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(71) Applicant: EVONIK OPERATIONS GMBH [DE/DE];
Rellinghauser Strasse 1-11, 45128 Essen (DE).

(72) Inventors: SCHWAB, Peter; Frankenstrasse 222, 45134
Essen (DE). JARECKI, Christine; 63 Northleach Drive
Hemlington, Middlesbrough Yorkshire TS8 9PP (GB).

(72) Inventor: LATINOVIC, Milan (deceased).

(74) Agent: EVONIK PATENT ASSOCIATION; c/o Evonik
Industries AG / IP-Management, Bau 1042A - PB 15, Paul-
Baumann-Straße 1, 45772 Marl (DE).

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(54) Title: OXIDATION PRODUCTS OF METHIONYLMETHIONINE

(57) Abstract: The present invention relates to sulfoxides and sulfones of the methionylmethionine stereoisomers D-methionyl-L-methionine, L-methionyl-D-methionine and D-methionyl-D-methionine. An additional object is cosmetic formulations comprising sulfoxides and sulfones of methionylmethionine and also the use of the sulfoxides and sulfones of methionylmethionine contained.

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Oxidation products of methionylmethionine

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Field of the invention

The invention relates to oxidation products of methionylmethionine, to their preparation and use.

10 Prior art

EP 2 835 151 discloses cosmetic formulations containing at least one methionylmethionine stereoisomer chosen from the group D-methionyl-L-methionine, L-methionyl-D-methionine and D-methionyl-D-methionine and also the use of methionylmethionine for nail and/or hair treatment.

15

Supplemental of J. Am. Chem. Soc., 1998, 120(14), 3345-3356, discloses the di- and monosulfoxides of the methionylmethionine stereoisomer L-methionyl-L-methionine.

It is an object of the invention to make available compositions which exhibit, compared with methionylmethionine, a reduced odour.

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Description of the invention25

It has been found that, surprisingly, the oxidation products of methionylmethionine described below are able to solve the problem addressed by the invention.

The present invention accordingly relates to sulfoxides and sulfones of the methionylmethionine stereoisomers D-methionyl-L-methionine, L-methionyl-D-methionine and D-methionyl-D-methionine.

30

An additional object is cosmetic formulations comprising sulfoxides and sulfones of methionylmethionine and also the use of the sulfoxides and sulfones of methionylmethionine contained.

35

It is an advantage of the oxidation products of methionylmethionine that these exhibit, compared with methionylmethionine itself, an increased solubility in water.

It is an advantage of the oxidation products of methionylmethionine that the solubility in water can be controlled via the oxidation stages.

It is a further advantage of the present invention that the oxidation products of methionylmethionine can be incorporated very well in cosmetic formulations

It is an additional advantage of the present invention that the oxidation products are odourless.

It is a further advantage of the present invention that the oxidation products are colourless.

It is an additional advantage of the present invention that the oxidation products are thermally stable.

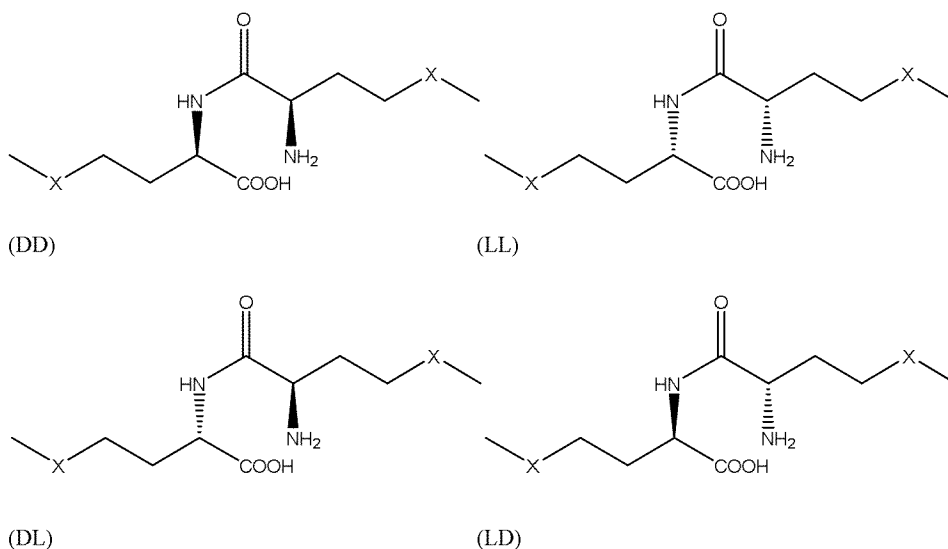
5 It is a further advantage of the present invention that the oxidation products are non-toxic.

It is an additional advantage of the present invention that the oxidation products can be easily prepared and isolated.

It is a further advantage of the present invention that the oxidation products are biodegradable.

10 It is a further advantage of the present invention that the oxidation products are hygroscopic and moisturizing.

The present invention accordingly relates to a cosmetic formulation comprising at least one oxidation product of methionylmethionine chosen from the group of the general formulae



15 with X, independently of one another, identically or differently chosen from S, SO and SO₂, with the proviso that at least one X in each general formula is not equal to S.

As can be seen above, four different stereoisomers of the oxidation product of methionylmethionine exist.

20 The letters D and L held in brackets describe the stereochemistry of the oxidation products of methionylmethionine.

Here, DD and LL behave towards each other as image and mirror image, i.e. they are enantiomers and therefore also have the same physical properties. The same is true for the pair DL and LD.

25 The two pairs DD/LL and DL/LD are in comparison diastereomeric relative to one another, i.e. they have different physical data.

The use according to the invention, where it is the case of a use on a living species, is exclusively a cosmetic and a non-therapeutic use.

Unless otherwise indicated, all stated percentages (%) are percentages by weight.

Preferred cosmetic formulations according to the invention are characterized in that at least one X is equal to SO or SO₂, particularly preferably SO; very particularly preferably, X is equal to SO.

5

Cosmetic formulations according to the invention are preferably characterized in that the total amount of the oxidation products of methionylmethionine present is from 0.01% by weight to 20% by weight, preferably from 0.1% by weight to 10% by weight, particularly preferably from 0.1% by weight to 10% by weight, the percentages by weight being with reference to the total formulation.

10

Preferably, the total amount of LL, with reference to the total weight of all oxidation products of methionylmethionine present in the formulation according to the invention, is less than or equal to 50% by weight, preferably less than 35% by weight, particularly preferably less than 18% by weight.

15

It is preferred according to the invention for the ratio by weight of DL and LD to DD and LL in the cosmetic formulation according to the invention to be from 9:1 to 2:3, preferably 8:2 to 1:1, in particular 6:3 to 4:2, where per enantiomer pair in each case the sum of the individual enantiomers is taken into consideration. The abovementioned formulation does not exclude the possibility of only one of the enantiomers of an enantiomer pair being present in the formulation.

20

In an alternatively preferred embodiment, the ratio by weight of DL and LD to DD and LL in the formulation according to the invention is from 10:80 to 0.01:110.

25 Preferred cosmetic formulations according to the invention are characterized in that they represent an aqueous solution, an emulsion or suspension.

The formulations according to the invention can comprise e.g. at least one additional component chosen from the group of

30

emollients,
surfactants,
emulsifiers,
thickeners/viscosity regulators/stabilizers,
UV light protection filters,

35

antioxidants,
hydrotropes (or polyols),
solids and fillers,
film formers,
pearlescence additives,

deodorant and antiperspirant active substances,
insect repellents,
self-tanning agents,
preservatives,
5 conditioning agents,
perfumes,
colourants,
odour absorbers,
cosmetic active substances,
10 care additives,
superfatting agents,
solvents.

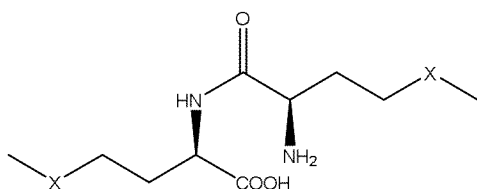
Substances which can be used as exemplary representatives of the individual groups are known to
15 a person skilled in the art and can be taken, for example, from German Patent Application DE
102008001788.4. This patent application is hereby incorporated as reference and thus forms part
of the disclosure.

As regards further optional components and also the amounts employed of these components,
20 reference is expressly made to the relevant handbooks known to a person skilled in the art, for
example K. Schrader, "Grundlagen und Rezepturen der Kosmetika" [Fundamentals and
Formulations of Cosmetics], 2nd edition, pages 329 to 341, Hüthig Buch Verlag, Heidelberg.

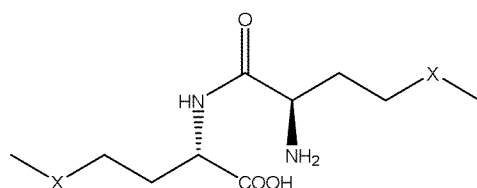
The amounts of the respective additives depend on the intended use.
25 Typical starting formulations for the relevant applications are known prior art and are contained for
example in the brochures of the manufacturers of the relevant base materials and active
substances. These existing formulations can generally be adopted unchanged. However, if
necessary, for adjustment and optimization, the desired modifications can be executed in a
straightforward manner through simple tests.

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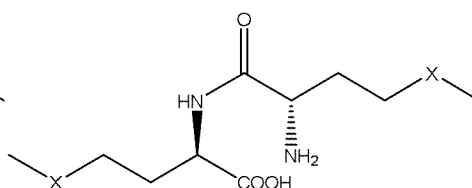
An additional object of the present invention is a compound chosen from the general formulae



(DD)



(DL)

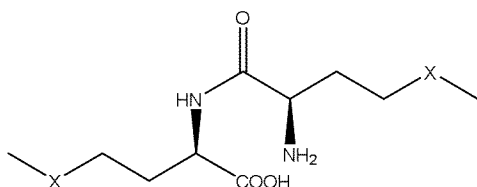


(LD)

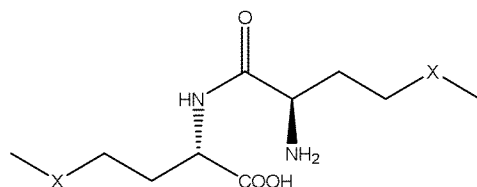
with X, independently of one another, identically or differently chosen from S, SO and SO₂, with the proviso that at least one X in each general formula is not equal to S.

- 5 Preferred compounds according to the invention are characterized in that X is equal to SO or SO₂, particularly preferably SO.

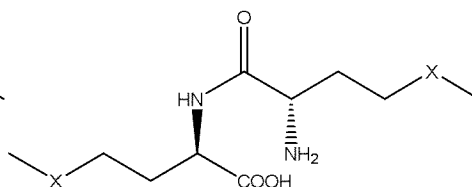
An additional object of the present invention is a process for the preparation of at least one compound chosen from the general formulae



(DD)



(DL)



(LD)

10

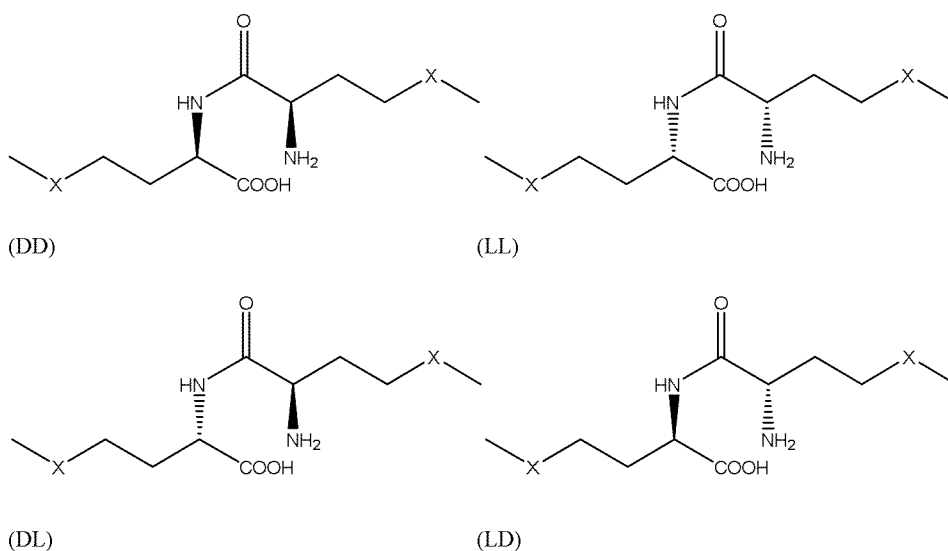
with X, independently of one another, identically or differently chosen from S, SO and SO₂, with the proviso that at least one X in each general formula is not equal to S, comprising the stages of:

- A) making available at least one compound chosen from DD, DL and LD, where all X = S,
 15 B) bringing the at least one compound chosen in process stage A) into contact with an oxidizing agent and oxidizing at least one X = S to give SO and/or SO₂, and
 C) optionally isolating the oxidized at least one compound.

A preferred process according to the invention is characterized in that the oxidizing agent is chosen from hydrogen peroxide, ozone, peracetic acid, sodium hypochlorite, potassium hypochlorite, perborates, percarbonates, iodine, bromine, chlorine, permanganate, dichromate and bromate, preferably hydrogen peroxide, peracetic acid and sodium hypochlorite, particularly preferably hydrogen peroxide.

Another object of the present invention is a process for the preparation of the cosmetic formulations according to the invention comprising the stages:

10 A2) making available at least one compound chosen from the group of the general formulae



with X, independently of one another, identically or differently chosen from S, SO and SO₂, with the proviso that at least one X in each general formula is not equal to S,

15 B2) bringing the at least one compound chosen in process stage A2) into contact with an oxidizing agent and oxidizing at least one X = S to give SO and/or SO₂, and

C2) incorporating the at least one oxidized compound, optionally isolated beforehand, in a cosmetic formulation, in particular in the form of an emulsion.

20 An additional object of the present invention is the use of at least one oxidation product of methionylmethionine as present in the formulations according to the invention for the treatment of nails and hair, for the conditioning of hair, for increasing the gloss of the hair, for increasing the tensile strength of the hair and/or for increasing the volume of hair.

25 An additional object of the present invention is the use of at least one oxidation product of methionylmethionine as present in the formulations according to the invention for increasing the colour intensity of the hair, for increasing the load-bearing capacity of the hair, for protecting the hair from UV damage, for protecting the hair from oxidative damage, for protecting the hair from thermal damage and/or for protecting the hair from chemical damage.

An additional object of the present invention is the use of at least one oxidation product of methionylmethionine as present in the formulations according to the invention known for improving the mechanical properties of nails.

5

According to the invention, the abovementioned formulations according to the invention can in particular be used, preferred formulations according to the invention preferably being used according to the invention.

10 The present invention is described by way of example in the examples cited below, without the invention, the scope of application of which results from the entirety of the description and from the claims, being restricted to the embodiments mentioned in the examples.

15 The following figures are an integral part of the examples:

Figure 1: mechanical properties of hair after oxidative damage.

Figure 2: skin moisture measurements

20 Examples:

For the present examples, the mixture of the stereoisomers of methionylmethionine was used. The possibility exists of separating the individual stereoisomers by crystallization to start with and thus of attaining the oxidation products enriched in a stereoisomer. Apart from this, the pure
25 stereoisomers of methionylmethionine can be prepared by selective synthesis according to Sharpless (asymmetric aminohydroxylation (AA) according to Sharpless a) G. Li, H.-T. Chang and K. B. Sharpless, Angew. Chem. Int. Ed., 1996, 35, 451-454; b) G. Li and K. B. Sharpless, Acta Chem. Scand., 1996, 50, 649-651) or according to Schöllkopf (the Schöllkopf bis-lactim ether method for the synthesis of enantiomerically pure α -amino acids a) U. Schöllkopf, T. Tiller and J.
30 Bardenhagen, Tetrahedron, 1988, 44, 5293-5305; b) U. Schöllkopf, Tetrahedron, 1983, 39, 2085-2091). Accordingly, even the pure stereoisomers of the oxidation products are consequently available.

Example 1: Oxidation of methionylmethionine to give the disulfoxide

35

5.6 g (0.02 mol) of methionylmethionine were suspended in 20 ml of demineralized water. 4.2 ml (0.04 mol) of 30% hydrogen peroxide were slowly added thereto dropwise at 20°C, so that the reaction temperature 35°C was not exceeded. After the total amount of hydrogen peroxide had been added, the mixture was heated at 50°C for one hour. The complete conversion of the starting

compounds was verified by HPLC. The water was subsequently distilled off and the white residue was dried at 50°C and 30 mbar. The complete conversion to the disulfoxide was analytically confirmed by ^1H NMR and ^{13}C NMR. The substance was odourless.

5

Example 2: Oxidation of methionylmethionine to give the disulfone

5.6 g (0.02 mol) of methionylmethionine were suspended in 20 ml of demineralized water. 8.4 ml (0.08 mol) of 30% hydrogen peroxide were slowly added thereto dropwise at 20°C, so that the reaction temperature 35°C was not exceeded. After the total amount of hydrogen peroxide had been added, the mixture was heated at 90°C for three hours. The complete conversion of the starting compounds was verified by HPLC. The water was subsequently distilled off and the white residue was dried at 50°C and 30 mbar. The complete conversion to the disulfone was analytically confirmed by ^1H NMR and ^{13}C NMR. The substance was odourless.

15

Example 3: Improvement in the mechanical properties of oxidatively damaged hair

Caucasian hair (21 cm long, colour 6/0, blend 852) from Kerling was chemically bleached. A mixture of 9% aqueous hydrogen peroxide and Basle bleach paste in the ratio 2:1 was prepared for this and was applied to the hair in the ratio 4 g/1 g of hair. After an action time of 50 min at AT, the hair was rinsed with warm water at 35°C for 2 min. The hair was subsequently dried. The hair thus bleached was immersed for 30 min in aqueous solutions of different concentrations of the substance obtained in Example 1. The hair was subsequently rinsed with tap water at a temperature of 35°C for a time of 1 min. The hair was finally dried. For the measurements, each time 50 hairs were tested in a Diastron Cyc 801 for fatigue (constant stress at 0.0145 g/ μm^2 , max 100 000 cycles, trigger load 10 gmf, frequency 50 mm/s).

Figure 1 shows the results and that the use of Example 1 restores the mechanical properties of hair after oxidative damage.

30

Example 4: Improvement in the moisture content of the skin

	Vehicle	Formulation 1
	to 100	to 100
Tego® Care LTP (Sorbitan Laurate; Polyglyceryl-4 Laurate; Dilauryl Citrate)	2.0%	2.0%

Tegosoft® CT (Caprylic/Capric Triglyceride)	5.0%	5.0%
Example 1 according to the invention		5.0%
Tegosoft® TN (C12-15 Alkyl Benzoate)	5.0%	5.0%
Tego® Carbomer 140 (Carbomer)	0.15%	0.15%
Tego® Carbomer 141 (Carbomer)	0.15%	0.15%
	Body cream	Body cream
Preservative, perfume	Body cream	Body cream

A moisture study was carried out. In this connection, two formulations were compared with each other (Vehicle and Formulation 1) 20 micrograms of the formulation were each time applied to the forearm. The skin moisture was measured after 2 hours and compared with the skin moisture before application.

Figure 2 shows the results and that the use of Example 1 improves the skin moisture.

Example 5: Improved smell

The following compositions were assessed by a trained panel of 10 persons regarding their smell from 0 to 5, with 0 = no detectable smell and 5 = very strong smell

Methionine (solid)	5
Methionylmethionine (solid)	3
example 1 (solid)	0
Formulation X containing 2% methionine	3
Formulation X containing 2% methionylmethionine	2
Formulation X	0
Formulation X containing 2% example 1	0
Formulation X containing 2% methionine. 3 months @ 40 °C	4
Formulation X containing 2% methionylmethionine. 3 months @ 40 °C	4
Formulation X containing 2% example 1. 3 months @ 40 °C	0
Formulation X. 3 months @ 40 °C	0

Formulation X had the basic recipe

5 % TEGO® Alkanol 1618

0.5 % TEGINACID C

1 % Varisoft BT85
 qs preservative
 ad 100% water
 were prepared additionally containing X:

5

Example 6: Effect on nails

The Formulation Example 8) Body Care Composition below was applied (2ml) onto one side's hand's nail only on a trained panel of 10 persons for 3 weeks daily until total absorption was achieved. The other side's hand was treated with the same Formulation without the active. All persons considered the nails of the side treated with example 1 containing composition to be stronger, less brittle and having a more even and glossy surface than the side treated with just the vehicle.

15

Formulation examples:

Formulation Example 1) Pearlized Shampoo

Texapon® NSO, Cognis, 28% strength (INCI: Sodium Laureth Sulfate)	32.25%
Example 1 according to the invention	0.25%
Perfume	0.25%
	55.25%
Tego® Betain F 50, Evonik Industries AG, 38% strength (INCI: Cocamidopropyl Betaine)	8.00%
Tego® Pearl N 300, Evonik Industries AG (INCI: Glycol Distearate; Laureth-4; Cocamidopropyl Betaine)	2.00%
Antil® 171, Evonik Industries AG (INCI: PEG-18 Glyceryl Oleate/Cocate)	1.50%
1% NaCl	0.50%
Preservative	Body cream

20

Formulation Example 2) Rinse-Off Conditioner

	91.0%
Teginacid® C, Evonik Industries AG Ceteareth-25)	0.5%

Example 1 according to the invention	
Varisoft® BT 85, Evonik Industries AG (INCI: Tego® Alkanol 1618, Evonik Industries AG (INCI: Cetearyl Alcohol)	2.50%
Preservative, perfume	5.00%
	q.s.

Formulation Example 3) Rinse-Off Conditioner

	91.0%
Example 1 according to the invention	2.00%
Varisoft® BT 85, Evonik Industries AG (INCI: Behentrimonium Chloride)	2.00%
Tego® Alkanol 1618, Evonik Industries AG (INCI: Cetearyl Alcohol)	5.00%
Preservative, perfume	q.s.

5

Formulation Example 4) Rinse-Off Conditioner

	90.20%
Example 1 according to the invention	2.00%
Varisoft® EQ 65, Evonik Industries AG (INCI: Distearoyl Dimonium Chloride, Cetearyl Alcohol)	2.00%
Tego® Alkanol 1618, Evonik Industries AG (INCI: Cetearyl Alcohol)	5.80%
Preservative, perfume	q.s.

Formulation Example 5) Leave-In Conditioner Spray

	0.40%
	94.30%
Example 1 according to the invention	1.20%
Varisoft® EQ 65, Evonik Industries AG (INCI: Distearoyl Dimonium Chloride, Cetearyl Alcohol)	
Tegin® G 1100 Pellets, Evonik Industries AG (INCI: Glycol Distearate)	0.60%
Tego® Care PS, Evonik Industries AG (INCI: Methyl Glucose Sesquistearate)	1.20%

Tegosoft® DEC, Evonik Industries AG (INCI: Diethylhexyl Carbonate)	1.30%
Preservative, perfume	Body cream

Formulation Example 6) Leave-in Conditioner Foam

Example 1 according to the invention	2.30%
Tagat® CH-40, Evonik Industries AG (INCI: PEG-40 Hydrogenated Castor Oil)	1.0%
Perfume	0.30%
Tego® Betain 810, Evonik Industries AG (INCI: Capryl/Capramidopropyl Betaine)	2.00%
	92.00%
Tego® Cosmo C 100, Evonik Industries AG (INCI: Creatine)	0.50%
Tegocel® HPM 50, Evonik Industries AG (INCI: Hydroxypropyl Methylcellulose)	0.30%
Varisoft® 300, Evonik Industries AG (INCI:	1.0%
Lactil®, Evonik Industries AG (INCI: Sodium Lactate; Sodium PCA; Glycine; Fructose; Urea; Niacinamide; Inositol; Sodium Benzoate; Lactic Acid)	0.50%
	0.10%
Preservative	q.s.

Formulation Example 7) Strong Hold Styling Gel

Tego® Carbomer 141, Evonik Industries AG (INCI:	1.20%
	65.70%
NaOH, 25%	2.70%
PVP/VA W-735, ISP (INCI: PVP/VA Copolymer)	16.00%
Example 1 according to the invention	1.30%
Denat. Alcohol	10.50%
Tagat® O 2 V, Evonik Industries AG (INCI: PEG-20 Glyceryl Oleate)	2.00%
Perfume	0.30%
Abil® B 88183, Evonik Industries AG (INCI:	0.30%
Preservative	q.s.

Formulation Example 8) Body Care Composition

Texapon® NSO, Cognis, 28% strength (INCI: Sodium Laureth Sulfate)	30.00%
Tegosoft® PC 31, Evonik Industries AG (INCI:	0.70%
Example 1 according to the invention	1.30%
Perfume	0.30%
	52.90%
Tegocel® HPM 4000, Evonik Industries AG (INCI: Hydroxypropyl Methylcellulose)	0.30%
Rewoteric® AM C, Evonik Industries AG, 32% strength (INCI: Sodium Cocoamphoacetate)	10.00%
Citric Acid Monohydrate	0.50%
Rewoderm® LI S 80, Evonik Industries AG (INCI: PEG-200 Hydrogenated Glyceryl Palmate; PEG-7 Glyceryl Cocoate)	2.00%
Tego® Pearl N 300, Evonik Industries AG (INCI: Glycol Distearate; Laureth-4; Cocamidopropyl Betaine)	2.00%

Formulation Example 9) Mild Foam Bath

Texapon® NSO, Cognis, 28% strength (INCI: Sodium Laureth Sulfate)	27.00%
Rewopol® SB FA 30, Evonik Industries AG, 40% strength (INCI: Disodium Laureth Sulfosuccinate)	12.00%
Tegosoft® LSE 65 K Soft, Evonik Industries AG (INCI:	2.00%
	39.00%
Rewoteric® AM C, Evonik Industries AG, 32% strength (INCI: Sodium Cocoamphoacetate)	13.00%
Example 1 according to the invention	0.40%
Citric Acid (30% in water)	3.00%
Antil® 171, Evonik Industries AG (INCI: PEG-18 Glyceryl Oleate/Cocoate)	1.60%
Tego® Pearl N 300, Evonik Industries AG (INCI: Glycol Distearate; Laureth-4; Cocamidopropyl Betaine)	2.00%

5

Formulation Example 10: Hot Oil Treatment

	96.5
Polyquaternium-10	1.0%
Hydroxyethylcellulose	0.5%

Example 1 according to the invention	1.0%
Varisoft® BT 85, Evonik Industries AG (INCI: Behentrimonium Chloride)	1.0%
Lauramide DEA	1.0%
Citric Acid, 30%	
Preservative, perfume	q.s.

Formulation Example 11: Moisturizing Cream

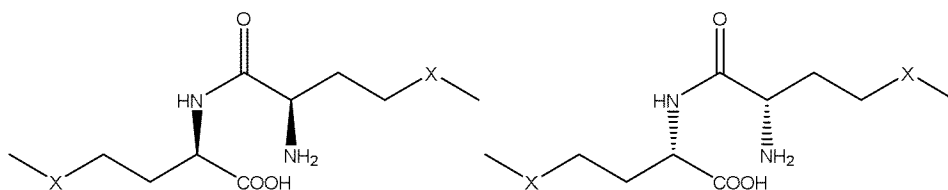
	to 100
Tego® Care LTP (Sorbitan Laurate; Polyglyceryl-4 Laurate; Dilauryl Citrate)	2.0%
Tegosoft® CT (Caprylic/Capric Triglyceride)	
Example 1 according to the invention	
Tegosoft® TN (C12-15 Alkyl Benzoate)	5.0%
Tego® Carbomer 140 (Carbomer)	0.15%
Tego® Carbomer 141 (Carbomer)	0.15%
	q.s.
Preservative, perfume	q.s.

5 Formulation Example 12: Moisturizing Cream

	to 100
Tego® Care LTP (Sorbitan Laurate; Polyglyceryl-4 Laurate; Dilauryl Citrate)	2.0%
Tegosoft® CT (Caprylic/Capric Triglyceride)	
Example 2 according to the invention	
Tegosoft® TN (C12-15 Alkyl Benzoate)	5.0%
Tego® Carbomer 140 (Carbomer)	0.15%
Tego® Carbomer 141 (Carbomer)	0.15%
NaOH (10%)	q.s.
Preservative, perfume	Body cream

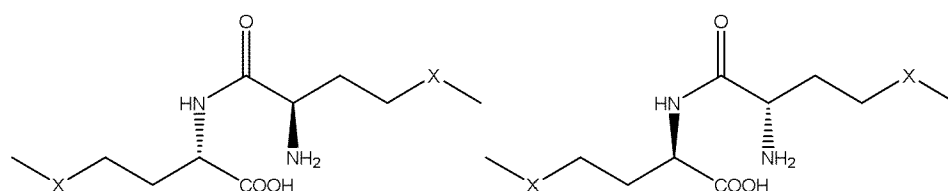
Claims

1. Cosmetic formulation comprising at least one oxidation product of methionylmethionine chosen from the group of the general formulae



(DD)

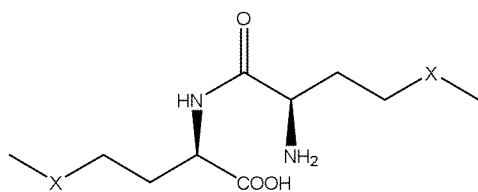
(LL)



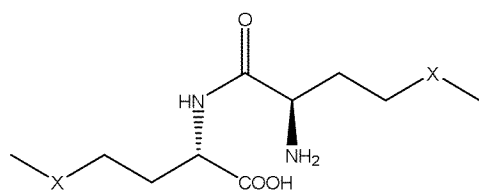
(DL)

(LD)

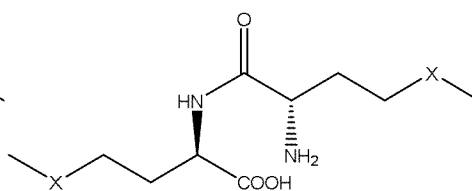
- 5 with X, independently of one another, identically or differently chosen from S, SO and SO₂, with the proviso that at least one X in each general formula is not equal to S.
- 10 2. Cosmetic formulation according to Claim 1, characterized in that at least one X is equal to SO or SO₂, particularly preferably SO; very particularly preferably, X is equal to SO.
- 15 3. Cosmetic formulation according to Claim 1 or 2, characterized in that the total amount of the oxidation products of methionylmethionine present is from 0.01% by weight to 20% by weight, preferably from 0.1% by weight to 10% by weight, particularly preferably from 0.1% by weight to 10% by weight, the percentages by weight being with reference to the total formulation.
- 20 4. Cosmetic formulation according to at least one of the preceding claims, characterized in that the ratio by weight of DL and LD to DD and LL is from 9:1 to 2:3, preferably 8:2 to 1:1, in particular 6:3 to 4:2.
5. Cosmetic formulation according to at least one of Claims 1 to 3, characterized in that the ratio by weight of DL and LD to DD and LL is from 10:80 to 0.01:110.
- 25 6. Cosmetic formulation according to at least one of the preceding claims, characterized in that it represents an aqueous solution, an emulsion or suspension.
7. Compound chosen from the general formulae



(DD)



(DL)



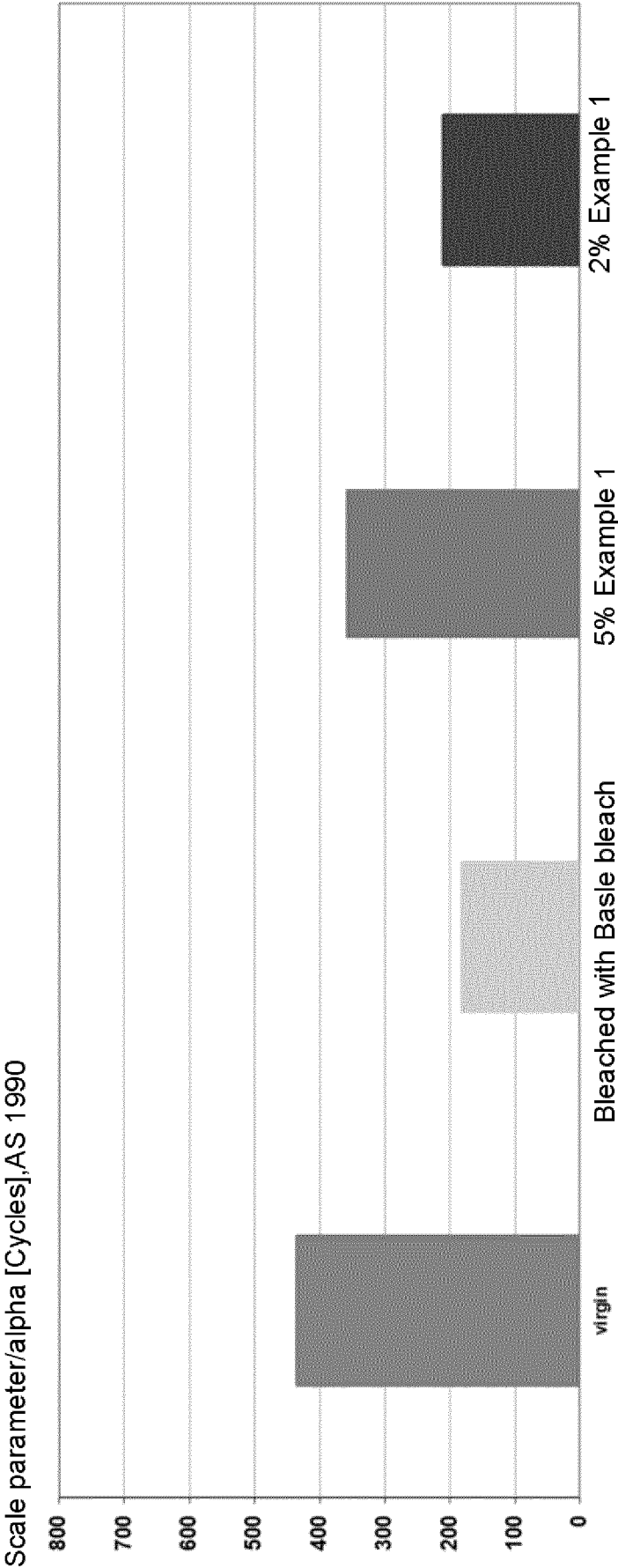
(LD)

with X, independently of one another, identically or differently chosen from S, SO and SO₂, with the proviso that at least one X in each general formula is not equal to S.

- 5 8. Compound according to Claim 7, characterized in that X is equal to SO or SO₂, particularly preferably is SO.
9. Process for the preparation of at least one compound according to Claim 7, comprising the stages:
 - 10 A) making available at least one compound chosen from DD, DL and LD, where all X = S,
 - B) bringing the at least one compound chosen in process stage A) into contact with an oxidizing agent and oxidizing at least one X = S to give SO and/or SO₂, and
 - C) optionally isolating the oxidized at least one compound.
- 15 10. Process according to Claim 9, characterized in that the oxidizing agent is chosen from hydrogen peroxide, ozone, peracetic acid, sodium hypochlorite, potassium hypochlorite, perborates, percarbonates, iodine, bromine, chlorine, permanganate, dichromate and bromate, preferably hydrogen peroxide, peracetic acid and sodium hypochlorite, particularly preferably hydrogen peroxide.
- 20 11. Process for the preparation of a cosmetic formulation according to at least one of Claims 1 to 6, comprising the stages
 - 25 A2) making available at least one compound chosen from DD, LL, DL and LD, where all X = S,
 - B2) bringing the at least one compound chosen in process stage A2) into contact with an oxidizing agent and oxidizing at least one X = S to give SO and/or SO₂, and

- C2) incorporating the at least one oxidized compound, optionally isolated beforehand, in a cosmetic formulation, in particular in the form of an emulsion.
12. Use of at least one oxidation product of methionylmethionine as mentioned in at
5 least one of Claims 1 to 6 for the treatment of nails and hair, for the conditioning of hair, for increasing the gloss of the hair, for increasing the tensile strength of the hair and/or for increasing the volume of hair.
13. Use of at least one oxidation product of methionylmethionine as mentioned in at
10 least one of Claims 1 to 6 for increasing the colour intensity of the hair, for increasing the load-bearing capacity of the hair, for protecting the hair from UV damage, for protecting the hair from oxidative damage, for protecting the hair from thermal damage and/or for protecting the hair from chemical damage.
14. Use of at least one oxidation product of methionylmethionine as mentioned in at
15 least one of Claims 1 to 6 for improving the mechanical properties of nails.
15. Use according to at least one of Claims 12 to 14, characterized in that a formulation according to one of Claims 1 to 6 is used.

Figure 1
Hair fibre fatigue after Basle bleaching
(repair)



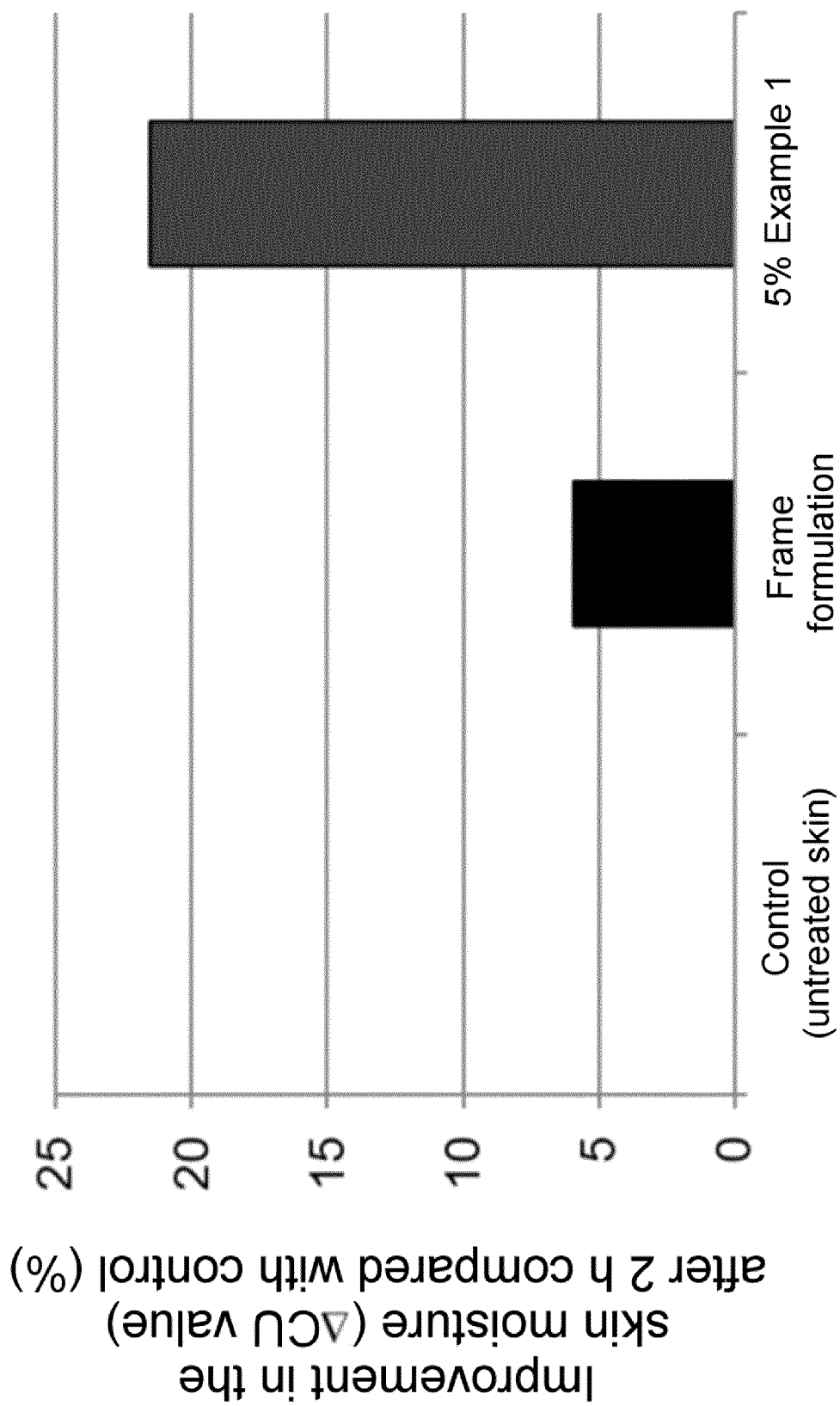


Figure 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2022/063139

A. CLASSIFICATION OF SUBJECT MATTER INV. A61K8/44 A61K8/64 A61Q5/12 A61Q5/02 A61Q5/00 A61Q19/00 ADD. 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) A61K A61Q 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, CHEM ABS Data, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	MILLER BRIAN L. ET AL: "One-Electron Photooxidation of N -Methionyl Peptides. Mechanism of Sulfoxide and Azasulfonium Diastereomer Formation through Reaction of Sulfide Radical Cation Complexes with Oxygen or Superoxide", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY / vol. 120, no. 14 1 April 1998 (1998-04-01), pages 3345-3356, XP055859666, ISSN: 0002-7863, DOI: 10.1021/ja973084t Retrieved from the Internet: URL:https://pubs.acs.org/doi/pdf/10.1021/j a973084t [retrieved on 2021-11-10] page 3348; table 1 ----- -/--	7-9
☒ 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		Date of mailing of the international search report
4 August 2022		26/08/2022
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 Bader, Karl Günther

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2022/063139

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	DE 10 2014 225221 A1 (HENKEL AG & CO KGAA [DE]) 21 January 2016 (2016-01-21)	1-3, 6-13, 15
Y	paragraph [0004] - paragraph [0009] paragraph [0077] - paragraph [0078] -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2022/063139

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		EP 2835151 A1	11-02-2015
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		US 2015044158 A1	12-02-2015

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