

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau



(10) International Publication Number  
**WO 2020/201273 A1**

(43) International Publication Date  
08 October 2020 (08.10.2020)

(51) International Patent Classification:

*A61K 8/85* (2006.01)      *C08K 5/20* (2006.01)  
*A61K 8/88* (2006.01)      *C08L 77/12* (2006.01)  
*A61Q 5/00* (2006.01)      *A61K 31/16* (2006.01)  
*C08G 69/44* (2006.01)      *A01N 37/18* (2006.01)  
*C08G 83/00* (2006.01)      *A61K 8/34* (2006.01)  
*C08L 101/00* (2006.01)      *A61K 8/42* (2006.01)  
*C08K 5/00* (2006.01)      *A61Q 17/00* (2006.01)  
*A01N 25/10* (2006.01)

**Declarations under Rule 4.17:**

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *of inventorship (Rule 4.17(iv))*

**Published:**

- *with international search report (Art. 21(3))*

(21) International Application Number:

PCT/EP2020/059102

(22) International Filing Date:

31 March 2020 (31.03.2020)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

19166543.9      01 April 2019 (01.04.2019)      EP

(71) Applicant: **DSM IP ASSETS B.V.** [NL/NL]; Het Overloon 1, 6411 TE Heerlen (NL).

(72) Inventor: **MENDROK-EDINGER, Christine**; c/o DSM Nutritional Products Ltd, Patent Department Wurmisweg 576, 4303 Kaiseraugst (CH).

(74) Agent: **DUX, Roland**; DSM Nutritional Products Ltd, Patent Department Wurmisweg 576, 4303 Kaiseraugst (CH).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(54) Title: COMPOSITION COMPRISING SPECIFIC HYPERBRANCHED COPOLYMERS AND 1,3-PROPANDIOL AND/OR N-HYDROXYOCTANAMIDE

(57) Abstract: The present invention relates to a composition comprising a specific hyperbranched copolymer (HBC) of the monomers dodecyl succinic acid anhydride, diisopropanol amine and bis-dimethylaminopropyl amine and the compound 1,3-propanediol and/or N-hydroxyoctanamide. It has been found that said hyperbranched copolymer synergistically enhances the antimicrobial action of 1,3-propanediol and/or N-hydroxy-octanamide.



## COMPOSITION COMPRISING SPECIFIC HYPERBRANCHED COPOLYMERS AND 1,3-PROPANDIOL AND/OR N-HYDROXYOCTANAMIDE

### Technical Field

5           The present invention relates to the field of antimicrobial agents, particularly in the field of cosmetic compositions.

### Background of the invention

          Antimicrobial agents are known ingredients to stabilize compositions, particularly cosmetic compositions, by reducing the growth of microorganisms. The reduction of growth of microorganisms is essential for the consumer's safety and health when using a cosmetic product. By reducing the growth of microorganisms, the shelf life of a cosmetic product can be increased. As the use of certain antimicrobial agents are under public discussion a reduction of antimicrobial agents is a strong desire, particularly in the cosmetic industry.

15           EP 2 794 729 B1 discloses the preparation of specific hyperbranched polyesters which can be used as flocculants in paper production and in dishwasher detergents.

          EP 2 296 619 B1 discloses that specific hyperbranched copolymers have an advantageous effect in a shampoo for increasing the volume of hair.

          1,3-propanediol and N-hydroxyoctanamide are compounds which are known to be used as an active antimicrobial adjuvant in cosmetic compositions.

### Summary of the invention

25           Therefore, the problem to be solved by the present invention is to offer a composition with enhanced antimicrobial properties.

          It has been surprisingly found that the composition of claim 1 is able to solve this problem. It has been particularly observed that a specific hyperbranched copolymer is able to enhance the antimicrobial action of antimicrobial agents used particularly in cosmetic compositions. This effect is a synergistic effect of the specific hyperbranched copolymer on the antimicrobial effect of an antimicrobial agent. This surprising finding is very advantageous as this invention can lead to higher stability, longer shelf life, respectively, to the reduction of antimicrobial

agents in compositions, particularly in cosmetic compositions, by, nevertheless, maintaining the antimicrobial properties.

Further aspects of the invention are subject of further independent claims. Particularly preferred embodiments are subject of dependent claims.

5

### Detailed description of the invention

In a first aspect the present invention relates to a composition comprising

a) a hyperbranched copolymer (**HBC**) of the monomers

(i) dodecanyl succinic acid anhydride

10

(ii) diisopropanol amine

(iii) bis-dimethylaminopropyl amine

having terminal groups of the formula



and having a molecular weight  $M_n$  of between 1200 and 4000 g/mol;

15

and

b) 1,3-propanediol and/or N-hydroxyoctanamide.

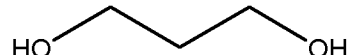
The term "molecular weight  $M_n$ " stands for the number average molecular weight.

20

The term "preparation" or "formulation" is used in this document as equivalent to the term "composition".

The term "antimicrobial agent" is used in this document for an organic chemical substance which reduces the growth of microorganisms. However, monohydroxy- $C_1$ - $C_6$  alkanes, such as methanol, ethanol, propanol or *iso*-propanol, 25 for this invention, are not considered to be antimicrobial agents. For sake of clarity, it is worthwhile that antioxidants are not to be regarded as antimicrobial agents.

- 3 -

1,3 propanediol has the formula . 1,3 propanediol is commercially readily available from different suppliers.

N-hydroxyoctanamide (CAS-Nr. 7377-03-9) is commercially readily available.

5

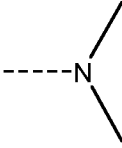
The hyperbranched copolymer (**HBC**) is preferably prepared by the following consecutive steps of:

- a1) polymerizing the monomers (i) and monomers (ii) and monomers (iii) to yield a polyesteramide having terminal dimethyl amino groups of the



- a2) quaternization of the dimethyl amino groups of the polyesteramide of step a1) by 2-chloroacetate, particularly by sodium 2-chloroacetate.

Details for the polymerization step a1) to yield the respective polyesteramide

15 having terminal dimethyl amino groups of the formula  are disclosed for example by EP 2 794 729 B1.

Preferably in the polymerization step a1) the monomer (iii) is added to a mixture of monomers (ii) and (iii) under stirring, followed by heating.

20 Details of the quaternization step a2) are disclosed as well by EP 2 794 729 B1. Therefore, the entire content of EP 2 794 729 B1 is hereby incorporated by reference.

It is preferred that the molar ratio of the monomers (i) to monomers (ii) is between 5 : 1 and 0.5 : 1, particularly between 4 : 1 and 1 : 1, preferably between 3 : 1 and 3 : 2.

25 It is further preferred that the molar ratio of the monomers (i) to monomers (iii) is between 5 : 1 and 0.5 : 1, particularly between 3 : 1 and 1 : 1, preferably between 2.5 : 1 and 1.1 : 1.

The hyperbranched copolymer (**HBC**) has preferably a number average molecular weight  $M_n$  of between 1400 and 3000 g/mol, preferably between 2100 and 2400 g/mol.

5 Preferably, the hyperbranched copolymer (**HBC**) is polyquaternium-110, also identified by CAS Number 1323977-82-7.

The composition comprises 1,3-propanediol and/or N-hydroxyoctanamide.

10 In one preferred embodiment, the composition comprises 1,3-propanediol and not N-hydroxyoctanamide. In another preferred embodiment, the composition comprises N-hydroxyoctanamide and not 1,3-propanediol.

In a still another preferred embodiment, the composition comprises both 1,3-propanediol and N-hydroxyoctanamide.

15 It is preferred that the composition comprises 1,3-propanediol and N-hydroxyoctanamide. In the case of mutual presence of comprises 1,3-propanediol and N-hydroxyoctanamide, it is preferred that the ratio of comprises 1,3-propanediol to N-hydroxyoctanamide is  $> 1$ , particularly  $> 3$ . In a very preferred embodiment the composition comprises a mixture of 1,3-propanediol and N-hydroxyoctanamide, as commercially available under the tradename Zeostat™  
20 from Inolex.

The weight ratio of said hyperbranched copolymer (**HBC**) and 1,3-propanediol and/or N-hydroxyoctanamide is preferably in the range of between 1:30 and 30:1, more preferred between 1:20 – 20:1, even more preferred between  
25 1:10 and 10:1.

In a preferred embodiment the weight ratio of said hyperbranched copolymer (**HBC**) and 1,3-propanediol and/or N-hydroxyoctanamide is larger than 1.

30 In one embodiment of the invention, the composition of hyperbranched copolymer (**HBC**) and 1,3-propanediol and/or N-hydroxyoctanamide is used as an antimicrobial agent mixture. Such an antimicrobial agent mixture can be added to any other composition to improve its resistance against microorganisms. Typically, the amounts of hyperbranched copolymer (**HBC**) and 1,3-propanediol and/or N-

hydroxyoctanamide in such an antimicrobial agent mixture is considerable, particularly the weight of hyperbranched copolymer **(HBC)** and 1,3-propanediol and/or N-hydroxyoctanamide is more than 10, particularly more than 30, preferably more than 50, % by weight based on the weight of the antimicrobial agent mixture. It is even possible that such an antimicrobial agent mixture consists of hyperbranched copolymer **(HBC)** and 1,3-propanediol and/or N-hydroxyoctanamide. Additionally, the antimicrobial agent mixture may also contain further antimicrobial agents.

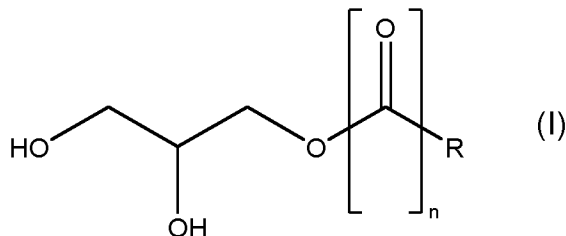
The composition may additionally comprise at least a further antimicrobial agent. Antimicrobial agents are known as such to the person skilled in the art. The field of use, however, limits the choice of antimicrobial agents which are mainly due particularly to regulatory issues. In the field of food and cosmetics the choice of antimicrobial agents is rather limited.

Therefore, preferred antimicrobial agents suitable for this invention, are antimicrobial agents which are acceptable in the field of food and cosmetics.

In one of the preferred embodiments the antimicrobial agent is selected from the group consisting of:

- monoesters or monoethers of glycerol;
- salts or esters of aromatic acids;
- alkylarylic alcohols;
- phenolic ether alcohols;
- hydroxyacetophenone
- aliphatic diols; and
- hydroxamic acids.

Preferred monoesters or monoethers of glycerol are those of formula (I)



wherein R is a C<sub>5</sub>-C<sub>10</sub> alkyl group or C<sub>5</sub>-C<sub>10</sub> cyclo alkyl group, preferably a C<sub>6</sub>-C<sub>9</sub> alkyl group or a C<sub>6</sub>-C<sub>9</sub> cyclo alkyl group, more preferably a C<sub>6</sub> alkyl group or a C<sub>8</sub> alkyl group or a C<sub>6</sub> cyclo alkyl group;

and wherein n is either 1 or 0, preferably 0.

5 In case, where n=0, R is preferably cyclohexyl or n-octyl or n-hexyl or a branched octyl group, preferably an n-hexyl group or an ethylhexyl group, more preferably a 2-ethylhexyl group. A preferred embodiment is glyceryl caprylate.

In case, where n=1, R is preferably a branched or unbranched saturated or olefinically unsaturated heptyl or nonyl group, preferably a saturated or olefinically unsaturated heptyl or nonyl group, more preferably n-octyl or n-nonyl group, 10 most preferred n-nonyl group.

The monoester or monoethers of glycerol of the formula (I) is preferably selected from the group consisting of cyclohexyl glycerin, hexyl glycerine, ethylhexyl glycerine, glyceryl caprate and glyceryl caprylate, more preferably, 15 hexyl glycerine, ethylhexyl glycerine or glyceryl caprate, most preferably ethylhexyl glycerine or hexyl glycerine. In the most preferred embodiment compound of the formula (I) is 3-(2-ethylhexyloxy)-1,2-propandiol.

Preferred salts of aromatic acids are salts of benzoic acid. Preferred salts 20 are salts of potassium or sodium, preferably sodium salts. Preferred esters of aromatic acids

Preferred esters of aromatic acids are alkylesters, particularly C<sub>1</sub>-C<sub>6</sub> alkyl esters of benzoic acid.

Most preferred salts or esters of aromatic acids is sodium benzoate. 25

Preferred alkylarylic alcohols are alcohols which have a C<sub>1</sub>-C<sub>6</sub> alkylene group, preferably a methylene group, between the hydroxyl group and the aromatic part of the alkylarylic alcohols. Benzyl alcohol is the most preferred alkylarylic alcohols.

30

Phenolic ether alcohols are alcohols which comprise an alcoholic hydroxyl group as well as a ether of a phenol. The aromatic ring of the phenol is optionally substituted. The ether oxygen and the hydroxyl group are preferably separated by

a C<sub>2</sub>-C<sub>4</sub> alkylene group, preferably by an ethylene group. Phenoxyethanol is the most preferred phenolic ether alcohol.

The preferred hydroxyacetophenone is p-hydroxyacetophenone.

5

Aliphatic diols are alkanes which have 2 hydroxyl groups. These hydroxyl groups are preferably separated by a linear or branched C<sub>2</sub>-C<sub>10</sub> alkylene group.

Preferred hydroxamic acids are hydroxamic acids of a saturated C<sub>3</sub>-C<sub>12</sub> alkanolic acid. Preferred hydroxamic acid is N-hydroxyoctanamide (=caprylhydroxamic acid).

10

Preferably the antimicrobial agent is selected from the group consisting of hexyl glycerine, ethylhexyl glycerine or glyceryl caprate, sodium benzoate, benzyl alcohol, phenoxyethanol and N-hydroxyoctanamide.

15

More preferably, the antimicrobial agent is selected from the group consisting of hexyl glycerine, ethylhexyl glycerine or glyceryl caprate and N-hydroxyoctanamide.

Most preferred, the antimicrobial agent is hexyl glycerine or ethylhexyl glycerine.

20

In a preferred embodiment the composition is a cosmetic composition.

It is preferred that the amount of 1,3-propanediol and/or N-hydroxyoctanamide is 0.01 – 6.0 % by weight, preferably 0.05 – 5.0 % by weight, more preferably 0.1 – 3.0 % by weight, based on the total weight of the cosmetic composition.

25

The amount of the hyperbranched copolymer (**HBC**) in a cosmetic composition is typically between 0.005 and 5.0 % by weight, preferably between 0.05 and 5.0 % by weight, more preferably between 0.1 and 3.0 % by weight, most preferably between 0.5 and 2.5 % by weight, based on the total weight of the cosmetic composition.

30

The cosmetic composition further preferably comprises at least one emulsifier, preferably an anionic emulsifier. Preferably the anionic emulsifier is an anionic emulsifier selected from the group consisting of potassium cetyl phosphate, disodium cetearyl sulfosuccinate, sodium stearyl glutamate, sodium stearyl lactylate, glyceryl stearate citrate and sodium cocoyl isethionate.

Potassium cetyl phosphate is commercially available as Amphisol® K at DSM Nutritional Products Ltd Kaiseraugst.

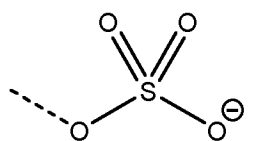
The amount of emulsifier is preferably in the range between 0.1 – 6.0 % by weight, more preferably between 0.25 – 5.0 % by weight, particularly between 0.5 - 4.0 % by weight, based on the total weight of the cosmetic composition.

The composition is preferably sulfate-free.

Hence, the cosmetic composition is preferably particularly free of sulfates of the group consisting of alkyl sulfates, alkyl ether sulfates, alkyl amido ether sulfates, alkylaryl polyether sulfates and monoglycerides sulfate as well as mixtures thereof.

The term "free" as used in the present document, for example in "sulfate-free", is used to mean that the respective substance is only present at amounts of less than 0.5 % by weight, particularly less than 0.1 % by weight, more particularly below 0.05 % by weight, relative to the weight of the composition. Preferably, "free" means that the respective substance is completely absent in the composition.

The term "sulfate-free" is used in the present document to mean that the composition is free of any anionic tenside having a terminal anionic group of the formula



The cosmetic composition is preferably free of cationic emulsifiers. Typical example for such cationic emulsifiers are isostearamidopropyl dimethylamine, stearamonium chloride, stearamidoethyl diethylamine, behentrimonium methosulfate, behenoyl PG-trimonium chloride, cetrimonium bromide, behenamidopropyl dimethylamine behenate, brassicamidopropyl dimethylamine, stearamidopropyl dimethylamine stearate, cocamidopropyl PG-dimonium chloride, distearoylethyl

hydroxyethylmonium methosulfate, dicocoylethyl hydroxyethylmonium metho-  
sulfate, distearoylethyl dimonium chloride, shea butteramidopropyltrimonium  
chloride, behenamidopropyl dimethylamine, brassicyl isoleucinate esylate,  
acrylamidopropyltrimonium chloride/acrylates copolymer, linoleamidopropyl  
5 ethyldimonium ethosulfate, dimethyl lauramine isostearate, isostearamidopropyl  
laurylacetodimonium chloride, particularly behentrimonium chloride, distearyldi-  
monium chloride, cetrimonium chloride, steartrimonium chloride, and palmitamido-  
propyltrimonium chloride.

10 The cosmetic composition further may comprise cosmetic carriers,  
excipients and diluents as well as additives and active ingredients commonly used  
in the skin care industry which are suitable for use in the cosmetic compositions of  
the present invention are for example described in the International Cosmetic  
Ingredient Dictionary & Handbook by Personal Care Product Council  
15 (<http://www.personalcarecouncil.org/>), accessible by the online INFO BASE  
(<http://online.personalcarecouncil.org/jsp/Home.jsp>), without being limited thereto.

Such possible ingredients of the cosmetic composition are particularly  
enhance the performance and/or consumer acceptability such as preservatives,  
antioxidants, fatty substances/oils, thickeners, softeners, light-screening agents,  
20 moisturizers, fragrances, co-surfactants, fillers, sequestering agents, cationic-,  
nonionic- or amphoteric polymers or mixtures thereof, acidifying or basifying  
agents, viscosity modifiers, and natural hair nutrients such as botanicals, fruit  
extracts, sugar derivatives and/or amino acids or any other ingredients usually  
formulated into cosmetic compositions. The necessary amounts of the adjuvants  
25 and additives can, based on the desired product, easily be chosen by a person  
skilled in the art in this field and will be illustrated in the examples, without being  
limited hereto.

The additional ingredients can either be added to the oily phase, the  
30 aqueous phase or separately as deemed appropriate.

In an advantageous embodiment, the compositions according to the  
present invention comprise from 50% to 99%, preferably from 60% to 98%, more

preferably from 70% to 98%, such as in particular from 80% to 95% of a carrier, based on the total weight of the cosmetic composition.

In a particular advantageous embodiment, the carrier consists furthermore  
5 of at least 40 wt. %, more preferably of at least 50 wt.-%, most preferably of at least 55 wt.-% of water, such as in particular of 55 to 90 wt.-% of water.

Furthermore, it is preferred that the cosmetic composition comprises at least one UV filter. The UV filter may be a liquid or solid UV filter. The UV filter  
10 may be a UV-A or UV-B filters.

Suitable liquid UV-filter absorb light in the UVB (280 - 315 nm) and/ or UVA (315 - 400 nm) range and are liquid at ambient temperature (i.e. 25°C). Such liquid UV-filter are well known to a person in the art and encompass in particular cinnamates such as e.g. octyl methoxycinnamate (PARSOL® MCX) and isoamyl  
15 methoxycinnamate (Neo Heliopan® E 1000), salicylates such as e.g. homosalate (3,3,5 trimethylcyclohexyl 2-hydroxybenzoate, PARSOL® HMS) and ethylhexyl salicylate (also known as ethylhexyl salicylate, 2 ethylhexyl 2-hydroxybenzoate, PARSOL® EHS), acrylates such as e.g. octocrylene (2 ethylhexyl 2-cyano-3,3-diphenylacrylate, PARSOL® 340) and ethyl 2-cyano-3,3 diphenylacrylate, esters  
20 of benzalmalonic acid such as in particular dialkyl benzalmalonates such as e.g. di (2-ethylhexyl) 4-methoxybenzalmalonate and polysilicone 15 (PARSOL® SLX), dialkylester of naphthalates such as e.g. diethylhexyl 2,6-naphthalate (Corapan® TQ), syringylidene malonates such as e.g. diethylhexyl syringylidene malonate (Oxynex® ST liquid) as well as benzotriazolyl dodecyl p-cresol (Tinoguard® TL)  
25 as well as benzophenone-3 and drometrizole trisiloxane.

Particular advantageous liquid UV-filter are octyl methoxycinnamate, homosalate, ethylhexyl salicylate, octocrylene, diethylhexyl 2,6-naphthalate, diethylhexyl syringylidene malonate, benzotriazolyl dodecyl p-cresol, benzo-  
30 phenone-3, drometrizole trisiloxane, Polysilicone-15 as well as mixtures thereof.

Suitable solid UV-filter absorb light in the UVB and/ or UVA range and are solid at ambient temperature (i.e. 25°C). They are particularly solid organic UV filters. Particularly suited solid UV-filters are of the group consisting of bis-ethyl-

hexyloxyphenol methoxyphenyl triazine, butyl methoxydibenzoyl methane, methylene bis-benzotriazolyl tetramethylbutylphenol, diethylamino hydroxybenzoyl hexyl benzoate, ethylhexyl triazone, diethylhexyl butamido triazone and 4-methylbenzylidene camphor.

5

The amount of an individual organic UV filter is preferably in the range of 0.1 to about 6 % by weight, preferable in the range of 0.5 to 5 % by weight, most preferably in the range of 1 to 4 % by weight, based on the total weight of the cosmetic composition.

10

In case of a sun care composition, the total amount of organic UV filter (s) depends strongly on the targeted UV protection of said composition and is typically in the range of between 1 to 50% by weight, preferably between 5 to 40% by weight, based on the total weight of said composition.

15

A sun creme with an SPF 15 (SPF=sun protection factor), for example, comprises preferably a total amount of organic UV filter (s) of between 4 to 20% by weight, more preferably between 7 and 15 % by weight, based on the total weight of said composition.

20

A sun creme with an SPF 30, for example, comprises preferably a total amount of organic UV filter (s) of between 10 to 40% by weight, more preferably between 15 and 25 % by weight, based on the total weight of said composition.

A sun creme with an SPF 50, for example, comprises preferably a total amount of organic UV filter (s) of between 15 to 50% by weight, more preferably between 20 and 40 % by weight, based on the total weight of said composition.

25

Particularly suitable thickeners in all embodiments of the present invention are xanthan gum, gellan gum and/ or carboxymethylcellulose. Most preferably in all embodiments of the present invention the thickener is xanthan gum or gellan gum. Further suitable thickeners are polyacrylates such as commercially available under the trade name Carbomer, or acrylate/C10-30 alkyl acrylate crosspolymers or salts of polyacrylic acid or polyacrylamides.

30

Such thickener(s) are preferably used in an amount (total) selected in the range from 0.1 to 1 wt.-%, more preferably in an amount of 0.1 to 0.5 wt.-%, based on the total weight of the cosmetic composition.

It is preferred that the composition is free of polyvinylpyrrolidones (PVP), particularly free of alkylated polyvinylpyrrolidones, such as copolymers of N-vinyl-

pyrrolidones and hexadecane or eicosene, e.g. as commercially available as Antaron V-216 or Antaron V-220.

The cosmetic compositions according to the invention in general have a pH in the range from 3 to 10, preferably a pH in the range from 4 to 8 and most preferably a pH in the range from 4 to 7.5. The pH is adjusted by methods known to a person skilled in the art, e.g. by using an acid such as a hydroxy acid including glycolic acid, lactic acid, malic acid, citric acid and tartaric acid or a base such as e.g. sodium or potassium hydroxide or ammonium hydroxide as well as mixtures thereof.

Preferably, in the compositions according to the invention citric acid in an amount of at least 0.0001 wt.-%, such as e.g. in an amount of 0.01-1 wt.-%, in particular in an amount of 0.01 to 0.5 wt.-% is used for pH adjustment.

The cosmetic composition is preferably sulfate-free and/or free of parabens, and/or silicon oils and/or silicone surfactants and/or methylisothiazolidine and/or free of polyvinylpyrrolidones (PVP), particularly free of alkylated polyvinylpyrrolidones.

The cosmetic composition is preferably a topical composition.

The term "topical" as used herein is understood here to mean external application to keratinous substances, which are in particular the skin, scalp, eyelashes, eyebrows, nails, mucous membranes and hair, preferably the skin.

As the topical compositions are intended for topical application, it is well understood that they comprise a physiologically acceptable medium, i.e. a medium compatible with keratinous substances, such as the skin, mucous membranes, and keratinous fibres. In particular, the physiologically acceptable medium is a cosmetically acceptable carrier.

The term "cosmetically acceptable carrier" refers to all carriers and/or excipients and/ or diluents conventionally used in cosmetic compositions such as in particular in sun care products.

Preferably the cosmetic composition is a skin care composition.

In a further embodiment, the cosmetic composition is a decorative preparation or a functional preparation.

Examples of skin care compositions are, in particular, light protective composition, anti-ageing composition, compositions/preparations for the treatment of photo-ageing, body oils, body lotions, body gels, treatment creams, skin protection ointments, skin powders, moisturizing gels, moisturizing sprays, face and/or body moisturizers, skin-tanning preparations (i.e. compositions for the artificial/sunless tanning and/or browning of human skin), for example self-tanning creams as well as skin lightening compositions.

Examples of functional preparations are cosmetic compositions containing active ingredients such as hormone preparations, vitamin preparations, vegetable extract preparations, anti-ageing preparations, and/or antimicrobial (antibacterial or antifungal) preparations without being limited thereto.

The cosmetic composition is preferably a skin care composition.

In a particular embodiment, the cosmetic composition is a sun care composition. Sun care compositions are light-protective composition (sun care products), such as sun protection milks, sun protection lotions, sun protection creams, sun protection oils, sun blocks or day care creams with a SPF (sun protection factor). Sun protection creams, sun protection lotions, sun protection milks and sun protection compositions are of particular interest.

20

The cosmetic compositions according to the present invention may be in the form of a suspension or dispersion in solvents or fatty substances, or alternatively in the form of an emulsion or micro emulsion (in particular of oil-in-water (O/W-) or water-in-oil (W/O-)type, silicone-in-water (Si/W-) or water-in-silicone (W/Si-)type, PIT-emulsion, multiple emulsion (e.g. oil-in-water-in oil (O/W/O-) or water-in-oil-in-water (W/O/W-)type), pickering emulsion, hydrogel, alcoholic gel, lipogel, one- or multiphase solution or vesicular dispersion or other usual forms, which can also be applied by pens, as masks or as sprays.

Preferred cosmetic compositions in all embodiments of the present invention are emulsions which contain an oily phase and an aqueous phase such as in particular O/W, W/O, Si/W, W/Si, O/W/O, W/O/W multiple or a pickering emulsions.

30

The total amount of the oily phase present in such emulsions is preferably at least 10 wt.-%, such as in the range from 10 to 60 wt.-%, preferably in the range from 15 to 50 wt.-%, most preferably in the range from 15 to 40 wt.-%, based on the total weight of the cosmetic composition.

5

The amount of the aqueous phase present in such emulsions is preferably at least 20 wt. %, such as in the range from 40 to 90 wt.-%, preferably in the range from 50 to 85 wt.-%, most preferably in the range from 60 to 85 wt.-%, based on the total weight of the cosmetic composition.

10

The cosmetic compositions can be in the form of a liquid, lotion, a thickened lotion, a gel, a cream, a milk, an ointment or a paste.

More preferably, the cosmetic compositions according to the present invention are in the form of an oil-in-water (O/W) emulsion comprising an oily phase dispersed in an aqueous phase in the presence of an O/W- respectively Si/W-emulsifier. The preparation of such O/W emulsions is well known to a person skilled in the art.

The compositions in form of O/W emulsions according to the invention can be provided, for example, in all the formulation forms for O/W emulsions, for example in the form of serum, milk or cream, and they are prepared according to the usual methods. The compositions which are subject-matters of the invention are preferably intended for topical application and can in particular constitute a dermatological or cosmetic composition, for example intended for protecting human skin against the adverse effects of UV radiation (antiwrinkle, anti-ageing, moisturizing, anti-sun protection and the like).

It is preferred that the cosmetic composition is a shampoo or a hair conditioner.

It is preferred that the cosmetic composition is a hair care composition.

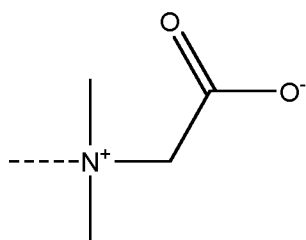
It is preferred that the cosmetic composition is a shampoo or a hair conditioner.

It is further preferred, that the cosmetic composition is a topical composition applied to the human skin, scalp and/ or hair.

It has been surprisingly found that hyperbranched copolymer **(HBC)** increases the antimicrobial action of antimicrobial agents in cosmetic compositions.

Hence, a further aspect of the present invention relates to the use of a  
5 hyperbranched copolymer **(HBC)** of the monomers

- (i) dodecanyl succinic acid anhydride
  - (ii) diisopropanol amine
  - (iii) bis-dimethylaminopropyl amine
- having terminal groups of the formula



10

and having a molecular weight  $M_n$  of between 1200 and 4000 g/mol; to enhance the antimicrobial action of 1,3-propanediol and/or N-hydroxyoctanamide.

Antimicrobial action has been observed particularly against the  
15 microorganisms which are selected from the group consisting *Kocuria rhizophila*, *Staphylococcus aureus*, *Enterobacter gergoviae*, *Escherichia coli*, *Klebsiella pneumoniae*, *Pseudomonas aeruginosa*, *Pseudomonas fluorescens*, *Pseudomonas putida*, *Aspergillus brasiliensis*, *Penicillium pinophilum* and *Candida albicans*, particularly against *Escherichia coli*.

20

The use of a hyperbranched copolymer **(HBC)** to enhance the antimicrobial action of 1,3-propanediol and/or N-hydroxyoctanamide can take place both in the cosmetic sense as well as in the pharmaceutical sense

25 It is preferred that the use is a non-therapeutic use.

In a cosmetic composition the use the non-therapeutic use is preferably a cosmetic use, such as for maintenance of skin homeostasis and/or balancing the skin microbiome and/or hair microbiome.

It has been observed that, when adding the above hyperbranched  
30 copolymer **(HBC)** to cosmetic compositions which comprises 1,3-propanediol

and/or N-hydroxyoctanamide, the antimicrobial action is increased significantly. In other words, by adding additionally the hyperbranched copolymer (**HBC**) to a cosmetic composition, which comprises 1,3-propanediol and/or N-hydroxyoctanamide, a smaller number of microbes are observed to grow than  
5 without the use of said hyperbranched copolymer (**HBC**). The above hyperbranched copolymer (**HBC**) has a synergistic effect on the antimicrobial action of 1,3-propanediol and/or N-hydroxyoctanamide in a composition, particularly in a cosmetic composition.

This is very advantageous also in such a way that the amount of 1,3-propanediol and/or N-hydroxyoctanamide can be reduced by adding the effective  
10 amount of the above hyperbranched copolymer (**HBC**) to maintain the same antimicrobial action.

It has been further observed that the antimicrobial action is particularly pronounced in an aqueous phase. This is very advantageous as it is known that it  
15 is typically the water phase of a product which is most susceptible to microbial growth.

## Examples

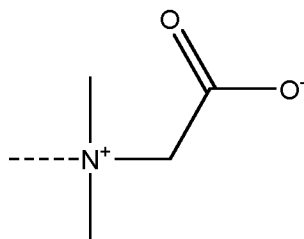
The present invention is further illustrated by the following experiments. These examples are illustrative only and are not intended to limit the scope of the invention in any way.

5

### Preparation of hyperbranched copolymer (**HBC1**)

The hyperbranched copolymer **HBC1** of the monomers dodecenyl succinic acid anhydride and diisopropanol amine and bis-dimethylaminopropyl amine has been prepared according to example 3 in EP 2 794 729 B1 using 237.59 g of N,N-bis(N,N'-dimethylaminopropyl)amine and 112.6 g diisopropanol amine and 426.89 g of dodecenylsuccinic anhydride. After heating and vacuum, the residual carboxylic acid content of < 0.3 meq/g (trimerical analysis) AV=9.8mg KOH/g and amine content of 2.99 meq/g (trimerical analysis) and a molecular weight Mn=2240 Da was obtained. This product has been reacted with sodium chloroacetate in water and stirred at 80°C until <sup>1</sup>H-NMR analysis shows a complete conversion of the chloroacetate to obtain the hyperbranched copolymer **HBC1** which has terminal groups of the formula

15



and a molecular weight Mn of 2.3 kDa.

The hyperbranched copolymer **HBC1** was used as a 50 % solution in water in the following experiments. The amounts indicated in table 1 are based on the amount of polymer.

20

### Testing of antimicrobial action (24 hours Challenge test)

Since it is known that typically a water phase of a product is most susceptible to microbial growth, the antimicrobial efficacy has been assessed in analogy to the regulatory challenge test method (NF EN ISO11930) for an aqueous solution.

25

Thus, a solution of **HPC1** and/or 1,3-propanediol and/or N-hydroxy-octanamide in an amount as indicated in table 1 were prepared under sterile conditions. For this, it was solubilized in physiological serum with 0.85 wt.-% NaCl.

30

The solutions were deposited in 96-deep well plates (1.6 ml/well). The wells were contaminated with *Escherichia coli* or *Aspergillus brasiliensis*, at  $6.3 \cdot 10^5$  or  $4.5 \cdot 10^4$  cfu/ml, respectively. After the contamination each well was thoroughly mixed to ensure a homogeneous distribution of the microorganism. Then each plate was incubated at 22°C for 24h. The counting of the (remaining) population was carried out 24h after contamination and reported in table 1.

	<b>Ref.1</b>	<b>Ref.2</b>	<b>Ref.3</b>	<b>1</b>	<b>Ref.4</b>	<b>2</b>	<b>Ref.5</b>	<b>3</b>
<b>HPC1</b> [wt. %]		0.5		0.5		0.5		0.5
1,3-propanediol [wt. %]			1.0	1.0				
Zeostat(1,3-propanediol/N-hydroxyoctanamide)[wt. %]					0.3	0.3		
N-hydroxyoctanamide [wt. %]							0.02	0.02
Colony counts after 24h [cfu/ml] with <i>E.coli</i> .	1'000'000	<1'000'000	1'000'000	4'000	700'000	0	700'000	400'000
Colony counts after 24h [cfu/ml] with <i>Aspergillus brasiliensis</i> .	45'000	700	n.m.	n.m.	n.m.	n.m.	700	100

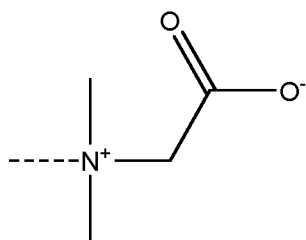
Table 1 Antimicrobial action in the 24 hours screen test with *E.coli*.  
n.m.: not measured.

The results of table 1 clearly show the effect that these specific copolymers, i.e. the hyperbranched copolymers, increase the antimicrobial action of 1,3-propanediol and/or N-hydroxyoctanamide. This effect is synergistic. It has been observed that **HPC1** and 1,3-propanediol and/or N-hydroxyoctanamide, particularly combined with N-hydroxyoctanamide, show in diverse cosmetic compositions such as shampoo or o/w skin care emulsions an increased antimicrobial effect.

**Claims**

1. A composition comprising  
 a) a hyperbranched copolymer (**HBC**) of the monomers

- 5 (i) dodecanyl succinic acid anhydride  
 (ii) diisopropanol amine  
 (iii) bis-dimethylaminopropyl amine  
 having terminal groups of the formula

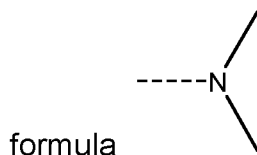


and having a molecular weight  $M_n$  of between 1200 and 4000 g/mol;

10 and

- b) 1,3-propanediol and/or N-hydroxyoctanamide.

2. The composition according to claim 1 characterized in that the  
 hyperbranched copolymer (**HBC**) is prepared by the consecutive steps of  
 15 a1) polymerizing the monomers (i) and monomers (ii) and monomers (iii) to  
 yield a polyesteramide having terminal dimethylamino groups of the



- a2) quaternization of the dimethyl amino groups of the polyesteramide of  
 step a1) by 2-chloroacetate, particularly by sodium 2-chloroacetate.

20

3. The composition according to anyone of the preceding claims characterized  
 in that the molar ratio of the monomers (i) to monomers (ii) is between 5 : 1  
 and 0.5 : 1, particularly between 4 : 1 and 1 : 1, preferably between 3 : 1 and  
 3 : 2.

25

4. The composition according to anyone of the preceding claims characterized  
 in that the molar ratio of the monomers (i) to monomers (iii) is between 5 : 1  
 and 0.5 : 1, particularly between 3 : 1 and 1 : 1, preferably between 2.5 : 1  
 and 1.1 : 1.

5. The composition according to anyone of the preceding claims characterized in that the hyperbranched copolymer has a number average molecular weight  $M_n$  of between 1400 and 3000 g/mol, preferably between 2100 and 2400 g/mol.  
5
6. The composition according to anyone of the preceding claims characterized in that the hyperbranched copolymer is polyquaternium-110.
7. The cosmetic composition according to anyone of the preceding claims,  
10 characterized in that the weight ratio of said hyperbranched copolymer **(HBC)** and 1,3-propanediol and/or N-hydroxyoctanamide is in the range of between 1:30 and 30:1, preferred between 1:20 – 20:1, more preferred between 1:10 and 10:1.
- 15 8. The composition according to anyone of the preceding claims, characterized in that composition is a cosmetic composition.
9. The cosmetic composition according to claim 8, characterized in that the  
20 amount of the hyperbranched copolymer **(HBC)** is between 0.005 and 5.0 % by weight, preferably between 0.05 and 5.0 % by weight, more preferably between 0.1 and 3.0 % by weight, most preferably between 0.5 and 2.5 % by weight, based on the total weight of the cosmetic composition.
10. The cosmetic composition according to claim 8 or 9, characterized in that the  
25 cosmetic composition is a skin care composition.
11. The cosmetic composition according to claim 8 or 9, characterized in that the cosmetic composition is a hair care composition.
- 30 12. The cosmetic composition according to anyone of the preceding claims 8 to 11, characterized in that the cosmetic composition is a shampoo or a hair conditioner.

13. The cosmetic composition according to anyone of the preceding claims 8 to 11, characterized in that the cosmetic composition is a topical composition applied to the human skin, scalp and/ or hair.

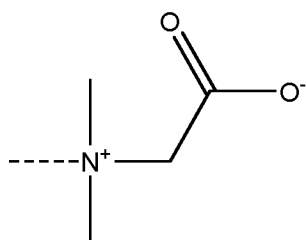
5 14. Use of a hyperbranched copolymer (**HBC**) of the monomers

(i) dodecanyl succinic acid anhydride

(ii) diisopropanol amine

(iii) bis-dimethylaminopropyl amine

having terminal groups of the formula



and having a molecular weight  $M_n$  of between 1200 and 4000 g/mol;  
to enhance the antimicrobial action of 1,3-propanediol and/or N-hydroxy-  
octanamide.

15 15. Use according to claim 14, characterized in that the use is a non-therapeutic  
use, particularly a cosmetic use.

**INTERNATIONAL SEARCH REPORT**

International application No  
PCT/EP2020/059102

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. A61K8/85	A61K8/88	A61Q5/00	C08G69/44	C08G83/00
C08L101/00	C08K5/00	A01N25/10	C08K5/20	C08L77/12
A61K31/16	A01N37/18	A61K8/34	A61K8/42	A61Q17/00

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)

C09J A61Q A61K C08G C08L C08K A01N

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)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 2 895 141 A1 (DSM IP ASSETS BV [NL]) 22 July 2015 (2015-07-22) claim 1 paragraph [0019]	1-15
A	EP 2 895 560 A1 (DSM IP ASSETS BV [NL]) 22 July 2015 (2015-07-22) claim 1 paragraph [0005] paragraph [0024]	1-15
A	KR 101 641 498 B1 (CWUIACF [KR]) 21 July 2016 (2016-07-21) claim 1	1-15

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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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

Date of the actual completion of the international search

8 April 2020

Date of mailing of the international search report

21/04/2020

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040,  
Fax: (+31-70) 340-3016

Authorized officer

Costantini, Nicola

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/EP2020/059102
---

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
EP 2895141	A1	22-07-2015	BR 112015005622 A2	04-07-2017
			CN 104619309 A	13-05-2015
			EP 2895141 A1	22-07-2015
			ES 2657604 T3	06-03-2018
			JP 6202449 B2	27-09-2017
			JP 2015529674 A	08-10-2015
			KR 20150056549 A	26-05-2015
			US 2015320670 A1	12-11-2015
			WO 2014041019 A1	20-03-2014
-----				
EP 2895560	A1	22-07-2015	BR 112015005614 A2	04-07-2017
			CN 104640931 A	20-05-2015
			EP 2895560 A1	22-07-2015
			ES 2596241 T3	05-01-2017
			JP 6085820 B2	01-03-2017
			JP 2015529737 A	08-10-2015
			KR 20150056775 A	27-05-2015
			US 2015216789 A1	06-08-2015
			WO 2014040811 A1	20-03-2014
-----				
KR 101641498	B1	21-07-2016	NONE	
-----				