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(54) Title: IMPROVED QUICK BREAKING WATER-IN-OIL EMULSION

(57) Abstract: Disclosed is a quick-breaking water-in-oil emulsion with an improved quick breaking effect.

WO 2020/227909 A1

## **An improved quick breaking water-in-oil emulsion**

### **Technical field**

The present invention belongs to the cosmetic field, and specifically relates to an improved quick breaking water-in-oil emulsion.

### **Background art**

In general, emulsions are understood as heterogeneous systems, which consist of at least two liquids, which are immiscible or have only a limited miscibility with one another and are usually referred to as phases. In an emulsion, one of the two liquids (water or oil) is dispersed in the form of very fine droplets in the other liquid (oil or water, respectively). In an emulsion the droplets (pure liquids or as solutions) are present in a more or less fine distribution. In general, without an emulsifier an emulsion is only of a limited stability.

Water-in-oil emulsions are characterized in that watery droplets are dispersed in a continuous oil phase. A Water-in-oil emulsion may be abbreviated as W/O emulsion. Both expressions are used synonymously in this specification. "Quick-breaking" means that shear forces acting upon a water-in-oil emulsion by distributing a suitable amount of the respective emulsion preparation on the skin and/or massaging the preparation in the skin, will decompose or "break" the emulsion and watery or milky droplets are released. The release of such droplets results in a refreshing and cooling effect.

Prior art already discloses water-in-oil emulsions being described as "quick-breaking". Water-in-oil emulsions according to CN 104968318 A, being classified as quick-breaking, contain specific emulsifiers, namely Amodimethicone Glycerocarbat and/or Diisostearoyl Polyglyceryl-3 Dimer Dilinoleat. Said emulsions are free from polyethylene glycols or derivatives of polyethylene glycols.

In JP 5477883 B2 a water-in-oil type emulsion composition is described. According to the teaching of this invention two different surfactants are necessary, namely a hydrophilic one and a lipophilic one, to stabilize the emulsion. The powders contained are hydrophobic powders or the powders after a hydrophobization treatment.

The product Nivea Men Hydration Water Burst Serum (Mintel number 3478277) is a W/O-emulsion characterized by a "quick-breaking" upon usage. The product contains the emulsifier Lauryl-PEG-9 Polymethyl siloxyethyl dimethicone. The product is available in China since September 2015.

The product Skin Nutrient Goat's Milk Magic Touch produced by the company Australia Health Research & Development Group contains the emulsifier PEG/PPG-10/1 dimethicone and is a quick-breaking emulsion.

An analysis of quick-breaking W/O-emulsions was published in 2008 (Personal Care, Hai Zhou Zhang, et. al., March 2008, page 45). All example formulations disclosed therein contain the emulsifier ABIL EM 90 (cetyl PEG/PPG-10/1 dimethicone).

Water in oil emulsions with quick breaking effect provide a special application experience for the consumer. During application watery (aqueous) or milky droplets become apparent. However, sometimes a perfect breaking effect is difficult to achieve. If the breaking effect is occurring too slowly or only to a small extent, the consumer will not notice the effect of quick-breaking water-in-oil emulsions, namely the watery or milky droplets leading to a cooling and/or a refreshing effect. Furthermore, if the droplets are too small or too big, the visual and tactile impression is not perfect.

Quick-breaking W/O emulsions usually contain a large amount of water and are very sensitive to changing temperatures and shearing forces; this is the reason why such emulsions break and separate, then showing watery or milky droplets during the massage on skin.

To improve the breaking effect, the amount of water contained in such emulsions may be increased; however this results in compositions, which are more unstable. To improve the stability, in general more oily components are added and the amount of water is reduced. This will lead to a worsening of the quick-breaking effect and a sensory impression of oiliness and greasiness after application of such an emulsion on the skin.

With regard to quick-breaking water-in-oil emulsion provided in form of "milks" or milky lotions the quick-breaking effect has to be optimized. A quick-breaking effect, which is not optimized, may lead to whitish or white residues on the skin after application of such a composition. Consumers do not like this and probably will not rebuy such a product.

Hence, a balance of an optimized quick-breaking effect and a sufficient stability of the compositions has to be achieved. Moreover, after application of the quick-breaking water-in-oil emulsion the skin should feel fresh and/or refreshed without any oiliness or greasiness. Also, the composition itself shall be perceived as a light, pleasant composition.

## **Summary of the invention**

Surprisingly, by the addition of one or more selected powder(s) the quick-breaking water-in-oil emulsions are improved significantly. The quick-breaking effect appears faster and is

more pronounced. Additionally, the sensory impression of the composition itself and the feeling of the skin are improved.

A quick-breaking water-in-oil emulsion containing

- at least one powder material, selected from starch powder, modified starch powder, talc, kaolin and the respective derivatives thereof ,
- an oily phase, containing at least one lipid component, chosen from at least one silicone oil, and/or at least one organic liquid oil,
- an aqueous phase,
- at least one W/O emulsifier, having a HLB value of 2 to 7,

wherein the at least one powder material has

- an average particle size from 1 to 100 micron;
- a specific surface area of 0.05 to 100 m<sup>2</sup>/g;
- an oil absorption rate of 10 to 100 g oil/100 g powder,

could bring about the desirable improvements.

As described above, the quick-breaking water-in-oil emulsion preferably contains

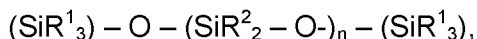
- 0.5 to 10% by weight of at least one powder material,
  - 3 to 20% by weight of an oily phase,
  - 60 to 97% by weight of an aqueous phase,
  - 0.5 to 10% by weight of at least one W/O emulsifier,
- in relation to the total weight of the emulsion.

As described above, the preparation of the present invention is a quick-breaking water-in-oil emulsion. In this application, the preparation, the composition and the emulsion are interchangeably used. By shear forces acting on said emulsion, the emulsion breaks (decomposes) and releases watery or milky droplets. For achieving this, the preparation according to the invention contains a considerable amount of water, namely from 50 to 97 % by weight, preferably 60 to 85 % by weight, in relation to the total weight of the preparation.

Preferably, the preparation according to the present invention is a cosmetic preparation, more preferably intended to stay on the skin (leave-on).

According to the present invention, the quick-breaking water-in-oil emulsion contains an oily phase containing at least one lipid component chosen from silicone oils, and/or organic liquid oils.

Silicone oils are silicones, which are fluid. Silicones may also be named polysiloxanes. Linear polysiloxanes may be described by the following formula



wherein  $\text{R}^1$  and  $\text{R}^2$  independently represent hydrogen, a methyl group, or a C2 to C30 linear saturated or unsaturated alkyl group, a phenyl group and or an aryl group;  $n$  is an integer from 0 to 50,000 and denotes the amount of siloxane units, being represented by the formula in the second bracket of the above shown complete formula.

Preferably, according to the invention the silicone components are represented by the above shown formula, where  $\text{R}^1$  and  $\text{R}^2$  are methyl groups only. Such silicone components are known as dimethicones. Depending on the number of  $n$  dimethicones may be fluid or rubbery semi-solid. According to the invention the silicones have to be fluid, therefore advantageously  $n$  is an integer of 2 to 2000, preferably 10 to 400.

A suitable dimethicone may be purchased as DM 20 from BRB or Xiameter PMX-200 Silicone Fluid 20cSt from Dow Corning, or Edlement14 PDMS 100 from Momentive.

According to the present invention at least one organic liquid oil is contained in the preparation of the present invention. Organic liquid oils may be polar or non-polar ones.

Non-polar oils comprise aliphatic, unbranched hydrocarbons having 12 to 40 carbon atoms, preferably 15 to 19 carbon atoms. Said hydrocarbons may be contained as components being characterized by one specific number of carbon atoms. However, it is preferred, if blends of hydrocarbons having 15 to 19 carbon atoms (e.g. C15-19 alkane) are contained. For example, such a blend may be purchased from Total as Gemseal 40.

Furthermore, non-polar oils comprise branched hydrocarbons having in total 12 to 40 carbon atoms, preferably 12 to 16 carbon atoms. It is preferred, if isohexadecane and/or isododecane are contained in the preparation according to the present invention.

It is more preferred, if combinations of one or more aliphatic, unbranched hydrocarbon(s) having 15 to 19 carbon atoms, especially as a blend, and one or more branched hydrocarbon(s) having in total 12 to 16 carbon atoms are contained in the preparation according to the invention.

Polar oils comprise esters of saturated and/or unsaturated, branched and/or unbranched alkane carboxylic acids with a chain length of from 3 to 20 carbon atoms and saturated and/or unsaturated, branched and/or unbranched alcohols with a chain length of from 1 to 20 carbon atoms, and esters of aromatic carboxylic acids and saturated and/or unsaturated, branched and/or unbranched alcohols with a chain length of from 3 to 20 carbon atoms, with

the proviso that said esters are fluid. Examples for such ester oils are methyl palmitate, isopropyl myristate, isopropyl palmitate and/or C12-15 alkyl benzoate.

Furthermore, the polar oils comprise components of the group of neopentyl glycol diheptanoate, propylene glycol dicaprylate/dicaprate, caprylic/capric/diglycerol succinate, butylene glycol dicaprylate/dicaprate, C12-13 alkyl lactate, di-C12-13 alkyl tartrate, triisostearin, dipentaerythrityl hexacaprylate/hexacaprate, propylene glycol monoisostearate, tricaprylin, dimethylisobisobutylidene and/or diisopropyl adipate.

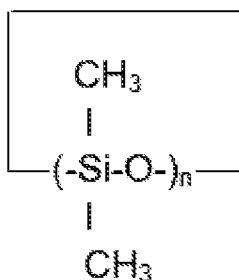
Still furthermore, the polar oils comprise components of the group of dialkyl ethers and dialkyl carbonates, advantageous examples being dicaprylyl ether, for example available under the trade name Cetiol OE from BASF, and dicaprylyl carbonate, for example available under the trade name Cetiol CC from BASF.

Advantageously, single organic liquid oils may be comprised in the preparation of the present invention. However, it is likewise advantageous, if two or more organic liquid oils are contained. The organic liquid oils may be chosen from one of the described groups or from different groups.

Advantageously, the total oil content of the preparation according to the invention is 3 to 20 % by weight, preferably 6 to 15 % by weight, in relation to the total weight of the preparation. The total oil content comprises the amount of at least one silicone oil, and/or at least one organic liquid oil. According to the invention, the oil content may have the same amount as the content of the oily phase. In the meaning of the present invention, the content of the emulsifiers is not included in the total oil content.

Single example contains at least one cyclomethicone.

Cyclomethicones may be characterized by the following formula:



wherein n is from 3 to 30.

In cosmetic preparations cyclomethicones with n representing 4 to 6 are mainly used. These components have the property to reduce the stickiness of cosmetic preparations. They are colorless and thin fluids.

According to new evaluations cyclotetrasiloxane (D4) is considered as presumably affecting fertility and being harmful for aquatic organisms. Furthermore, the degradability is slow and therefore this substance is accumulated in living organisms.

Cyclopentasiloxane (D5) may be absorbed and resorbed by the human organisms because of its high volatility.

Hence, the preparation according to the invention is preferably free from cyclomethicones.

Advantageously, the preparation according to the invention is free from cyclomethicones. In the meaning of the present invention "free from" in relation to cyclomethicones means that less than 0.01 % by weight, preferably less than 0.001 % by weight, and more preferably 0 % by weight of the respective substance is contained, in relation to the total weight of the composition.

To stabilize an emulsion, one or more emulsifier(s) is/are contained in general.

Emulsifiers help to combine two immiscible liquids (for example oil in water) in a way to result in a stable preparation, an emulsion. For that reason emulsifiers have to have an amphiphilic character, the hydrophobic part interacts with the oily or lipid phase and the hydrophilic part interacts with the aqueous phase. By stirring or homogenizing, droplets are generated, which are dispersed in the respective environment, namely aqueous droplets in a lipid environment or lipid droplets in an aqueous environment. Primarily, emulsifiers do not have a deterative, surfactant character. Emulsifiers reduce the interfacial tension between the two phases and, besides reducing the interfacial work, also achieve a stabilization of the formed emulsion. They stabilize the emulsion by means of interfacial films, as well as by forming steric or electrical barriers, as a result of which the merging (coalescence) of the emulsified particles is prevented.

HLB values are suitable to characterize emulsifiers, said values specify the hydrophilicity of a given emulsifier. The HLB value may be determined by the following formula:

$$HLB=20\times(1-M_{\text{lipophile}}/M),$$

where  $M_{\text{lipophile}}$  represents the molar mass of the lipophilic fraction of a given emulsifier and M represents the molar mass of the total emulsifier.

In general, emulsifiers with an HLB value up to about 8 are considered to be W/O-emulsifiers. By contrast, O/W-emulsifiers have HLB values of greater than 8 to 15. Substances with HLB values greater than 15 are often referred to as solubilizers.

Advantageously, according to the invention, the at least one W/O-emulsifier is dimethicone based.

A preferred dimethicone based emulsifier is Lauryl PEG-10 Tris(Trimethylsiloxy)silylethyl Dimethicone, which may be purchased from Dow Corning as Dowsil ES 5300 Formulation Aid or Dowsil ES 5227 Formulation Aid.

It is likewise preferred, if the dimethicone based emulsifier is Cetyl PEG/PPG-10/1 Dimethicone, which may be purchased from Evonic as Abil EM 90 or Abil EM 180.

Likewise advantageously, according to the invention, the at least one W/O-emulsifier is a non-silicone-based, PEG-free emulsifier. Preferred examples of said emulsifiers are Glyceryl monooleate available as Monomuls® 90-O18 from BASF, Polyglyceryl-4 Diisostearate/Polyhydroxystearate/Sebacate available as ISOLAN GPS, and Diisostearyl Polyglyceryl-3 Dimer Dilinoleate, available as ISOLAN PDI, both from the company Evonic.

In the meaning of the present invention PEG-free means that the respective emulsifier does not contain any polyethylene glycol residue. Moreover, it may be advantageous, if the complete preparation according to the invention is free from polyethylene glycol(s) (PEG) and/or polyethylene glycol derivatives. In the meaning of the present invention in relation to aforementioned substances the term "free from" means that polyethylene glycol(s) (PEG) and/or polyethylene glycol derivatives are contained in an amount less than 1% by weight, preferably less than 0.1 % by weight, and more preferably 0% by weight, based on the total weight of the preparation.

Advantageously, in the preparation according to the present invention the at least one W/O-emulsifier is contained in a total amount of 0.3 to 10.0 % by weight, preferably 0.5 to 3 % by weight, in relation to the total weight of the preparation.

According to the present invention at least one powder material, selected from starch powder, modified starch powder, talc, kaolin and the respective derivatives thereof, is contained in the preparation of the present invention. The at least one powder material has to fulfill specific criteria, namely

- an average particle size from 1 to 100 micron;
- a specific surface area of 0.05 to 100 m<sup>2</sup>/g; and
- an oil absorption rate of 10 to 100 g oil /100g powder.

The average particle size is determined according to ISO13320:2009 using a Malvern Mastersizer 3000.

The specific surface area is a BET surface area determined according to the method ISO 4652.

The oil absorption rate is determined according to the method ISO 4656-1-1992.

The starch powder is selected from modified starch powders, non-modified starch powders and mixtures thereof. It is preferred, if the non-modified starch powder is a tapioca starch, extracted from cassava plant. Tapioca starch may be purchased from Akzo Nobel as Tapioca Pure.

If the starch powder is selected from modified starch, it is preferred, if tapioca starch together with polymethylsilsesquioxane is contained. It is more preferred, if said combination contains about 98% by weight of tapioca starch and about 2% by weight of polymethylsilsesquioxane, in relation to the raw material. This raw material may be purchased from Akzo Nobel as DRY-FLO® TS Starch.

It is likewise preferred, if the modified starch is distarch phosphate, which may be from Solvadis with the tradename Corn PO4 PH"B".

The at least one powder material may be selected from talc, modified talc and/or kaolin.

Talc may be purchased from Omya with the trade name Microtalc Pharma 8. Talc modified with magnesium myristate, for example provided by KOBOL as TALC N/MM3, talc modified with stearyl glutamic acid, for example provided by KOBOL as TALC N-ASG4 and talc treated with Dimethicone (and) Cetearyl Alcohol (and) Stearic Acid (and) Ceramide NP (and) Phytosterols, for example provided by KOBOL as TALC G8-DS-PDL3, are examples for modified talc powders.

Kaolin may be purchased from Quarzwerke as Pharmakaolin B 860, from Merck as "Weisser Ton innerlich" Art Nr 105006.

In the present preparation the at least one powder material is contained in an amount of 0.5 to 10%wt, preferably 0.7 to 5.0 % by weight, in relation to the total weight of the preparation.

Advantageously, according to the invention additionally at least one polyol is contained in the composition of the present invention. Polyols contain at least two hydroxyl groups, which may bind water in a considerable amount. Thus, polyols are hygroscopic substances, which may be addressed as moisturizers, providing moisture to the skin. Examples of suitable polyols are propylene glycol, hexylene glycol, and butylene glycol, glycerol, sorbitol, xylitol, maltitol. Preferred polyols are glycerol, butylene glycol and/or propylene glycol.

If at least one polyglycol is contained in the composition of the present invention, the at least one polyol is preferably contained in a total amount of 3.0 to 50.0 % by weight, more preferably 5.0 to 20.0 % by weight, in relation to the total weight of the composition.

Advantageously, according to the invention additionally at least one preservative is contained in the composition of the present invention. All preservatives, which are allowed and suitable for cosmetic preparations may be contained. However, it is preferred, if methylparaben, ethylparaben, and Phenoxyethanol, or mixtures thereof are contained. Additionally, ethanol may be contained. Ethanol has a preservative effect and is often classified as a preservative. Ethanol may be contained as denatured alcohol. If ethanol is contained in the preparation of the present invention, the amount of ethanol ranges from 0.5 to 20 % by weight, preferably 0.7 to 10 % by weight, in relation to the total weight of the preparation.

Other preservatives may also be used, for example Benzyl Alcohol, Methylisothiazolinone, Methylchlorisothiazolinone and/or DMDM Hydantoin. These preservatives may be used alone or in combination or in combination with the above mentioned preferred preservatives and/or ethanol.

If at least one preservative is contained in the composition of the present invention, the at least one preservative is preferably contained in a total amount of 0.01 to 4.0 % by weight, more preferably 0.1 to 1.0 % by weight, relative to the total weight of the composition, with the proviso that the amount of ethanol is not contained in the above mentioned range. The values are referring to the active content of the preservatives. These values refer to all preservatives except for ethanol.

Advantageously, according to the invention additionally components stabilizing the preparation may be contained. Preferably, physiologically compatible salts may be contained, more preferably sodium chloride is contained.

If at least one stabilizing component, especially sodium chloride is contained in the composition of the present invention, the at least one stabilizing component, especially sodium chloride is preferably contained in a total amount of 0.1 to 5.0 % by weight, more preferably 0.5 to 1.5 % by weight, relative to the total weight of the composition.

Advantageously, according to the invention additionally complexing components may be contained. Preferably, the complexing components are chosen from EDTA, [S,S]-ethylenediamine disuccinate (EDDS), pentasodium ethylenediamine tetramethylenephosphonate and/or iminodisuccinic acid. If at least one complexing component is contained in the preparation of the present invention, the at least one complexing component is present in an amount of 0.1 to 5 % by weight, preferably 0.5 to 2 % by weight, in relation to the total weight of the preparation.

Advantageously, according to the invention additionally colorants may be contained in the preparation of the present invention. The colorants may be in form of dyes or pigments. Advantageous color pigments are, for example, titanium dioxide, mica, iron oxides (e.g.  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{FeO}(\text{OH})$ ) and/or tin oxide. Advantageous dyes are, for example, carmine, Prussian blue, chromium oxide green, ultramarine blue and/or manganese violet. It is particularly advantageous to choose the dyes and/or the color pigments from the Rowe Color Index, 3rd Edition, Society of Dyers and Colorists, Bradford, England, 1971.

Also advantageous are oil-soluble natural dyes, such as, for example, paprika extracts,  $\beta$ -carotene or cochineal.

If at least one colorant is contained in preparation of the present invention, the at least one colorant is present in an amount of 0.01 to 1.0 % by weight, in relation to the total weight of the preparation.

Advantageously, according to the invention additionally at least one UV filter is contained in the preparation of the present invention, which may be in form of UV-A, UV-B and/or broadband filter substance. Optionally, the preparation may also comprise one or more organic and/or inorganic pigments as UV filter substances, which may be present in the water phase and/or the oil phase.

Suitable UV filter substances are homomenthyl salicylate (INCI: Homosalate), 2-ethylhexyl 2-cyano-3,3-diphenylacrylate (INCI: Octocrylene), 2-ethylhexyl 2-hydroxybenzoate (2-ethylhexyl salicylate, octyl salicylate, INCI: Ethylhexyl Salicylate) and esters of cinnamic acid, preferably 2-ethylhexyl 4-methoxycinnamate (INCI: Ethylhexyl Methoxycinnamate) and isopentyl 4-methoxycinnamate (INCI: Isoamyl p-Methoxycinnamate), 3-(4-(2,2-bis-ethoxycarbonylvinyl) phenoxy)propenyl)methoxysiloxane/dimethylsiloxane copolymer.

Suitable inorganic pigments are metal oxides and/or other metal compounds, which are insoluble or sparingly soluble in water, in particular oxides of titanium ( $\text{TiO}_2$ ), zinc ( $\text{ZnO}$ ), iron (e.g.  $\text{Fe}_2\text{O}_3$ ), zirconium ( $\text{ZrO}_2$ ), silicon ( $\text{SiO}_2$ ), manganese (e.g.  $\text{MnO}$ ), aluminum ( $\text{Al}_2\text{O}_3$ ), cerium (e.g.  $\text{Ce}_2\text{O}_3$ ), mixed oxides of the corresponding metals, and mixtures of such oxides, and also the sulfate of barium ( $\text{BaSO}_4$ ).

Suitable UV-A filter substances for the purposes of the present invention are dibenzoylmethane derivatives, in particular 4-(tert-butyl)-4'-methoxydibenzoyl-methane (CAS No. 70356-09-1).

Further suitable UV filter substances for the purposes of the present invention are sulfonated, water-soluble UV filters, such as, for example:

- phenylene-1,4-bis(2-benzimidazolyl)-3,3'-5,5'-tetrasulfonic acid and its salts, particularly the corresponding sodium, potassium or triethanolammonium salts, in particular the phenylene-1,4-bis(2-benzimidazolyl)-3,3'-5,5'-tetrasulfonic acid bis-sodium salt with the INCI name Disodium Phenyl Dibenzimidazole Tetrasulfonate (CAS No.: 180898-37-7);
- salts of 2-phenylbenzimidazole-5-sulfonic acid, such as its sodium, potassium or its triethanolammonium salt, and the sulfonic acid itself with the INCI name Phenylbenzimidazole Sulfonic Acid (CAS No. 27503-81-7);
- 1,4-di(2-oxo-10-sulfo-3-bornylidenemethyl)benzene (also: 3,3'-(1,4-phenylene-dimethylene)bis(7,7-dimethyl-2-oxobicyclo[2.2.1]hept-1-ylmethanesulfonic acid) and salts thereof (particularly the corresponding 10-sulfato compounds, in particular the corresponding sodium, potassium or triethanolammonium salt), which is also referred to as benzene-1,4-di(2-oxo-3-bornylidenemethyl-10-sulfonic acid). Benzene-1, 4-di(2-oxo-3-bornylidenemethyl-10-sulfonic acid) has the INCI name Terephthalidene Dicamphor Sulfonic Acid (CAS No.: 90457-82-2);
- sulfonic acid derivatives of 3-benzylidenecamphor, such as, for example, 4-(2-oxo-3-bornylidenemethyl)benzenesulfonic acid, 2-methyl-5-(2-oxo-3-bornylidene-methyl)sulfonic acid and salts thereof.

Further suitable UV filter substances for the purposes of the present invention are also so-called broadband filters, i.e. filter substances which absorb both UV-A and also UV-B radiation. Examples for broadband filters or UV-B filter substances are, for example, triazine derivatives, such as, for example,

- 2,4-bis[[4-(2-ethylhexyloxy)-2-hydroxy]phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine (INCI: Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine;
- dioctylbutylamidotriazone (INCI: Diethylhexyl Butamido Triazone;
- Tris(2-ethylhexyl) 4,4',4''-(1,3,5-triazine-2,4,6-triyltriimino)trisbenzoate, also: 2,4,6-tris[anilino(p-carbo-2'-ethyl-1'-hexyloxy)]-1,3,5-triazine (INCI: Ethylhexyl Triazone;
- 2-[4,6-bis(2,4-dimethylphenyl)-1,3,5-triazin-2-yl]-5-(octyloxy)phenol (CAS No.: 2725-22-6).

Furthermore, 2,2'-methylenebis(6-(2H-benzotriazol-2-yl)-4-(1, 1,3,3-tetramethylbutyl)phenol), (INCI: Methylene Bis-Benztriazolyl Tetramethylbutylphenol) may be comprised in the preparation of the present invention.

Still furthermore 2-(2H-benzotriazol-2-yl)-4-methyl-6-[2-methyl-3-[1,3,3,3-tetramethyl-1-[(trimethylsilyl)oxy]disiloxanyl]propyl]phenol (CAS No.: 155633-54-8) with the INCI name Drometrizole Trisiloxane may be contained in the preparation of the present invention.

If at least one UV Filter is contained in the preparation according to the present invention, the at least one UV filter is present in an amount of 0.5 to 10 % by weight, preferably 1.0 to 5 % by weight, in relation to the total weight of the preparation.

The preparation according to the present invention has preferably a pH value of 4 to 8. The pH value is adjusted by every suitable, physiologically acceptable means, however it is preferred, if the pH value is adjusted by an inorganic base, such as for example sodium hydroxide.

The cosmetic preparation according to the invention may comprise cosmetic auxiliaries in general being contained in such preparations, e.g. preservative aids, perfumes, and other customary constituents of a cosmetic formulation.

## **Examples**

The examples below are intended to illustrate the present invention without limiting it. The numerical values in the examples are percentages by weight, based on the total weight of the particular preparations, given as active content.

### Preparation method

The composition of the present invention may be prepared by any technique known or effective to prepare a “quick-breaking” water-in-oil emulsion. The process to prepare the composition of the present invention comprises conventional formulating and mixing techniques.

### Test method

Preparations according to the example 1.1 and a comparative example (without powder raw material) were prepared and compared to the market product Nivea Men Hydrating Water Burst Serum. The INCI listing of Nivea Men Hydrating Water Burst Serum discloses the following components: Aqua, Glycerin, Cyclomethicone, Dimethicone, Propylene Glycol, Sodium Chloride, Sodium Hyaluronate, Sodium Ascorbyl Phosphate, Tocopheryl Acetate, Caprylic/Capric Triglyceride, Glyceryl Glucoside, Dimethicone Crosspolymer, PEG/PPG-18/18 Dimethicone, Glycyrrhiza Glabra Root Extract, Fucus Vesiculosus Extract, Maris Limus Extract, Ostrea Shell Extract, Phenoxyethanol, Ethylhexylglycerin, Perfume.

The preparations were used to conduct a Sensory Panel Evaluation. The evaluation was performed according to the following method:

- Panelists: 10 trained panelists joined the evaluation. The skin of the panelists was characterized as normal, the test was performed on their arms.
- Panel Room: Temperature: 23-27°C, humidity: 50-60%,
- Process:
  - Panelists are sitting at a desk for 10 minutes (acclimation time).
  - The skin area of applying the respective product is marked by using a stamp. Maximal 3 areas are marked on each arm, and on each area one product will be applied. In total, 6 products may be evaluated in one panel (including 1 standard product, which is used for providing the score for calibration).
  - The panel organizer dispenses one product on each marked area and starts the beeper for massaging the product with a certain frequency.
  - The panelists start a timer and massage the product, meanwhile evaluating the sensory criteria during application. Touch the skin and evaluate the sensory criteria immediately after absorption.
- Scale:
  - Water breaking time: Counted by circles of massage.
  - Watery: 0: Extremely dry, 10: Extremely watery.
  - Less oily: 0: Extremely oily, 10: Not oily at all.
  - Less Greasy: 0: Extremely greasy, 10: Not greasy at all.
  - Less Residue: 0: High amount of residues, 10: Clean and no residues.
  - Smoothness: 0: Rough and not smooth, 10: Extremely smooth.

The results of the evaluation are shown in the table below.

| Preparations                          | Water breaking time | Watery | Less oily | Less Greasy | Less Residue | Smoothness |
|---------------------------------------|---------------------|--------|-----------|-------------|--------------|------------|
| Nivea Men Hydrating Water Burst Serum | 9.1                 | 7.10   | 5.50      | 8.60        | 7.50         | 7.10       |
| Comparative formula without powder    | 14.7                | 7.20   | 6.10      | 8.60        | 7.40         | 7.05       |
| Example 1.1                           | 3.5                 | 8.05   | 7.50      | 8.70        | 7.60         | 7.60       |

It becomes apparent that the water breaking time of the preparation according to the inventive example was shortened compared to the preparation without powder and the

market product; the evaluation of the quality “watery” showing similar results. Referring to smoothness, residues left on the skin, and greasiness, the preparation according to the invention is evaluated in about the range as the comparative preparation and the market product. The preparation according to the invention is evaluated less oily than the market product and the comparative preparation. The results show, that product according to the invention solves the above mentioned problem, namely providing a significant higher (better) emulsion breaking effect and providing a higher amount of water to the skin, thereby causing a considerable cooling and refreshing effect.

Furthermore, the stability was analyzed.

To evaluate long-term storage, the example preparations (examples 1.1, 1 to 12) were prepared and filled in to 50ml transparent glass bottle with plastic cap. The comparative product (Nivea Men Hydrating Water Burst Serum) was filled in the same glass bottles. The test samples were stored as indicated below.

| Preparations                          | Storage       |                |
|---------------------------------------|---------------|----------------|
|                                       | 50°C, 30 days | -10°C, 30 days |
| Nivea Men Hydrating Water Burst Serum | OK            | OK             |
| Example 1.1                           | OK            | OK             |
| Example 1                             | OK            | OK             |
| Example 2                             | OK            | OK             |
| Example 3                             | OK            | OK             |
| Example 4                             | OK            | OK             |
| Example 5                             | OK            | OK             |
| Example 6                             | OK            | OK             |
| Example 7                             | OK            | OK             |
| Example 8                             | OK            | OK             |
| Example 9                             | OK            | OK             |
| Example 10                            | OK            | OK             |
| Example 11                            | OK            | OK             |
| Example 12                            | OK            | OK             |

OK means no obvious water or oil separation, no color change.

**Examples:**

| INCI name                                                 | Comparative example (without powder raw material) | Example 1.1 | Example 1 | Example 2 | Example 3 | Example 4 | Example 5 | Example 6 | Example 7 | Example 8 | Example 9 | Example 10 | Example 11 | Example 12 |
|-----------------------------------------------------------|---------------------------------------------------|-------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|------------|------------|------------|
| CI 77891                                                  | 0.8                                               | 0.8         | 0.8       | 0.8       | 0.8       | 0.8       | 0.8       | 0.8       | 0.8       | 0.8       | 0         | 0.8        | 0          | 0.8        |
| Cyclomethicone                                            | 0                                                 | 0           | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 4         | 0         | 0          | 0          | 4          |
| Dimethicone                                               | 0.5                                               | 0.5         | 4         | 4         | 4         | 4         | 4         | 4         | 4         | 2         | 2.5       | 0          | 0.5        | 2          |
| C12-15 Alkyl Benzoate                                     |                                                   | 0.5         | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5        | 0          | 0.5        |
| Isohexadecane                                             | 0                                                 | 0           | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 3          | 0          | 0          |
| Isododecane                                               | 2                                                 | 2           | 2         | 2         | 2         | 2         | 2         | 2         | 2         | 0         | 0         | 2.5        | 2          | 0          |
| Butylene Glycol Dicaprylate/Dicaprate                     | 4                                                 | 4           | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 0          | 4          | 0          |
| Lauryl PEG-10 Tris(trimethylsiloxy)silylethyl Dimethicone | 0.8                                               | 0.8         | 0.8       | 0.8       | 0.8       | 0.8       | 0.8       | 0.8       | 0.8       | 0.8       | 0.8       | 0.8        |            | 0.8        |
| Cetyl PEG/PPG-10/1 Dimethicone                            | 0                                                 | 0           | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 0          | 0.8        | 0          |
| Distarch Phosphate                                        | 0                                                 | 1           | 1.5       | 0         | 0         | 0         | 1         | 1         | 1         | 3         | 3         | 3          | 1          | 3          |
| Tapioca Starch                                            | 0                                                 | 0           | 0         | 1.5       | 0         | 0         | 0         | 0         | 0.5       | 0         | 0         | 0          | 0          | 0          |
| Talc                                                      | 0                                                 | 1           | 0         | 0         | 1.5       | 0         | 0         | 0.5       | 0         | 0         | 0         | 0          | 1          | 0          |
| Silica                                                    | 0                                                 | 0           | 0         | 0         | 0         | 0.5       | 0         | 0         | 0         | 0         | 0         | 0          | 0          | 0          |
| Tapioca Starch                                            | 0                                                 | 0           | 0         | 0         | 0         | 0         | 1         | 0         | 0         | 0         | 0         | 0          | 0          | 0          |
| (98%)+Polymethylsilsesquioxane(2%)*                       | 0                                                 | 0           | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 0          | 0          | 0          |
| Parfum                                                    | 0.1                                               | 0.1         | 0.1       | 0.1       | 0.1       | 0.1       | 0.1       | 0.1       | 0.1       | 0.1       | 0.1       | 0.1        | 0.1        | 0.1        |
| Glycerin                                                  | 3                                                 | 3           | 3         | 3         | 3         | 3         | 3         | 3         | 3         | 3         | 6         | 3          | 3          | 8          |
| Butylene Glycol                                           | 2                                                 | 2           | 2         | 2         | 2         | 2         | 2         | 2         | 2         | 2         | 2         | 2          | 2          | 2          |
| Propylene Glycol                                          | 2.5                                               | 2.5         | 2.5       | 2.5       | 2.5       | 2.5       | 2.5       | 2.5       | 2.5       | 2.5       | 2.5       | 2.5        | 2.5        | 2.5        |
| Aqua(55%) + Sodium Hydroxide (45%)*                       | 0                                                 | 0           | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 0          | 0          | 0.6        |
| Methylparaben                                             | 0.1                                               | 0.1         | 0.1       | 0.1       | 0.1       | 0.1       | 0.1       | 0.1       | 0.1       | 0.1       | 0.1       | 0.1        | 0.1        | 0.1        |
| Phenoxyethanol                                            | 0.5                                               | 0.5         | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5       | 0.5        | 0.5        | 0.5        |
| Sodium Chloride                                           | 1.5                                               | 1.5         | 1.5       | 1.5       | 1.5       | 1.5       | 1.5       | 1.5       | 1.5       | 1.5       | 1.5       | 1.5        | 1.5        | 1.5        |
| Aqua(80%) + Trisodium EDTA(20%)*                          | 1                                                 | 1           | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 1         | 1         | 1          | 1          | 1          |
| Alcohol Denat. (95%)+ Aqua(5%)*                           | 5                                                 | 5           | 0         | 5         | 5         | 5         | 5         | 5         | 5         | 5         | 15        | 5          | 5          | 5          |
| Aqua                                                      | 76.2                                              | 74.2        | 80.7      | 75.7      | 75.7      | 76.7      | 75.2      | 75.7      | 80.7      | 73.2      | 64.5      | 73.7       | 75         | 65.8       |
| Phenylbenzimidazole Sulfonic Acid                         | 0                                                 | 0           | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 0         | 0          | 0          | 1.8        |
| Sum                                                       | 100                                               | 100         | 100       | 100       | 100       | 100       | 100       | 100       | 100       | 100       | 100       | 100        | 100        | 100        |

## **Claims**

- 1) A quick-breaking water-in-oil emulsion, containing
  - at least one powder material, selected from starch powder, modified starch powder, talc, kaolin and the respective derivatives thereof ,
  - an oily phase, containing at least one lipid component, chosen from at least one silicone oil, and/or at least one organic liquid oil,
  - an aqueous phase,
  - at least one W/O emulsifier, having a HLB value of 2 to 7, wherein the at least one powder material has
    - an average particle size from 1 to 100 micron;
    - a specific surface area of 0.05 to 100 m<sup>2</sup>/g; and
    - an oil absorption rate of 10 to 100 g oil /100g powder.
- 2) The water-in-oil emulsion according to claim 1, containing
  - 0.5 to 10% by weight of at least one powder material,
  - 3 to 20% by weight of an oily phase,
  - 70 to 97% by weight of an aqueous phase,
  - 0.5 to 10% by weight of at least one W/O emulsifier,in relation to the total weight of the emulsion.
- 3) The water-in-oil emulsion according to claim 1 or 2 characterized in that water is contained in an amount of 50 to 97 % by weight, preferably 60 to 85 % by weight, in relation to the total weight of the emulsion.
- 4) The water-in-oil emulsion according to any of the preceding claims characterized in that the water-in-oil emulsion is a cosmetic preparation, preferably intended to stay on the skin (leave-on).
- 5) The water-in-oil emulsion according to any of the preceding claims characterized in that the at least one organic liquid oil is at least one silicone oil, preferably a dimethicone, having 2 to 2000 siloxane units, especially 10 to 400 siloxane units.
- 6) The water-in-oil emulsion according to any of the preceding claims characterized in that the at least one organic liquid oil is at least one non-polar organic oil chosen from
  - aliphatic, unbranched hydrocarbons having 12 to 40 carbon atoms, preferably 15 to 19 carbon atoms, and/or
  - aliphatic branched hydrocarbons having in total 12 to 40 carbon atoms, preferably 12 to 16 carbon atoms, more preferably isohexadecane and/or isododecane.
- 7) The water-in-oil emulsion according to any of the preceding claims characterized in that the at least one organic liquid oil is at least one polar oil chosen from

- esters of saturated and/or unsaturated, branched and/or unbranched alkane carboxylic acids with a chain length of from 3 to 20 carbon atoms and saturated and/or unsaturated, branched and/or unbranched alcohols with a chain length of from 1 to 20 carbon atoms, and esters of aromatic carboxylic acids and saturated and/or unsaturated, branched and/or unbranched alcohols with a chain length of from 3 to 20 carbon atoms, with the proviso that said esters are fluid, preferably from methyl palmitate, isopropyl myristate, isopropyl palmitate and/or C12-15 alkyl benzoate,
  - the group of neopentyl glycol diheptanoate, propylene glycol dicaprylate/dicaprate, caprylic/capric/diglyceryl succinate, butylene glycol dicaprylate/dicaprate, C12-13 alkyl lactate, di-C12-13 alkyl tartrate, triisostearin, dipentaerythrityl hexacaprylate/hexacaprate, propylene glycol monoisostearate, tricaprylin, dimethylisosorbide and/or diisopropyl adipate, and
  - the group of dialkyl ethers and dialkyl carbonates, preferably dicaprylyl ether and/or dicaprylyl carbonate.
- 8) The water-in-oil emulsion according to any of the preceding claims characterized in that a combination of at least one non-polar oil, at least one polar oil, and/or at least one silicone oil is contained.
- 9) The water-in-oil emulsion according to any of the preceding claims characterized in that the total oil content ranges from 3 to 20 % by weight, preferably 6 to 15 % by weight, in relation to the total weight of the emulsion.
- 10) The water-in-oil emulsion according to any of the preceding claims characterized in that the at least one W/O emulsifier, having a HLB value of 2 to 7, is dimethicone based, preferably Lauryl PEG-10 Tris(Trimethylsiloxy)silylethyl Dimethicone, and/or Cetyl PEG/PPG-10/1 Dimethicone.
- 11) The water-in-oil emulsion according to any of the preceding claims characterized in that the at least one W/O emulsifier, having a HLB value of 2 to 7, is a non-silicone-based, PEG-free emulsifier, preferably Glyceryl monooleate, Polyglyceryl-4 Diisostearate/Polyhydroxystearate/Sebacate, and/or Diisostearyl Polyglyceryl-3 Dimer Dilinoleate.
- 12) The water-in-oil emulsion according to any of the preceding claims characterized in that the at least one W/O emulsifier, having a HLB value of 2 to 7 is contained in a total amount of 0.3 to 10.0 % by weight, preferably 0.5 to 3 % by weight, in relation to the total weight of the emulsion.
- 13) The water-in-oil emulsion according to any of the preceding claims characterized in that the at least one powder material is contained in an amount of 0.5 to 10 % by weight, preferably 0.7 to 5.0 % by weight, in relation to the total weight of the emulsion.

- 14) The water-in-oil emulsion according to any of the preceding claims characterized in that additionally at least one polyol is contained, preferably chosen from propylene glycol, hexylene glycol, and butylene glycol, glycerol, sorbitol, xylitol, maltitol, more preferably from glycerol, butylene glycol and/or propylene glycol.
- 15) The water-in-oil emulsion according to claim 14 characterized in that the at least one polyol is contained in a total amount of 3.0 to 50.0 % by weight, more preferably 5.0 to 20.0 % by weight, in relation to the total weight of the emulsion.
- 16) The water-in-oil emulsion according to any of the preceding claims characterized in that additionally at least one colorant is contained, preferably in a total amount of 0.01 to 1.0 % by weight, in relation to the total weight of the emulsion.
- 17) The water-in-oil emulsion according to any of the preceding claims characterized in that additionally at least one UV filter is contained, preferably chosen from salts of 2-phenylbenzimidazole-5-sulfonic acid, more preferably Phenylbenzimidazole Sulfonic Acid.
- 18) The water-in-oil emulsion according to claim 17 characterized in that the at least one UV Filter is contained a total amount of 0.5 to 10 % by weight, preferably 1.0 to 5 % by weight, in relation to the total weight of the emulsion.
- 19) The water-in-oil emulsion according to any of the preceding claims characterized in that the water-in-oil emulsion is free from cyclomethicones.
- 20) Use of at least one one powder material, selected from starch powder, modified starch powder, talc, kaolin and the respective derivatives thereof specified by
  - an average particle size from 1 to 100 micron;
  - a specific surface area of 0.05 to 100 m<sup>2</sup>/g; and
  - an oil absorption rate of 10 to 100 g oil /100 g powder,to improve the quick breaking effect in a quick-breaking water-in-oil emulsion, preferably in the emulsion according to any of the claims 1 to 19.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2019/086727

**A. CLASSIFICATION OF SUBJECT MATTER**

A61K 8/06(2006.01)i; A61Q 1/00(2006.01)i; A61Q 19/00(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

A61K8/-; A61Q1/-; A61Q19/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNPAT,CA,CNKI,WPLEPODOC,ISI,STN: quick breaking, water-in-oil, emulsion, powder, starch, talc, kaolin, oil phase, aqueous phase, emulsifier, surfactant

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                  | Relevant to claim No. |
|-----------|-----------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X         | JP 2008208045 A (SHISEIDO CO. LTD.) 11 September 2008 (2008-09-11)<br>description, paragraphs [0006], [0011], [0017], [0027], [0029]-[0032], [0038] | 1-20                  |
| A         | CN 104968318 A (BEIERSDORF) 07 October 2015 (2015-10-07)<br>claims 1-13                                                                             | 1-20                  |
| A         | US 2018280279 A1 (L'OREAL) 04 October 2018 (2018-10-04)<br>claims 1-19                                                                              | 1-20                  |



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

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“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

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**INTERNATIONAL SEARCH REPORT**  
**Information on patent family members**

International application No.

**PCT/CN2019/086727**

| Patent document<br>cited in search report |            |    | Publication date<br>(day/month/year) | Patent family member(s) |                 | Publication date<br>(day/month/year) |
|-------------------------------------------|------------|----|--------------------------------------|-------------------------|-----------------|--------------------------------------|
| JP                                        | 2008208045 | A  | 11 September 2008                    | None                    |                 |                                      |
| CN                                        | 104968318  | A  | 07 October 2015                      | EP                      | 2931210 B1      | 20 June 2018                         |
|                                           |            |    |                                      | WO                      | 2014090615 A2   | 19 June 2014                         |
|                                           |            |    |                                      | WO                      | 2014090615 A3   | 22 January 2015                      |
|                                           |            |    |                                      | DE                      | 102012222797 A1 | 12 June 2014                         |
|                                           |            |    |                                      | BR                      | 112015013190 B1 | 29 October 2019                      |
|                                           |            |    |                                      | EP                      | 2931210 A2      | 21 October 2015                      |
|                                           |            |    |                                      | CN                      | 104968318 B     | 19 April 2019                        |
|                                           |            |    |                                      | BR                      | 112015013190 A2 | 11 July 2017                         |
| US                                        | 2018280279 | A1 | 04 October 2018                      | None                    |                 |                                      |