	Yes	Yes	NA	(2)

General information						Properties						Texture				
Classification 1	Classification 2	Type	INCI name	Price ($/Kg)		HLB		Usage concen-tration		CMC (M) - 25°C		Cream	Lotion	Spray	Gel	
			Caprylic/Capric Triglyceride													
nonionic	**silicone derivatives**	W/o Emulsifiers	Cetyl PEG/PPG-10/1 Dimethicone	NA	-	~5	(1)	NA	-	NA	-	Yes	Yes	-	NA	(2)
nonionic	**silicone derivatives**	O/W	Polyglyceryl-6 Stearate; Polyglyceryl-6 Behenate	NA	-	~13	(1)	NA	-	NA	-	NA	NA	NA	NA	-
nonionic	Sorbitans	NA	Sorbitan isostearate	NA	-	4.7	(7)	NA	-	NA	-	NA	NA	NA	NA	-
nonionic	Sorbitans	O/W	Sorbitan Laurate	NA	-	~9	(1)	NA	-	6.13E-05	(6)	NA	NA	NA	NA	-
nonionic	Sorbitans	NA	Sorbitan Monopalmitate	NA	-	6.7	(7)	NA	-	NA	-	NA	NA	NA	NA	-
nonionic	Sorbitans	NA	Sorbitan Monostearate	12.5	(9)	4.7	(7)	NA	-	NA	-	NA	NA	NA	NA	-
nonionic	Sorbitans	NA	Sorbitan Oleate (and) Polyglyceryl-3 Polyricinoleate	NA	-	3.5	(7)	NA	-	NA	-	Yes	Yes	NA	NA	(7)
nonionic	Sorbitans	W/o Emulsifiers	Sorbitan sesquioleate	NA	-	3.7	(7)	NA	-	NA	-	NA	NA	NA	NA	-
nonionic	Sorbitans	W/o Emulsifiers	Sorbitan trioleate	NA	-	1.8	(7)	NA	-	NA	-	NA	NA	NA	NA	-
nonionic	Sorbitans/ Polyglycerol esters of fatty acids	W/o Emulsifiers	Sorbitan Oleate	16.2	(9)	4.3	(7)	NA	-	NA	-	Yes	Yes	NA	NA	(7)
nonionic	Sucrose ester	NA	Sucrose Distearate	NA	-	3	(7)	NA	-	NA	-	Yes	NA	NA	NA	(7)
nonionic	Sucrose ester	O/W	Sucrose Polystearate(and) CetylPalmitate	NA	-	10	(3)	2 –5	(3)	NA	-	Yes	Yes	Yes	Yes	(3)
nonionic	Sucrose ester	O/W	Sucrose Polystearate(and) Hydrogenated Polyisobutene	NA	-	10	(3)	1 –5	(3)	NA	-	Yes	Yes	Yes	Yes	(3)
nonionic	Sucrose ester	O/W	Sucrose Stearate	NA	-	~ 13	(1)	NA	-	NA	-	NA	NA	NA	NA	-
nonionic	Sucrose ester	NA	Sucrose Stearate	NA	-	14.5	(7)	NA	-	NA	-	NA	NA	NA	NA	(7)

General information						**Properties**						Texture				
Classification 1	**Classification 2**	**Type**	**INCI name**	**Price ($/Kg)**		**HLB**		**Usage concen-tration**		**CMC (M) - 25°C**		**Cream**	**Lotion**	**Spray**	**Gel**	
nonionic	Sucrose ester	NA	Sucrose Stearate (and) Sucrose Distearate	NA	-	12	(7)	NA	-	NA	-	NA	NA	NA	NA	(7)
Anionic	Sulfo-succinates	O/W	Disodium CetearylSulfosuccinate	NA	-	31	(3)	0.25 –1.5	(3)	NA	-	Yes	Yes	Yes	Yes	(3)

References: (1) Evonik industries. Personal Care Catalog of products. 2015, (2) Evonik Industries. Emulsifiers for Skin Care Applications. March 2008. Essen - Germany, (3) BASF. Emulsifiers & Cream Bases. May 2016, (4) Rosen, M.J., 2004. Surfactants and interfacial phenomena, Third. ed. John Wiley & Sons, Inc, New York. doi:10.1016/0166-6622(89)80030-7, (5) Hait, S.K., Moulik S. P., Determination of critical micelle concentration (CMC) of nonionic surfactants by donor-acceptor interaction with Iodine and correlation of CMC with hydrophile-lipophile balance and other parameters of the surfactants, American Oil Chemists' Society (AOCS), 2001. doi: 10.1007/s11743-001-0184-2, (6) Kim, C., Hsieh, Y-L., Wetting and absorbency of nonionic surfactant solutions on cotton fabrics, Colloids and Surfaces A Physicochemical and Engineering, 2001, DOI: 10.1016/S0927-7757(01)00653-7, (7) Croda datasheet, (8) Evonik datasheet, (9) Making cosmetics - ingredient supplier information

G. Droplet size distribution frequency for the emulsion prototypes

This annex presents the droplet size distribution frequency for the emulsion prototypes prepared in the experimental section of Chapter 4. The Figures present both: the frequency histogram and the accumulated.

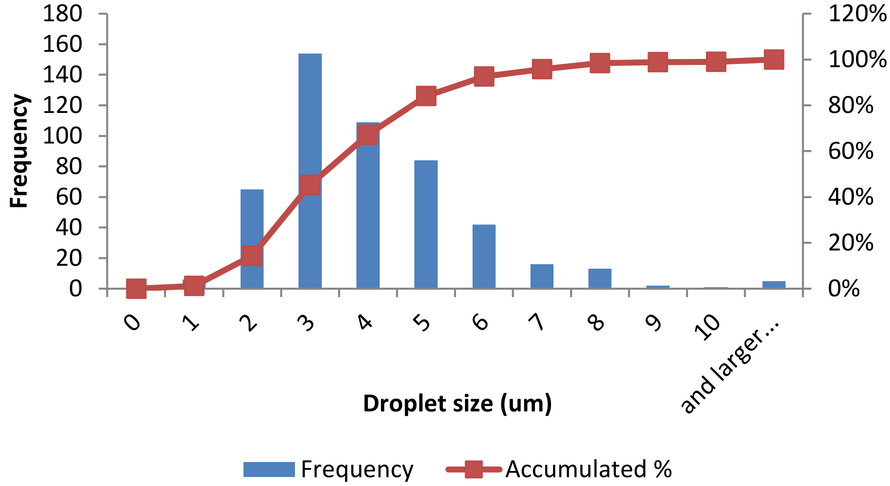

Figure G-1 - Droplet size frequency distribution for Prototype 1

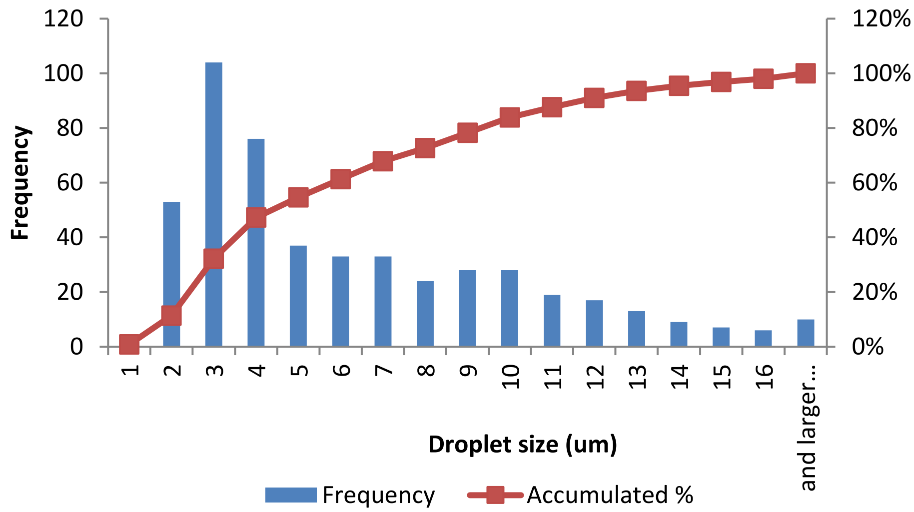

Figure G-2 - Droplet size frequency distribution for Prototype 2

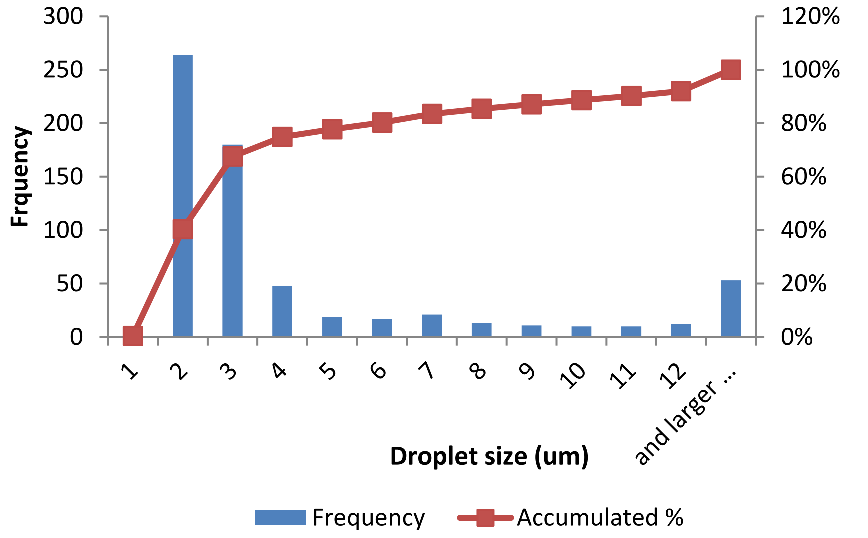

Figure G-3 - Droplet size frequency distribution for Prototype 3

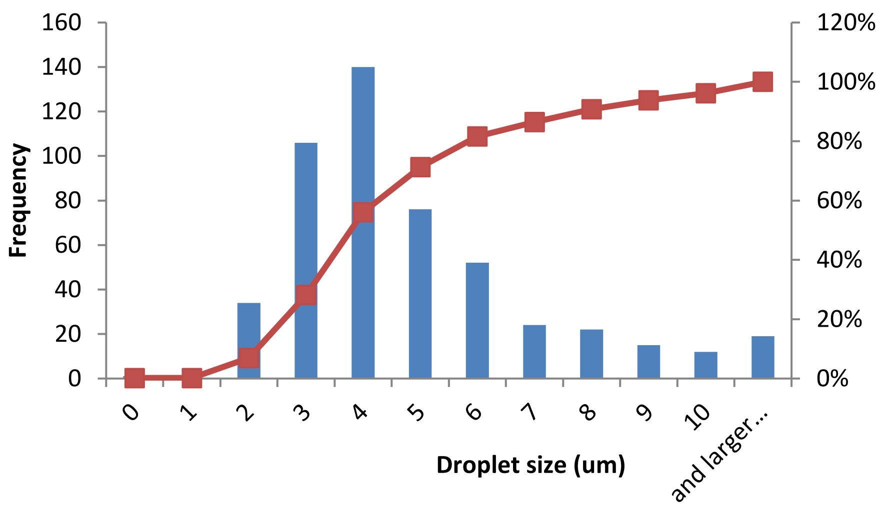

Figure G-4 - Droplet size frequency distribution for Prototype 4

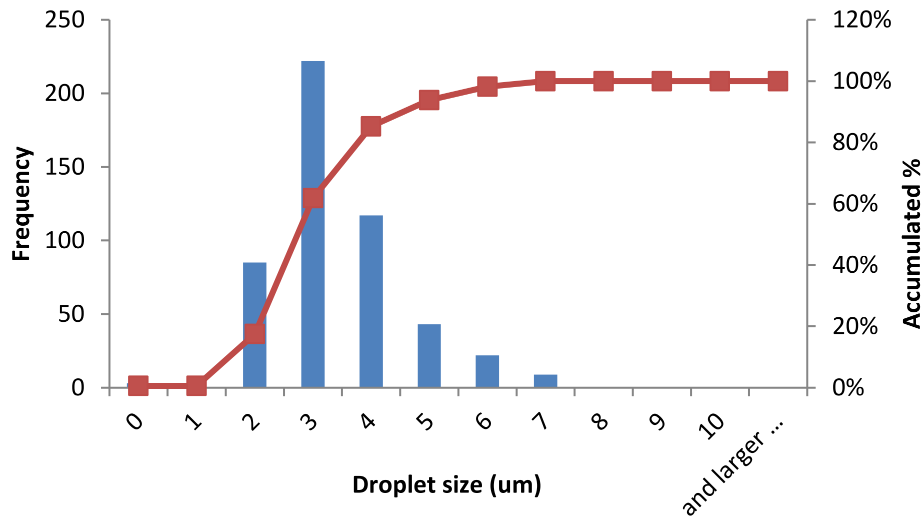

Figure G-5 - Droplet size frequency distribution for Prototype 5

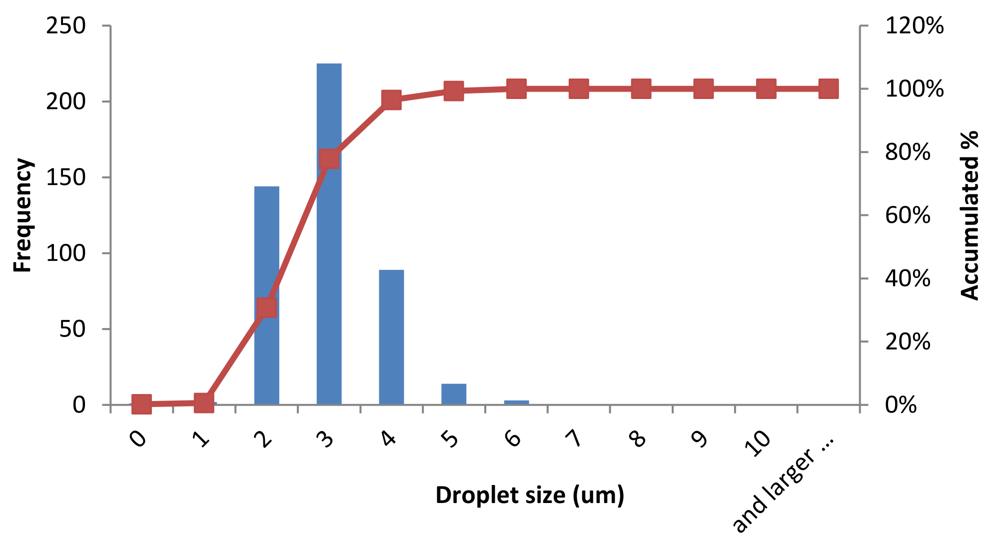

Figure G-6 - Droplet size frequency distribution for Prototype 6

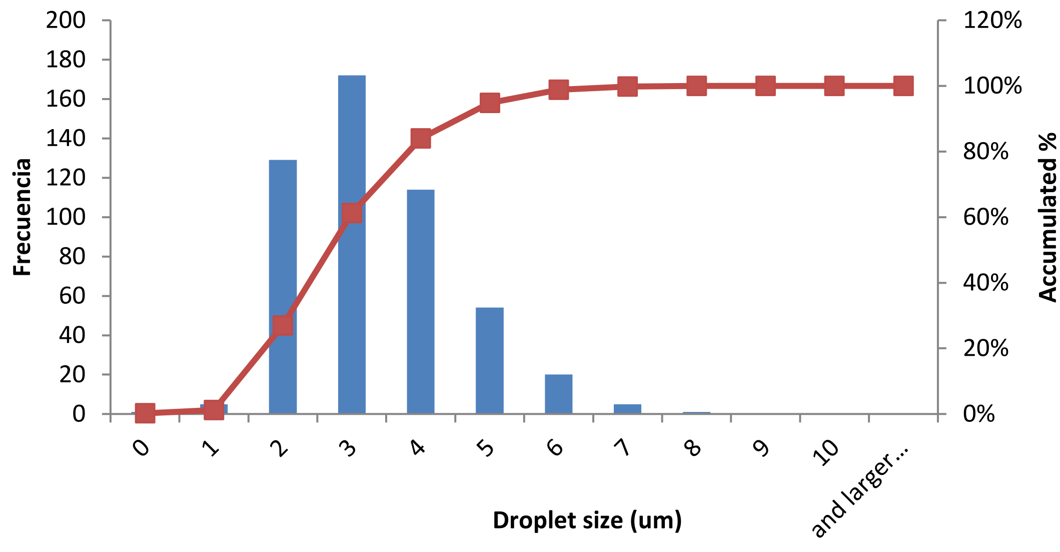

Figure G-7 - Droplet size frequency distribution for Prototype 7

H. Short version of the document in English and french

Methodological approach for the sustainable design of structured chemical products during early design stage

Emulsion based chemical products, which belong to the category of micro-structured chemical products, have a broad range of commercial applications. Despite their importance, there is not a general methodology for their design. With the aim to contribute to the progress on this matter, this research presents a product design methodology focused on emulsion design with the following characteristics: it proposes methods for customer needs analysis, product ideas generation and selection of the best product alternative. It considers the multivariate nature of emulsion design by taking into account the multiple effects of design variables into product properties. It integrates sustainability concepts into the product design process.

The methodology comprises three design stages: needs stage, ideas generation stage and ideas selection stage.

In the needs stage, customer needs are first analyzed and classified according to their effect on customer satisfaction and second translated into product specifications with the aid of experts and customers. The input is customer needs, i.e., statements expressing customers' desires about the product, and the output corresponds to product specifications, i.e., product characteristics that can be measured. To perform this stage two methods are used: Kano model and Quality Functional Deployment.

In ideas generation stage, product concepts accomplishing product specifications are generated in three sub-steps: First, problem specifications are classified into a predefined group of design sub-problems. Second, each sub-problem is connected with one or more pre-defined solution strategies through a prefilled relational matrix. Third, compatible solution strategies are selected and connected to ingredients and processing conditions through a second relational matrix. As result, a set of product concepts is generated. This

procedure is developed by the implementation of two relational matrices proposed in this research based on emulsion science and expert knowledge. The first connects sub-problems with solution strategies and the second connects solution strategies with ingredients and processing conditions.

In the selection stage, generated product concepts are evaluated according to product specifications. In addition, appropriated sustainability indicators are included to assess and rank product alternatives according to a global sustainability index. To perform this stage, a set of indicators are selected and integrated by the implementation of multi-criteria analysis methods.

The application of the methodology is exposed with a case study: the design of a moisturizing cream.

Key words: Chemical Product Design, Design Methodology, Customer Needs, Emulsion design, Sustainability, Cosmetic Products

Approche méthodologique pour la conception durable de produits chimiques structurés dans les premières phases de la conception

En raison de la compétitivité dans le marché des produits chimiques et la demande croissante pour les produits de qualité, l'industrie et l'académie sont à la recherche de nouvelles méthodes pour la conception des produits chimiques. Par conséquent, cette étude propose une approche méthodologique pour faciliter la prise de décisions dans la conception de produits de type émulsion. Les caractéristiques de la méthodologie proposée sont les suivantes: elle propose des méthodes pour l'analyse des besoins de consommateurs, la génération d'idées pour la conception du produit et la sélection du meilleur produit, en prenant en compte la nature multi- variée du problème de conception avec l'intégration de la notion de durabilité dans le processus de conception.

La méthodologie comporte trois étapes de conception: Étape de besoins, étape de génération d'idées et étape de sélection d'idées.

Dans la première étape, les besoins sont analysés et classifiés en fonction de leur impact sur la satisfaction du client. Ensuite, ils sont traduits aux spécifications du produit avec l'aide des experts et des clients. Les informations de saisie correspondent aux besoins des clients et celles de sortie correspondent aux spécifications du produit, c'est-à-dire des caractéristiques du produit qui peuvent être évaluées. Également, deux méthodes sont utilisées: le modèle de kano et la méthode QFD (Déploiement des Fonctions Qualités).

Dans la seconde étape, les produits répondant aux spécifications sont conçus en suivant une démarche en trois phases: 1) le problème de conception est divisé selon un groupe défini de sous-problèmes généraux. 2) Chaque sous-problème est connecté à un groupe de stratégies de solution selon une première matrice de décision prédéfinie. 3) Les stratégies de solution sont connectées avec des ingrédients et des conditions opératoires selon une deuxième matrice de décision. Cette démarche est faite en utilisant deux matrices

de décision développées dans cette recherche sur la base de la connaissance de science d'émulsion, ainsi que sur des connaissances des experts.

Dans la troisième étape, les alternatives de produit sont évaluées selon le cahier de spécifications définis dans la première étape et les indicateurs de durabilité appropriés. Ces indicateurs sont utilisés pour évaluer et classer les alternatives de produit selon un indice de développement durable global. Pour développer cette étape un ensemble d'indicateurs évaluant la dimension économique, environnementale et sociale de produits est choisi et ils sont intégrés par la mise en œuvre d'une méthode d'analyse de multi-critère.

Finalement, afin d'illustrer la méthodologie, une étude de cas est développée: la conception d'une crème hydratante.

Mots clés : Conception de Produit Chimique, Méthodologie de Conception, Besoins, Conception d'Émulsion, Durabilité, Produits Cosmétiques