Natural triphasic essence with light and velvety touch without silicone and mineral oil.

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Abstract

For cosmetics, triphases are a technology that has existed for several years. They are composed of 3 distinct phases (1 aqueous phase and 2 oily phases). Very often, oily phases of these galenic forms include a significant proportion of silicones (dimethicone), mineral oils (paraffin oil) or their derivatives. On one hand, silicones are among the controversial ingredients because they are derived from chemical synthesis and are not easily biodegradable, which implies a negative impact on the environment. On the other hand, the mineral oils are fats of fossil origin (petroleum and coal), in fact, they are polluting and not easily biodegradable. Moreover, they may contain carcinogenic residues and are also suspected of being comedogenic.

Finding alternatives to these controversial ingredients is therefore of importance to meet consumer’s needs in terms of health and environment protection. **We thus developed a triphase on a natural basis containing neither silicone nor mineral oil.**

Before starting the practical study, we studied the physical mechanisms allowing to obtain a triphase galenic such as interfacial tension, the polarity of phases and the density of the phases. Then, we worked on the selection of the components and on the improvement of the interfaces with 3 great stages:

- Find a natural **low density non polar oil**: we selected alkanes which are cosmetic ingredients used in particular for their very light sensory properties similar to those of silicones. These raw materials are non-polar and have low density, so we sourced them and added them in a biphasic formula made castor oil and water.

The immiscibility of water, castor oil and alkanes allowed us to obtain three phases.

- Find a **high density polar oil** combination to constitute the middle phase: we selected the castor oil known to have these two properties. Then, in order to lighten the sensoriality, we tried to mix the castor oil with another vegetable oil. For this, we tested different ratio of castor oil / sunflower oil until we found the threshold below which the percentage of castor oil could not be decreased without loosing the visual of the three phases. This allowed us to show that the most optimized weight ratio of castor oil to other vegetable oil s between 3:2 and 4:1.
- **Improving the interfaces**: we selected two types of raw materials to improve the interfaces of our product: sodium chloride and glycerin. Indeed, during our studies on the biphases we had noticed a real improvement of the interfaces thanks to the sodium chloride. Due to the high density of Glycerin, it allowed to increase the density of the aqueous phase. So, the difference in density between the aqueous phase and the oily phase 1 is more important. Thus, it improved the interface between these 2 phases. To find the optimal amount of sodium chloride and glycerin we screened at different percentages of each of these two materials. With 1% sodium chloride and 10% glycerin we were able to obtain visibly flatter interfaces.

Then, we used this base (water + sodium chloride + glycerin/castor oil + sunflower oil/alkane) to develop a triphasic face essence with more than 99% of natural ingredients that we have patented. After optimization, we found the ideal proportions to obtain a velvety and light texture when applied: 8:1:1 (aqueous phase/oily phase 1/oily phase 2).

Consumer testing result on 34 women aged 22 to 61, all skin types, in Asia, immediately after application of the product showed that 97% of the panel said that the triphase formula was easy to apply and 91% found the formula to be the perfect blend for preparing the skin to receive daily cares.

This development allowed us to stop using raw materials that are dangerous for humans and the environment while maintaining the sensoriality expected by the consumer. Based on this success in developing a natural-based triphase, new applications can be envisioned such as make-up remover.

1. Introduction

Triphase technology has been around for many years but most formulas on the market contain controversial raw materials that are harmful to the environment and to humans. Indeed, most often at least one of the phases contains silicone or mineral oils or their derivatives.

The chemical synthesis used to obtain silicones makes them not easily biodegradable polymers, so they are harmful to the environment [1]. As for mineral oils, they are fats of fossil origin (petroleum and coal). Therefore, they are polluting and not easily biodegradable [2]. Moreover, they may contain carcinogenic residues and are also suspected of being comedogenic [3].

In this new era where the consumer and nature are at the heart of our concern, we wanted to develop a natural formula, respectful of man and the environment. For that we looked at replacing the synthetic raw materials classically used in these galenics.

The principle of the triphasic formula is based on the non-miscibility of the phases. The phases must mix when the product is agitated and then separate and return to the initial state when it is at rest. It is the immiscibility of the phases, the important difference in density and the important difference in polarity of the phases that allow the constitution of a multiphase product.

After a study of the three-phase products of the competition, it was decided to start from a texture having an aqueous lower phase (constituted of water), an oily intermediate phase (constituted of castor oil) and an oily upper phase (whose composition was not known at the beginning).

The first step was to screen the raw materials for the upper phase. Then, studies were conducted to improve the sensoriality of the intermediate phase. The research continued with the aim of obtaining better quality interfaces (flatter and neater). Finally, we tried to improve the sensoriality of our galenic by playing with the phase ratios.

All these trials have allowed us to develop a three-phase galenic for the brand L'Occitane en Provence, whose technology we have patented. Consumer tests were conducted in order to evaluate the appreciation of our formula with more than 99% of ingredients of natural origin without silicones or mineral oils.

2. Materials and Methods

2.1. Raw material screening

2.1.1. Ester / castor oil / water miscibility

The first researches on the competition triphases determined that the best raw material for a natural intermediate phase is castor oil because it is very dense and very polar. Moreover, it's immiscible with water, which is the lower phase of the formula.

Thereafter, researches on esters were carried out in order to select those with a low density. The goal was to find an ester immiscible with castor oil. Low density esters of natural origin were selected and added to 30% in a bi-phasic formula containing 30% castor oil and 40% water. Lines were drawn on the transparent glass containers at the level of each phase in order to ensure that there is no migration of one part of a phase to another during mixing. The formula was then stirred with a blender for 30 seconds at 300 rpm (revolutions per minute). The formula was then left to rest for 3 hours in order to observe or not the good separation of the phases.

2.1.2. Alkane / castor oil / water miscibility

The density but also the polarity of the oils play a key role in the construction of a triphase. The further apart the densities and polarities of the oils are, the less miscible the phases are. The tests focused on alkanes, natural oily raw materials, low density and apolar unlike castor oil.

Several alkanes were tested at 25% in a biphasic formula containing 25% castor oil and 50% water. Lines were drawn on the transparent bottle as in the previous experiment to ensure that there was no migration between the alkane and the castor oil. The formula was stirred at 300 rpm for 3 minutes and then left to stand for 3 hours before observing the results.

2.2.Modification of the sensoriality of the intermediate phase

2.2.1. Castor oil substitution

Tests were conducted to substitute castor oil, which is very greasy and viscous, in order to lighten the sensoriality of the formula.

Three types of raw materials were tested to replace castor oil. On one hand, the esters of high density. On the other hand, esters and polar vegetable oils [4].

The most interesting candidates were incorporated up to 25% in a formula containing 50% water and 25% alkane. As in the previous tests, lines on the transparent bottles were used to mark the level of each phase before stirring to ensure that there was no migration between the two oil phases during mixing. Stirring was done under a mixer at 300 rpm for 3 minutes. Then the formula was left to rest for 3 hours before observing the results.

2.2.2. Mixing castor oil with another vegetable oil

With this idea in mind to lighten the intermediate fatty phase consisting of castor oil, new tests have been conducted to replace a part of this castor oil by another vegetable oil with a lighter sensory.

To begin with, only 10% of the castor oil was substituted by argan oil, then other ratios were tested up to 40% argan oil for 60% castor oil. The study was conducted first on argan oil and then on other vegetable oils.

To carry out these tests, mixtures of castor oil / other vegetable oil are prepared in beakers, stirred at 500 rpm for 5 minutes. Then each mixture is added at 25% to a formula consisting of 50% water and 25% alkane. Lines were drawn on the containers to ensure that there was no transfer from one oil phase to the other. The formulas were shaken for 3 minutes at 300 rpm, then we left them to rest for 3h before observing the results of the phase shifts.

2.3. Interfaces improvements

2.3.1. Influence of soduim chloride on the interfaces

According to the literature research that has been conducted, the addition of sodium chloride ($NaCl$) in the aqueous phase could improve the interfaces of the product. Indeed, the sodium chloride is a material allowing to increase the density of the aqueous phase, it allows to increase the difference of density between the aqueous phase and the intermediate oily phase. Moreover, the sodium chloride increases the surface tension of water. The lower the interfacial tension between two immiscible liquids, the less external energy is required to form a stable emulsion. Thus, in order to form a multiphase product the interfacial tension must be as high as possible [5]. So sodium chloride should help to improve the interfaces and phase separation.

Premixes were made at different percentages of calcium chloride (NaCl) in the aqueous phase to see the impact in the triphase formula composed of 50% aqueous phase (water + sodium chloride), 35% intermediate oil phase (castor oil + other vegetable oil), 15% alkane (upper phase).

The premix of water and NaCl was made in a beaker under agitation until complete dissolution of sodium chloride. Then the three-phase formula was stirred for 3 minutes at 300 rpm. The formula was put to rest for 3h before observation of the results.

2.3.2. Influence of glycerin on the interface Water / castor oil

Glycerin was tested in order to improve the interface between the water phase and the intermediate oil phase of the product. Indeed, glycerin has a higher density than water, the addition of this raw material in the aqueous phase could improve the interfaces by increasing the density difference between the lower phase (aqueous) and the intermediate phase (oily).

As in the previous experiment, glycerin was added to water at various percentages and stirred until it was homogeneous. Then, this mixture was used to form a triphase containing 50% water phase (water + glycerin), 25% oil intermediate phase (castor oil) and 25% oil upper phase. The triphasic formula was stirred at 300 rpm for 3 minutes and then left to rest for 3 hours.

2.4. Improvement of the sensoriality of the formula

After selecting the best natural raw materials to obtain a triphase with clear interfaces, it was decided to vary the ratios of the different phases in order to obtain the best sensoriality to develop a face lotion. Several ratios were tested until an optimal touch formula was obtained. In order to evaluate the touch, the formula was shaken and applied on the back of the hand.

2.5. Consumer test : texture evaluation

A new texture was developed by L'Occitane en Provence with the key ingredients necessary for the development of a natural triphase. This product was then evaluated during a consumer test in Thailand. The test took place over 4 weeks on a panel of 34 women aged 22 to 61. The product must be applied under the following conditions: Shake before use. Spray a minimum of 3 doses directly on face or in the palm of your hand to pat on skin right after. The product can be applied on cleansed skin or after your toner or lotion on morning and evening, before your usual care routine.

User testing questions adapted to the product, elaborated by the monitor of the study, were completed by each subject at application, immediately after application, after 1 day of use, after 7 consecutive days of use and after 28 consecutive days of use. The evaluation parameters are assessment scores and the descriptive analysis is in percentage of satisfied test subjects.

Panelists were also asked about their overall satisfaction rate, their purchase intention and the overall rating they would give the product.

3. Results

3.1. Raw material screening

3.1.1. Ester / castor oil / water miscibility

Two low density esters were tested to obtain a triphase: Dicaprylyl Ether with a density of 0.80 and Coco-Caprylate/Caprate with a density of 0.86. The table below shows the results obtained.

		Percentage of use (%)	
Upper phase composition	*Dicaprylyl Ether*	20	
	Coco-Caprylate/Caprate		20
Intermediate phase composition	Castor oil	30	30
Lower phase composition	Osmosis water	50	50
Results after stirring		Biphase	Biphase

Table 1 : Result of low density esters screening

The results show that despite the low density of these esters, the 2 oil phases are miscible, creating a biphase.

3.1.2. Alkan / castor oil / water miscibility

Four alkanes were tested for the purpose of obtaining a triphase in combination with castor oil and water:

- Undecane & Tridecane (density of 0.75)
- C15-19 Alkane (density of 0.77)
- Coconut Alkanes & Coco Caprylate/Caprate (specific gravity 0.76)
- C13-15 Alkane (specific gravity 0.77)

The results are compiled in the table below:

		Percentage of use (%)			
Upper phase composition	*Undecane & Tridecane*	25			
	C15-19 Alkane		25		
	Coconut Alkanes & Coco Caprylate/Caprate			25	
	C13-15 Alkane				25
Intermediate phase composition	Castor oil	25	25	25	25
Lower phase composition	Osmosis water	50	50	50	50
Results after stirring		Triphase (but migration between oil phases)	Triphase	Triphase	Triphase

Table 2: Results of alkan screening

The results show that alkanes are good candidates for triphase formulation. They are natural raw materials, allowing good phase separation after stirring. C15-19 Alkane is selected as the top phase for further formulation trials.

3.2.Modification of the sensoriality of the intermediate phase

3.2.1. Castor oil substitution

In this experience, several raw materials were tested. First, three high density esters:

- *Dibutyl Adipate* (density = 0.96)
- *C12-15 Alkyl Benzoate* (density = 0.93)
- *Caprylic/Capric/Succinic Triglyceride* (density = 1.01)

Next, 3 high polarity esters:

- *Isostearyl Neopentanoate*
- *Isodecyl Oleate*
- *Isocetyl Stearate*

Then four vegetable oils of high polarity:

- Olive oil
- Macadamia oil
- Jojoba oil
- Wheat germ oil

		Percentage of use (%)										
Upper phase composition	*C15-19 Alkane*	25	25	25	25	25	25	25	25	25	25	25
Intermediate phase composition	*Dibutyl Adipate*	25										
	C12-15 Alkyl Benzoate		25									
	Caprylic/Capric /Succinic Triglyceride			25								
	Isostearyl Neopentanoate				25							
	Isodecyl Oleate					25						
	Isocetyl Stearate						25					
	Olive oil							25				
	Macadamia oil								25			
	Jojoba oil									25		
	Wheat germ oil										25	
Lower phase composition	Osmosis water	50	50	50	50	50	50	50	50	50	50	50
Results after stirring		Biphase	Biphase	Biphase	Biphase	Biphase	Biphase	Biphase	Biphase	Biphase	Biphase	Biphase

Table 3 : Results of tests on the substitution of castor oil by esters or other vegetable oils

The results show that neither high density esters nor polar oils or esters can totally replace castor oil because after stirring the two oil phases mix, we obtain biphases.

3.2.2. Mixing castor oil with another vegetable oil

In this test phase, several vegetable oils were tested to substitute part of the castor oil.

		Percentage of use (%)									
Upper phase composition	*C15-19 Alkane*	25	25	25	25	25	25	25	25	25	25
Intermediate phase composition	Castor oil	22,5	20	17,5	16,25	15	16,25	16,25	16,25	16,25	16,25
	Argan oil	2,5	5	7,5	8,75	10					
	Sunflower oil						8,75				
	Sweet almond oil							8,75			
	Rapeseed oil								8,75		
	Grappe seed oil									8,75	
	Avocado oil										8,75
Lower phase composition	Osmosis water	50	50	50	50	50	50	50	50	50	50
Results after stirring		Triphase	Triphase	Triphase	Triphase	Triphase (but migration between oil phases)	Triphase	Triphase	Triphase	Triphase	Triphase

Table 4 : Results of the tests of substitution of a part of castor oil by other vegetable oils

The table above shows that it is possible to replace part of the castor oil by other vegetable oils up to a maximum of 35% of the intermediate phase in order to lighten its sensoriality.

3.3. Interfaces improvements

3.3.1. Influence of sodium chloride on the interfaces

Sodium chloride (NaCl) was tested at different percentages to evaluate the impact on the triphase interfaces. The results are compiled in the table below:

		Percentage of use (%)										
Upper phase composition	*C15-19 Alkane*	25	25	25	25	25	25	25	25	25	25	25
Intermediate phase composition	Castor oil	16,25	16,25	16,25	16,25	16,25	16,25	16,25	16,25	16,25	16,25	16,25
	Sunflower oil	8,75	8,75	8,75	8,75	8,75	8,75	8,75	8,75	8,75	8,75	8,75
Lower phase composition	Osmosis water	50	49,5	49	48,5	48	47,5	47	46,5	46	45,5	45
	NaCl	0	0,5	1	1,5	2	2,5	3	3,5	4	4,5	5
Results after stirring (interface appearance between lower and intermediate phase)		Curved interface	Slightly curved interface	Flat interface	Flat interface	Flat interface	Flat interface	Very flat interface	Very flat interface	Very flat interface	Very flat interface	Very flat interface

Table 5 : Influence of sodium chloride addition in the triphase

During these tests, it was observed that the sodium chloride allows to obtain a flatter interface between the intermediate phase and the lower phase, for this, the best is to add between 1 and 5% of sodium chloride.

3.3.2. Influence of glycerin on the interface water / castor oil

Glycerin is tested at different percentages in the aqueous lower phase. The tests and the results are shown in the table below:

		Percentage of use (%)								
Upper phase composition	*C15-19 Alkane*	25	25	25	25	25	25	25	25	25
Intermediate phase composition	Castor oil	25	25	25	25	25	25	25	25	25
Lower phase composition	Osmosis water	50	49	48	47	46	45	40	35	30
	Glycerin	0	1	2	3	4	5	10	15	20
Results after stirring (interface appearance)		Curved interface	Flat interface	Flat interface	Flat interface	Flat interface	Very flat interface	Very flat interface	Very flat interface	Very flat interface

Table 6 : Influence of glycerin addition in the triphase

The results show that the higher the percentage of glycerin, the flatter the interface.

3.4.Improvement of the sensoriality of the formula

In order to have a product with a light sensoriality for a face lotion application, several ratios were tested. On one hand, the intermediate phase being the richest, it was decided to reduce it as much as possible while keeping an aesthetic visual. On the other hand, the watery phase being the lightest, its percentage was increased. As for the upper phase, it is the lightest fatty phase, but still brings richness to the formula, therefore, it was reduced to lighten the sensoriality but still allowing to keep an aesthetic visual.

		Percentage of use (%)				
Upper phase	20	25	15	10	10	5
Intermediate phase	20	15	15	15	10	5
Lower phase	60	60	70	75	80	90
Sensory and visual results	Aesthetic appearance but texture too greasy	Aesthetic appearance but texture too greasy	Aesthetic appearance but texture too greasy	Aesthetic appearance and light texture	Aesthetic appearance and light texture	Non-aesthetic apparence but light texture

Table 7 : Influence of the phase ratio on the sensoriality of the triphase

The results show that the optimal ratio of this formula for a face lotion allowing to have an aesthetic visual with 3 distinct phases and an adequate sensoriality is between 75%/15%/10% and 80%/10%/10% (lower aqueous phase / intermediate oily phase / upper oily phase).

Indeed, the use of these ratios allow to have a fresh and velvety texture to the application which penetrates quickly.

3.5. Consumer test: texture evaluation

Only the results of the consumer test "during application" are shown in the table below because 38 other items were evaluated immediately after application, after 1 day of use, after 7 days of use and after 1 month of use. But this study was too large to be included in this report.

The results of our consumer test showed that our triphase texture is appreciated by consumers, the texture is easy to apply (97%) penetrates quickly (97%), provides a nourishing and fresh effect (97%). In addition, 94% of panelists said that the triphase offers a surprising sensory experience.

	% of subjects (agree / rather agree)
	At the application
The triphase formula is easy to apply	97%
The triphase formula offers a surprising sensorial experience	94%
The triphase formula fastly penetrates into the skin	97%
The triphase formula offers yet nourishing feeling, yet still offering a fresh finish	97%
The triphase formula seems to be the perfect blend for preparing the skin to receive following daily cares	91%
Complexion looks like fresh	91%

Table 8 : Results of consumer tests during the application of the product

Finally, the overall satisfaction rate and the purchase intention of the consumers are both 94%. And the overall product rating is 8.8/10.

4. Discussion and Conclusion

The various tests have shown that for the formulation of a triphasis composition, several conditions are necessary: to have an upper phase consisting of an alkane because they are raw materials apolar with a low density, to have an intermediate phase containing a minimum of 65% castor oil because it is polar and a high density. These two phases are both oily but the significant difference in polarity and density between them allows the non-miscibility of the blend. The last condition is to have an aqueous phase containing sodium chloride and glycerin in sufficient quantity to improve the interfaces of the product and to allow a good phase separation after stirring.

It is then possible to vary the ratios of each phase in different proportions in order to have the sensoriality required. For the face lotion developed in the laboratories of L'Occitane en Provence, we were looking to have the lightest possible sensoriality while keeping an aesthetic visual, for that the ratios must be included between 75%/15%/10% and 80%/10%/10% (lower aqueous phase / intermediate oily phase / upper oily phase).

All these researches have allowed us to develop a triessence formula with an adequate sensoriality, with more than 99% of ingredients of natural origin, without silicone or mineral oils, resulting to the technology being patented.

As a result of this research, we imagined that we could develop a triphasic formula for a make-up remover application. Indeed, by increasing the ratio of the oil phases, and by adding a surfactant in quantity lower than its critical micellar concentration, it could be possible to preserve the visual of the three phases. Micelle nor emulsion will be form during the mixing and a make-up removing power will be added to the product.

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