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(54) Titre : PROCEDE PERMETTANT DE STABILISER LE CONTENU BACTERIEN DE PREPARATIONS MINERALES AQUEUSES COMPRENANT DU CARBONATE DE CALCIUM NATUREL TERRESTRE ET/OU DU CARBONATE DE CALCIUM PRECIPITE ET/OU DE LA DOLOMIE ET/OU DU CARBONATE DE CALCIUM A SURFACE AYANT REAGI

(54) Title: PROCESS FOR STABILIZING BACTERIAL CONTENT OF AQUEOUS GROUND NATURAL CALCIUM CARBONATE AND/OR PRECIPITATED CALCIUM CARBONATE AND/OR DOLOMITE AND/OR SURFACE-REACTED CALCIUM CARBONATE-COMPRISING MINERAL PREPARATIONS

(57) **Abrégé/Abstract**:

This invention discloses a process for bacterial stabilising an aqueous mineral preparation, wherein the bacterial stabilization entails a lack of significant growth of bacteria, with a reduction and/or maintenance of the Total Viable Count of bacteria of less than 4 cfu/ml, comprising a step of adding at least one aldehyde-containing, aldehyde-releasing, phenolic and/or isothiazoline biocide to said aqueous mineral preparation.

ABSTRACT

This invention discloses a process for bacterial stabilising an aqueous mineral preparation, wherein the bacterial stabilization entails a lack of significant growth of bacteria, with a reduction and/or maintenance of the Total Viable Count of bacteria of less than 10^4 cfu/ml, comprising a step of adding at least one aldehyde-containing, aldehyde-releasing, phenolic and/or isothiazoline biocide to said aqueous mineral preparation.

Process for stabilizing bacterial content of aqueous ground natural calcium carbonate and/or precipitated calcium carbonate and/or dolomite and/or surface-reacted calcium carbonate-comprising mineral preparations

The invention relates to a process for stabilizing bacterial content of aqueous mineral preparations comprising at least one of ground natural calcium carbonate, precipitated calcium carbonate, dolomite, surface-reacted calcium carbonate, clay, talc, TiO_2, kaolin, kaolinitic clay, calcined kaolinitic clay, calcium sulfate, quartz, attapulgite, montmorillonite, diatomaceous earth, finely divided silica, aluminium oxide, aluminium hydroxide, silicates such as aluminium silicate, pumice and sepiolite, or a mixture thereof, and to the use of biocidal activity enhancing compounds.

In practice, aqueous preparations and especially suspensions or dispersions of water-insoluble mineral solids are used extensively in the paper, paint, rubber and plastics industries as coatings, fillers, extenders and pigments for papermaking as well as aqueous lacquers and paints. For example, suspensions or dispersions of mineral solids are used in the paper industry in large amounts as filler and/or as a component in the preparation of coated paper. Typical aqueous preparations of water-insoluble solids are characterized in that they comprise water, a water-insoluble solid compound and optionally further additives, such as dispersing agents, in the form of a suspension or dispersion. Water-soluble polymers and copolymers which may be used as e.g. dispersant and/or grinding aid in such preparation are, for example, described in US 5,278,248.

The aforementioned aqueous preparations are often subject to contamination by microorganisms such as aerobic and anaerobic bacteria resulting in changes in the preparation properties, such as discolorations or reductions in other quality parameters, which negatively affect their commercial value. Therefore, the manufacturers of such aqueous preparations usually take measures for stabilizing the suspensions, dispersions or slurries. For example, it is known that aldehyde-releasing biocides reduce the growth and accumulation of such microorganisms in aqueous preparations and, thus, reduce the tendency of undesired alterations of these preparations, like unpleasant odours.

For ensuring an acceptable microbiological quality of aqueous preparations, biocides are used over the entire life cycle of the preparation (production, storage, transport, use). In the art, several approaches for improving the microbiological quality of aqueous preparations have been proposed. For example, EP 1 139 741 describes aqueous suspensions or dispersions of minerals, fillers and/or pigments, containing a microbicidal agent in the form of a solution and derivatives of phenol in partially neutralized form. US 5,496,398 relates to a process for the reduction of microorganisms in kaolin clay slurries by a combination of low temperature heat and reduced levels of a microbiocidal agent. WO 02/052941 describes biocide compositions for incorporation into paints, coating, plasters and plastics comprising at least one metal oxide and at least one metal salt. US 2006/0111410 mentions a mixture comprising 1,2-benzisothiazolinone (BIT) and tetramethylolacetylenediurea (TMAD) for protecting industrial materials and products against attack and destruction by microorganisms. Furthermore, it is suggested in the art to add formaldehyde-releasing substances to such aqueous preparations for improving the microbiologically related quality. For example, US 4,655,815 mentions an antimicrobial composition comprising a formaldehyde donor. Furthermore, WO 2006/079911 describes a method of protection against microorganisms by increasing the OH^- ion concentration of the suspension.

WO 2004/040979 A1 relates to synergistic antimicrobial mixtures containing 1,2-benzisothiazolinon (BIT) and benzylhemiformal (BHF). The corresponding mixtures are used, for example, for suspensions of pigments.

EP 1 661 587 A1 relates to germicidal compositions including phthalaldehyde as an active ingredient. It is indicated in EP 1 661 587 A1 that carbonate salts and bicarbonate salts may enhance the germicidal efficacy of phthalaldehydes.

US 2001/0009682 A1 relates to disinfectant concentrates having improved biocidal activity which may contain an aldehyde such as glutaraldehyde, a glycol and a lithium based buffer.

EP 2 108 260 refers to a process for bacterial stabilizing of an aqueous preparation, said preparation comprising at least one mineral and at least one strain of bacteria which is resistant to, tolerant to and/or degrade aldehyde-releasing and/or aldehyde-based biocides, wherein the process comprises the steps of: (a) adding to the aqueous preparation one or more aldehyde-releasing and/or aldehyde-based biocides in an amount such that the total amount of aldehyde-releasing and/or aldehyde-based biocides in the aqueous preparation is from 250 ppm to 5 000 ppm, calculated relative to the water in the preparation; (b) adding at least one water soluble lithium compound to the aqueous preparation in an amount such that the total amount of solubilised lithium in the aqueous preparation is from 1 000 to 3 000 ppm, calculated relative to the weight of water in the preparation, where steps (a) and (b) may be carried out simultaneously, or separately in any order.

Finally, EP 2329 712 discloses a process for stabilising an aqueous mineral preparation comprising a step of: (a) adding at least one aldehyde-containing and/or aldehyde-releasing and/or phenolic and/or isothiazoline biocide to said aqueous mineral preparation; wherein said mineral comprises at least one of: a ground natural calcium carbonate, a precipitated calcium carbonate, a dolomite, a surface-reacted calcium carbonate, or a mixture thereof; said process comprises a step (b), which may be simultaneous and/or distinct relative to step (a), of adding at least one monoalcohol primary alkanol amine to said aqueous mineral preparation; said biocide(s) are added to said aqueous preparation in an amount corresponding to from 90 to 1 350 ppm based on the weight of the aqueous phase of said aqueous preparation; and wherein said monoalcohol primary alkanol amine(s) are added to said aqueous preparation in an amount corresponding to from 600 to 1 200 ppm based on the weight of the aqueous phase of said aqueous preparation.

Because of the limited activity spectrum of several biocides, the efficacy of such biocides against bacteria is not always satisfactory and, thus, the obtained action is in some cases insufficient to avoid microbially induced alteration of aqueous preparations.

Thus, there is still a need for adequate compositions providing sufficient biocidal activity in aqueous preparations such as suspensions and dispersions of mineral materials comprising ground natural calcium carbonate in order to achieve a longer lasting and sufficient stabilization.

These and other objectives of the present invention can be solved by a process and a use as described in the present invention and defined in the claims.

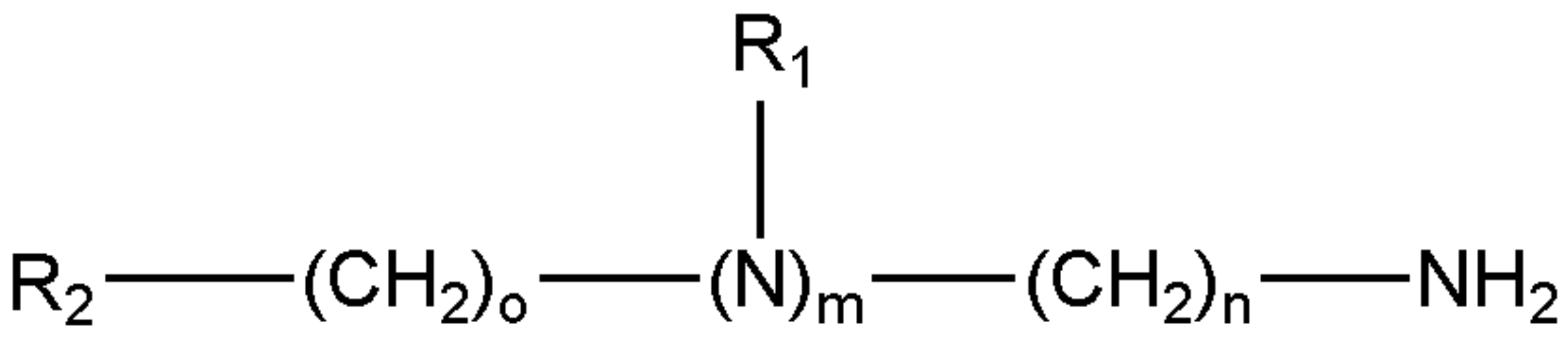
One aspect of the present application resides in a process for stabilising an aqueous mineral preparation comprising a step of:

(a) adding at least one aldehyde-containing and/or aldehyde-releasing and/or phenolic and/or isothiazoline biocide to said aqueous mineral preparation;

characterised in that:

- said mineral comprises at least one of: a ground natural calcium carbonate, a precipitated calcium carbonate, a dolomite, a surface-reacted calcium carbonate, clay, talc, TiO_2, kaolin, kaolinitic clay, calcined kaolinitic clay, calcium sulfate, quartz, attapulgite, montmorillonite, diatomaceous earth, finely divided silica, aluminium oxide, aluminium hydroxide, silicates such as aluminium silicate, pumice and sepiolite, or a mixture thereof;

- said process comprises a step (b), which may be simultaneous and/or distinct relative to step (a), of adding at least one linear or cyclic diamine or triamine compound to said aqueous mineral preparation, the linear or cyclic diamine or triamine compound having at least one primary amine group, and where the linear diamine or triamine compound has the following formula (I):



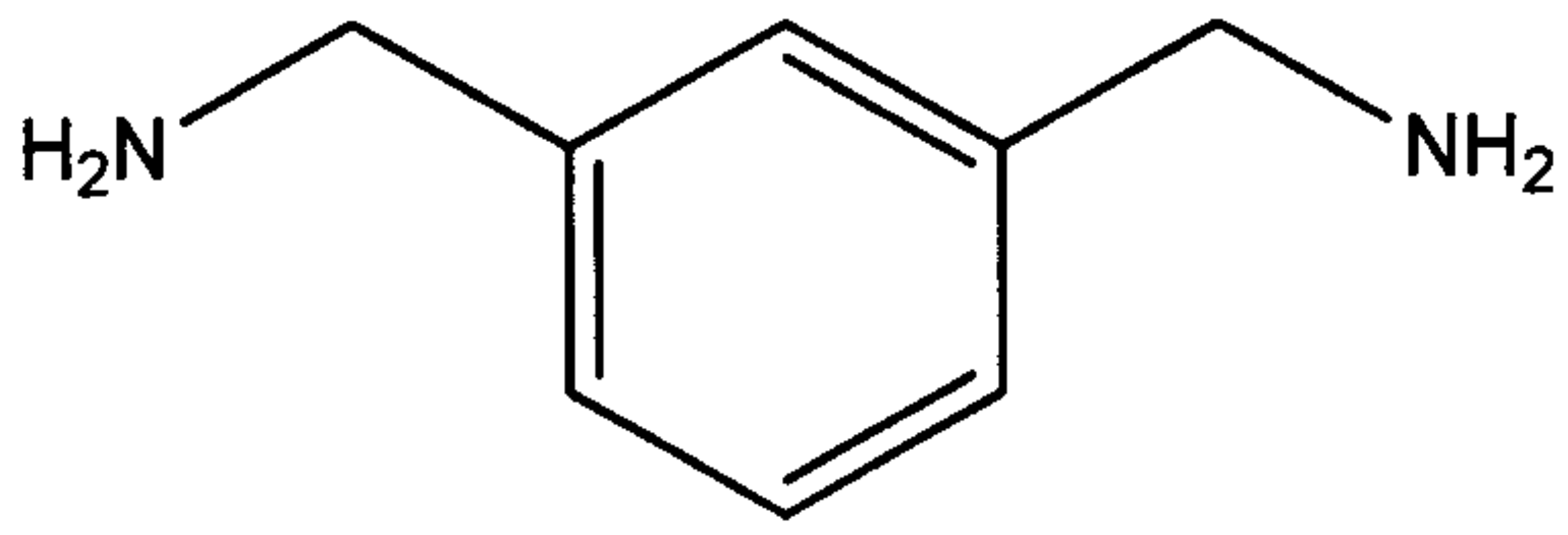
$$R_2-(CH_2)_o-\overset{R_1}{\overset{|}{(N)_m}}-(CH_2)_n-NH_2$$

(I)

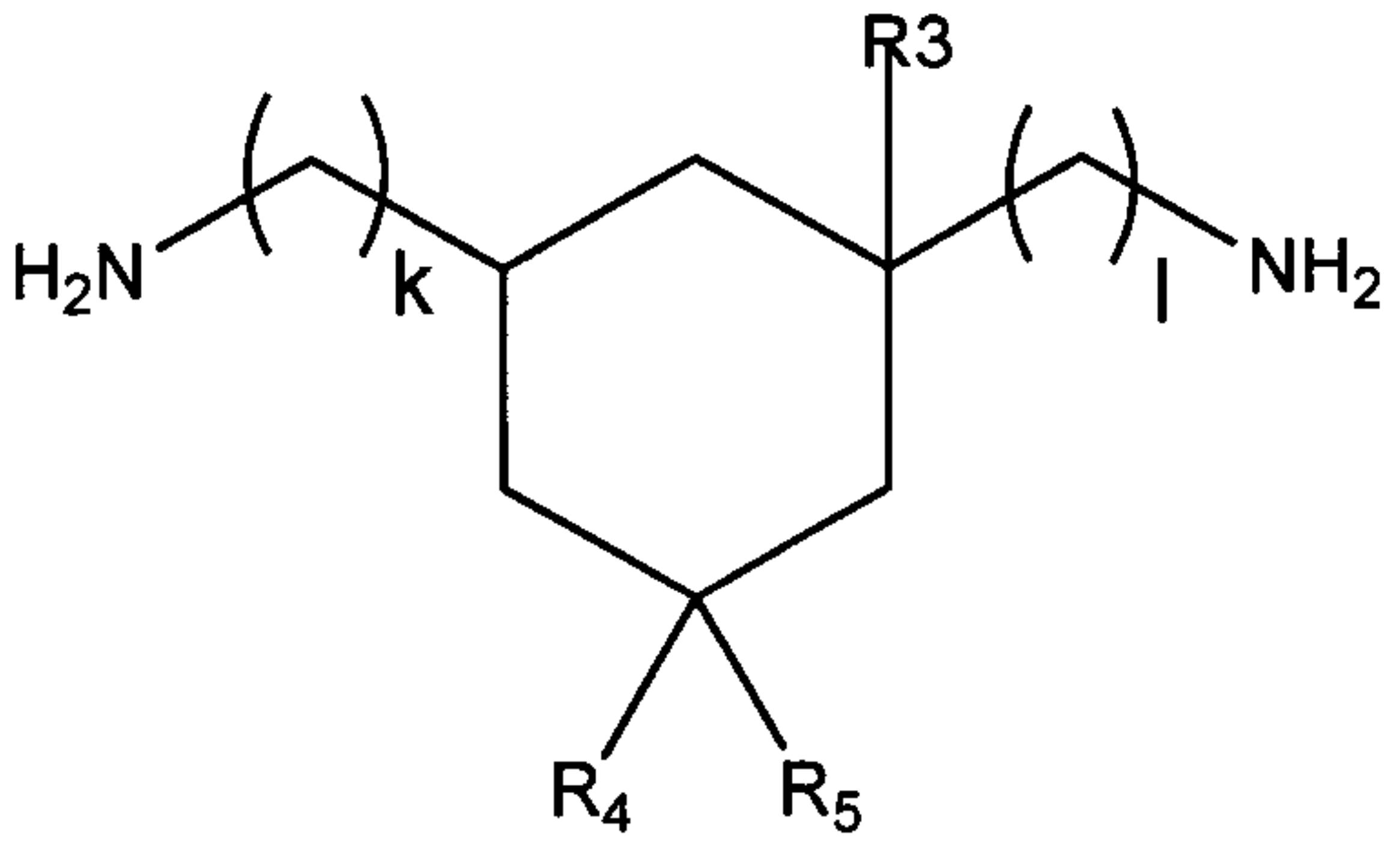
wherein:

m is an integer and is either 0 or 1, n is an integer and is from 2 to 8, o is an integer and is from 0 to 3, R_1 is a C_1 to C_{12} alkyl group, and is in particular CH_3, CH_2CH_3 or a linear $C_{12}H_{25}$ alkyl group, and R_2 is CH_3 or NH_2, and with the proviso that when m = 0, then o = 0 and R_2 is NH_2;

and where the cyclic diamine or triamine compound has one of the following formulas (II) and (III):



(II)



(III)

wherein:

k and l are the same or different and are either 0 or 1, R_3 is either H or CH_3, and R_4 and R_5 are the same or different and selected from H and CH_3;

- said biocide(s) are added to said aqueous preparation in an amount corresponding to from 90 to 1 350 ppm, based on the weight of the aqueous phase of said aqueous preparation; and

- said linear or cyclic diamine or triamine compound(s) are added to said aqueous preparation in an amount corresponding to from 600 to 1 200 ppm, based on the weight of the aqueous phase of said aqueous preparation.

According to the present invention, the wording “stabilising an aqueous preparation” implies no “significant growth” of bacteria. Preferably, the stabilization leads to a reduction and/or maintenance of the Total Viable Count (TVC, given in colony forming units per milliliter (cfu/ml), as measured according to the measurement method defined in the Examples section hereafter) of the treated aqueous preparation to a value of less than 10^4 cfu/ml, more preferably to a value of less than 10^3 cfu/ml, and even more preferably to a value of less than or equal to 10^2 cfu/ml.

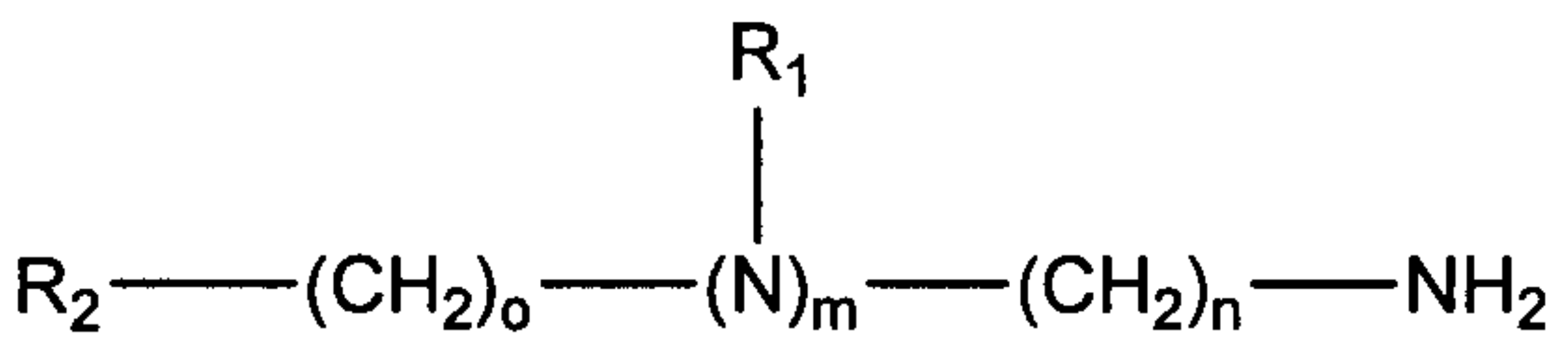
Another aspect of the present invention resides in a process for bacterial stabilization of an aqueous mineral preparation, comprising a step of:

(a) adding at least one aldehyde-containing, aldehyde-releasing, phenolic and/or isothiazoline biocide to said aqueous mineral preparation;

characterised in that:

- the bacterial stabilization entails a lack of significant growth of bacteria, with a reduction and/or maintenance of the Total Viable Count of bacteria of less than 10^4 cfu/ml;
- said mineral comprises at least one of: a ground natural calcium carbonate, a precipitated calcium carbonate, a dolomite, a surface-reacted calcium carbonate, clay, talc, TiO_2, kaolin, kaolinitic clay, calcined kaolinitic clay, calcium sulfate, quartz, attapulgite, montmorillonite, diatomaceous earth, finely divided silica, aluminium oxide, aluminium hydroxide, silicates, or a mixture thereof;

- said process comprises a step (b), which is simultaneous and/or distinct relative to step (a), of adding at least one linear or cyclic diamine or triamine compound to said aqueous mineral preparation, the linear or cyclic diamine or triamine compound having at least one primary amine group, and where the linear diamine or triamine compound has the following formula (I):



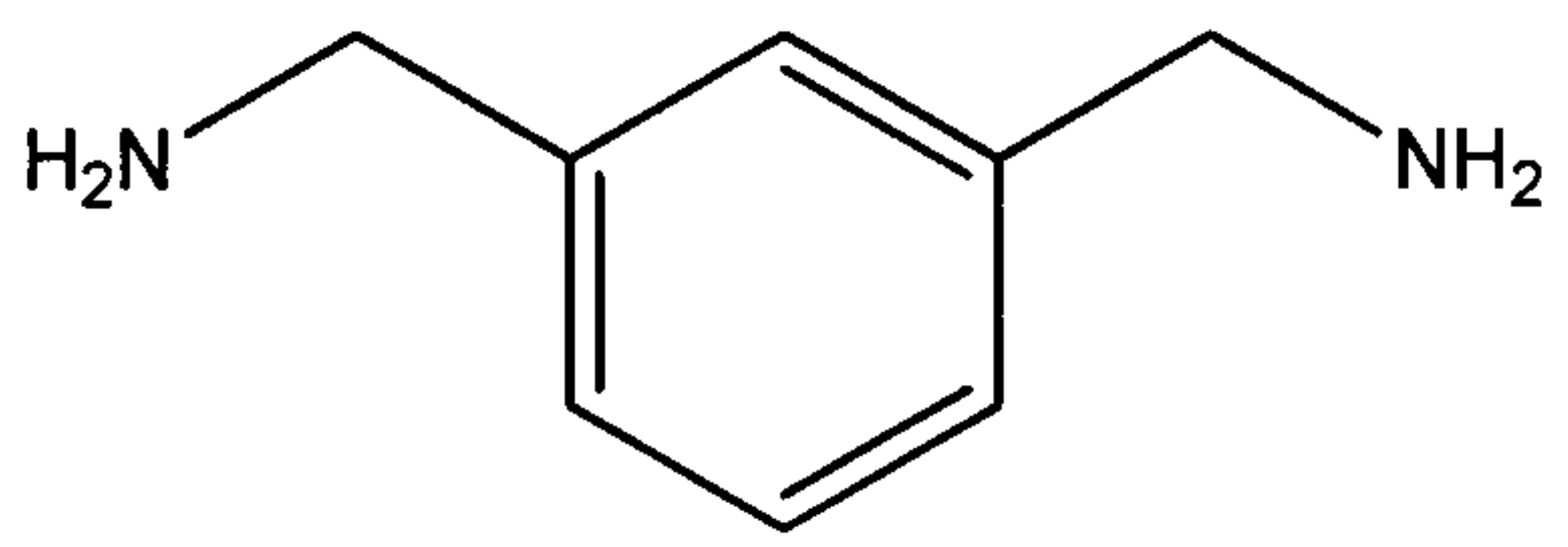
$$R_2 - (CH_2)_o - \overset{\overset{R_1}{|}}{(N)_m} - (CH_2)_n - NH_2$$

(I)

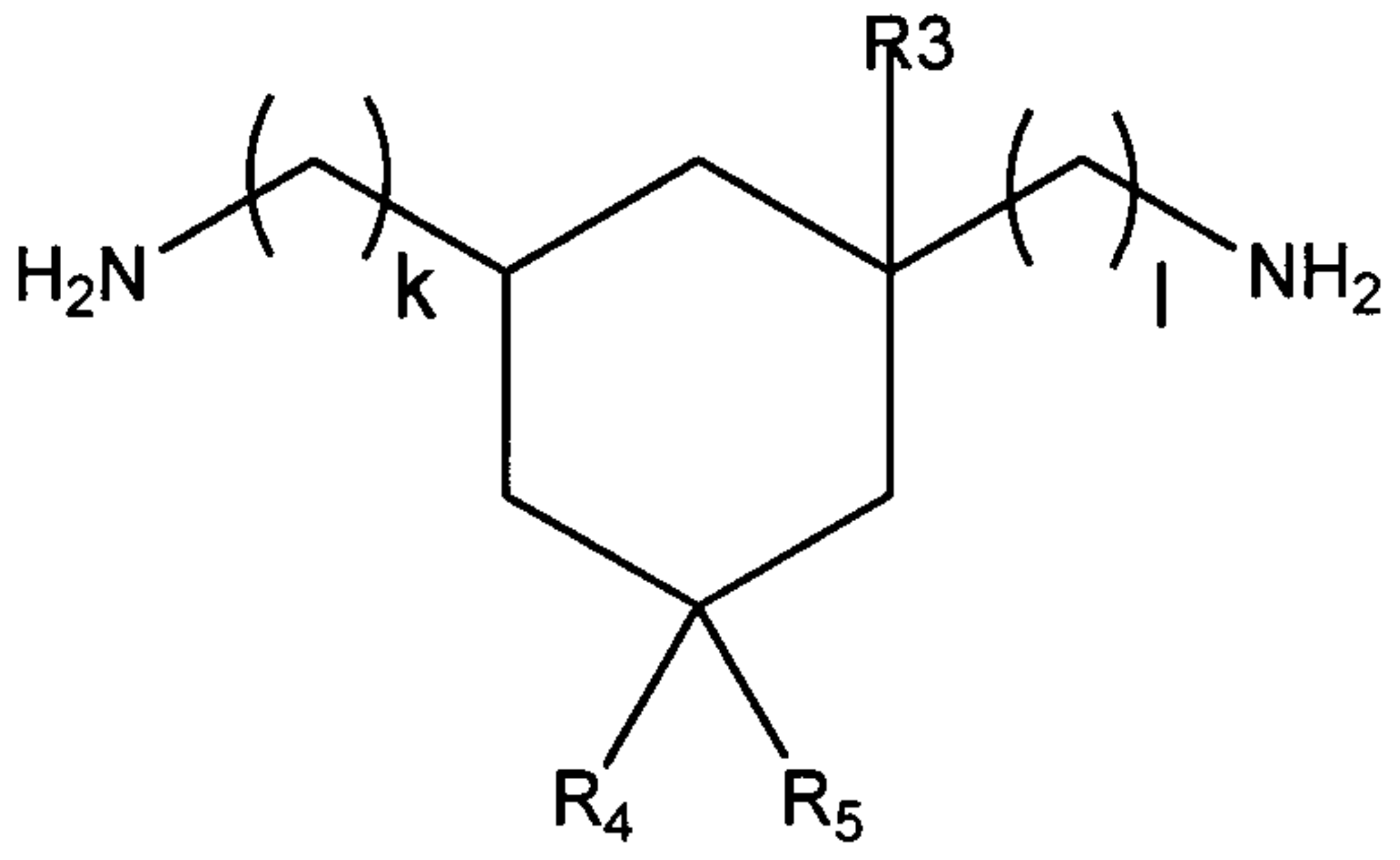
wherein:

m is an integer and is either 0 or 1, n is an integer and is from 2 to 8, o is an integer and is from 0 to 3, R_1 is a C_1 to C_{12} alkyl group, and R_2 is CH_3 or NH_2, and with the proviso that when m = 0, then o = 0 and R_2 is NH_2;

and where the cyclic diamine or triamine compound has one of the following formulas (II) and (III):



(II)



(III)

wherein:

k and l are the same or different and are either 0 or 1, R_3 is either H or CH_3, and R_4 and R_5 are the same or different and selected from H and CH_3,

- said biocide(s) are added to said aqueous preparation in an amount corresponding to from 90 to 1 350 ppm based on the weight of the aqueous phase of said aqueous preparation; and
- said linear or cyclic diamine or triamine compound(s) are added to said aqueous preparation in an amount corresponding to from 600 to 1 200 ppm, based on the weight of the aqueous phase of said aqueous preparation.

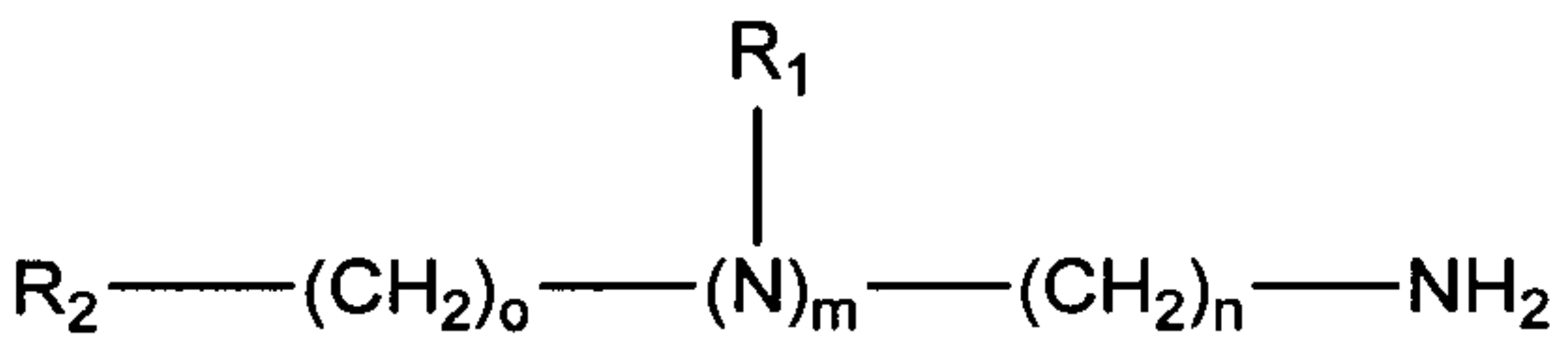
Another aspect of the invention resides in the process for bacterial stabilization of an aqueous mineral preparation, comprising a step of:

(a) adding at least one aldehyde-containing, aldehyde-releasing, phenolic and/or isothiazoline biocide to said aqueous mineral preparation;

characterised in that:

- the bacterial stabilization entails a lack of significant growth of bacteria, with a reduction and/or maintenance of the Total Viable Count of bacteria of less than 10^4 cfu/ml;
- said mineral comprises at least one of: a ground natural calcium carbonate, a precipitated calcium carbonate, a dolomite, a surface-reacted calcium carbonate, clay, talc, TiO_2, kaolin, kaolinitic clay, calcined kaolinitic clay, calcium sulfate, quartz, attapulgite, montmorillonite, diatomaceous earth, finely divided silica, aluminium oxide, aluminium hydroxide, silicates, or a mixture thereof;

- said process comprises a step (b), which is simultaneous and/or distinct relative to step (a), of adding at least one linear diamine, linear triamine or cyclic diamine compound to said aqueous mineral preparation, the linear diamine, linear triamine or cyclic diamine compound having at least one primary amine group, and where the linear diamine or linear triamine compound has the following formula (I):



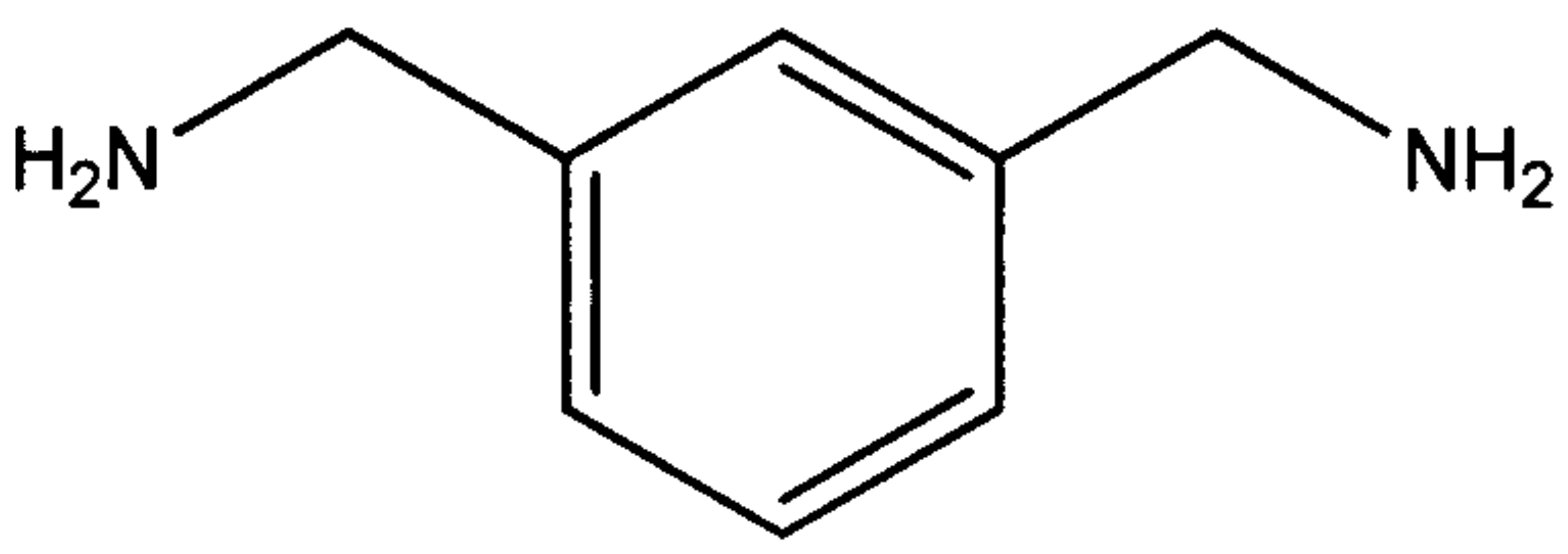
$$R_2-(CH_2)_o-\underset{}{\overset{\displaystyle R_1}{\overset{|}{(N)_m}}}-(CH_2)_n-NH_2$$

(I)

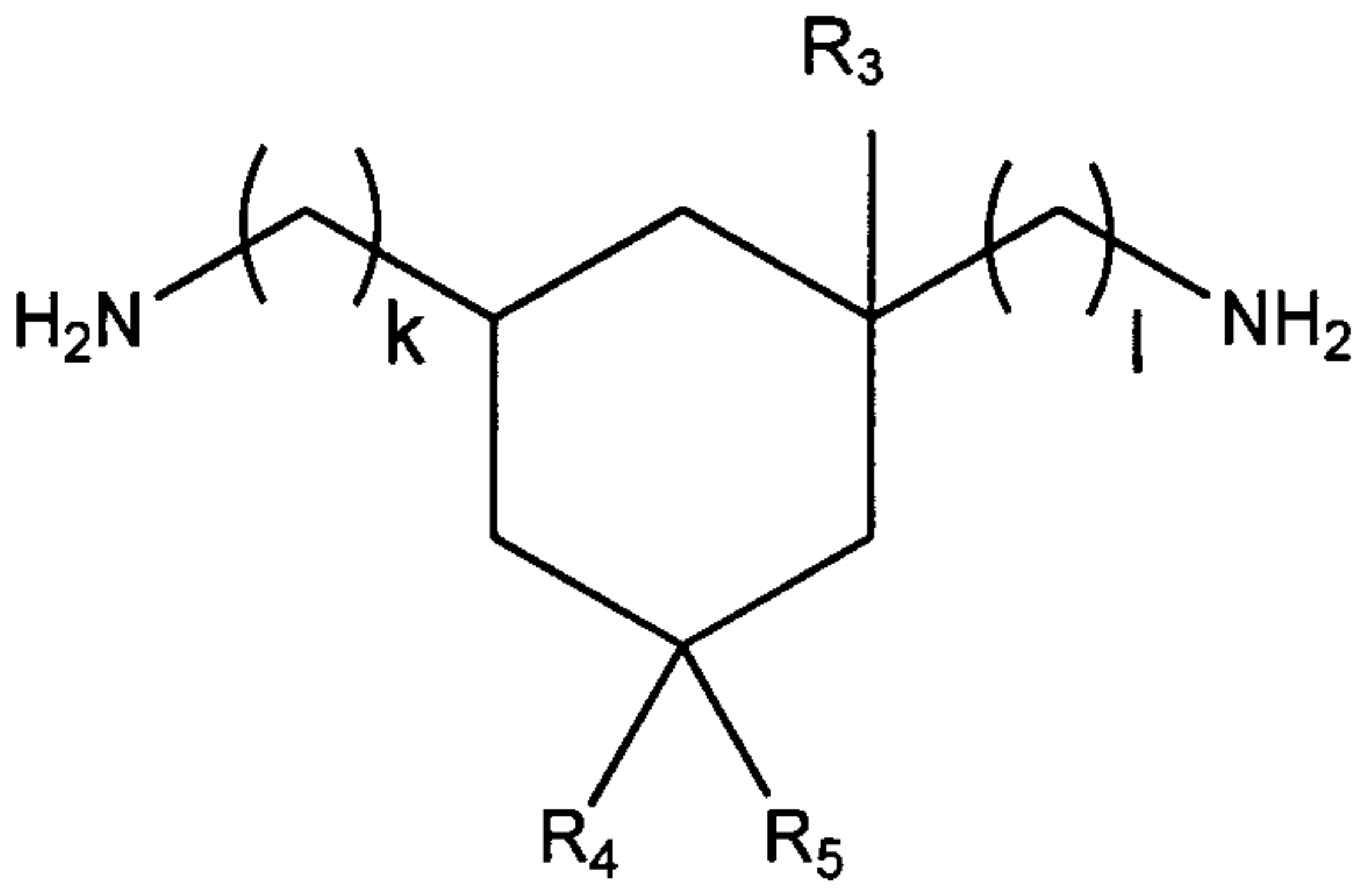
wherein:

m is an integer and is either 0 or 1, n is an integer and is from 2 to 8, o is an integer and is from 0 to 3, R_1 is a C_1 to C_{12} alkyl group, and R_2 is CH_3 or NH_2, and with the proviso that when m = 0, then o = 0 and R_2 is NH_2;

and where the cyclic diamine compound has one of the following formulas (II) and (III):



(II)



(III)

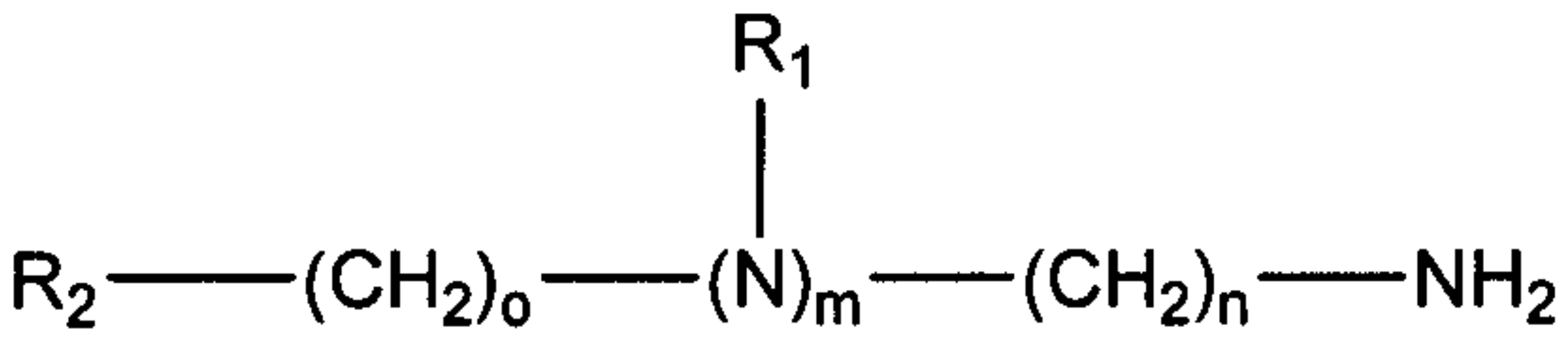
wherein:

k and l are the same or different and are either 0 or 1, R_3 is either H or CH_3, and R_4 and R_5 are the same or different and selected from H and CH_3,

- said biocide(s) are added to said aqueous preparation in an amount corresponding to from 90 to 1 350 ppm based on the weight of the aqueous phase of said aqueous preparation; and
- said linear diamine, linear triamine or cyclic diamine compound(s) are added to said aqueous preparation in an amount corresponding to from 600 to 1 200 ppm, based on the weight of the aqueous phase of said aqueous preparation.

Another aspect of the present invention resides in an aqueous preparation obtained by the process as defined by the invention.

Another aspect of the present invention resides in the use of at least one linear or cyclic diamine or triamine compound, the linear or cyclic diamine or triamine compound having at least one primary amine group, and where the linear diamine or triamine compound has the following formula (I):



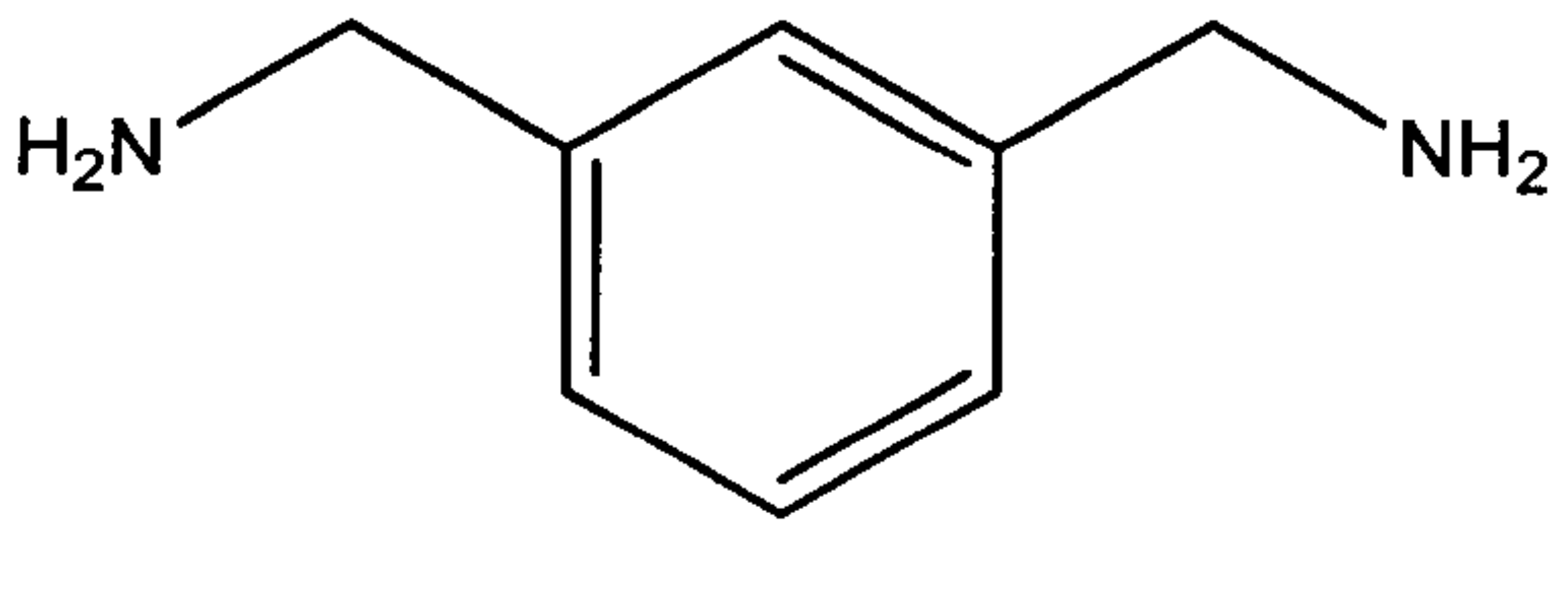
$$R_2-(CH_2)_o-\overset{\overset{R_1}{|}}{(N)_m}-(CH_2)_n-NH_2$$

(I)

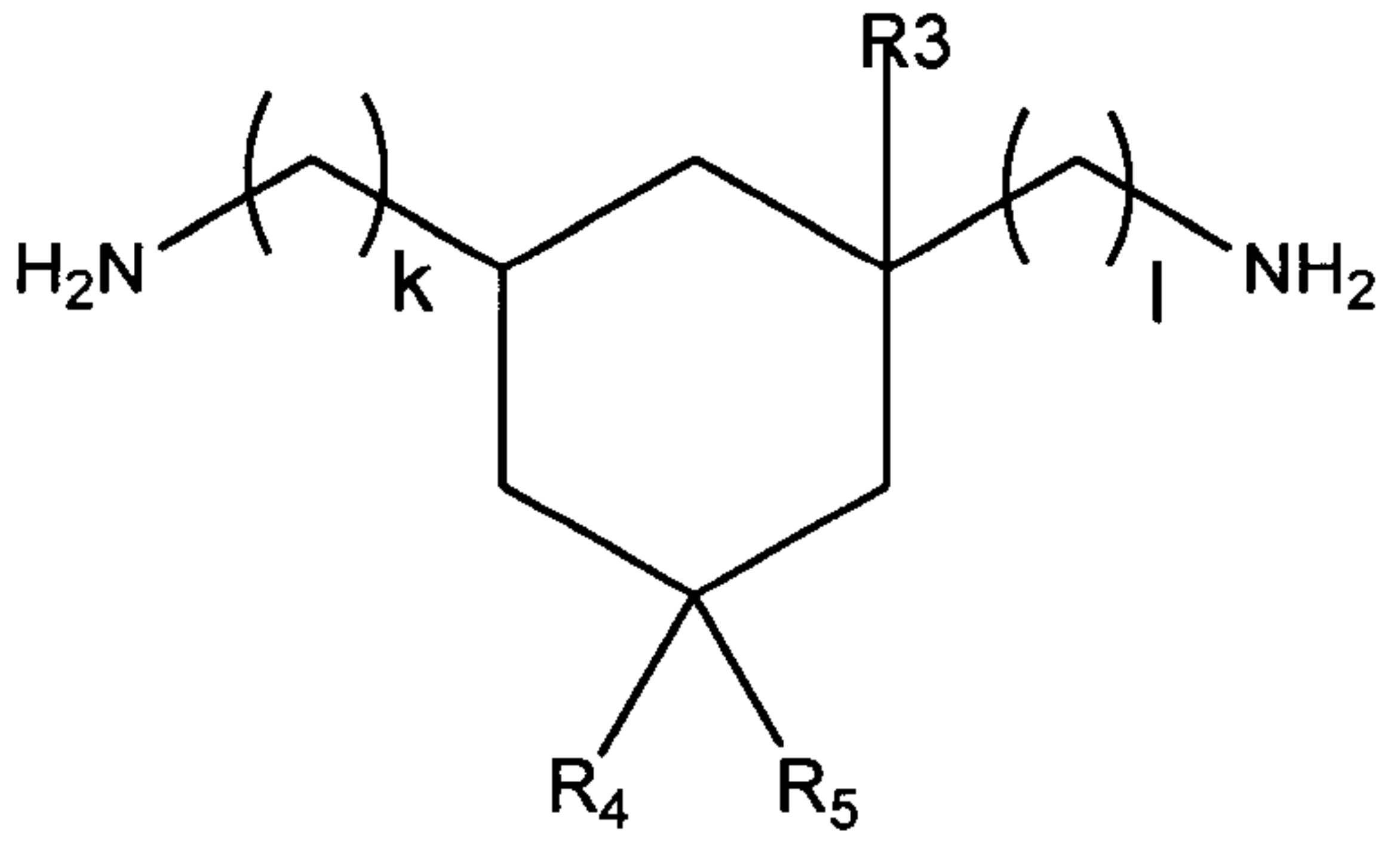
wherein:

m is an integer and is either 0 or 1, n is an integer and is from 2 to 8, o is an integer and is from 0 to 3, R_1 is a C_1 to C_{12} alkyl group, and R_2 is CH_3 or NH_2, and with the proviso that when m = 0, then o = 0 and R_2 is NH_2;

and where the cyclic diamine or triamine compound has one of the following formulas (II) and (III):



(II)

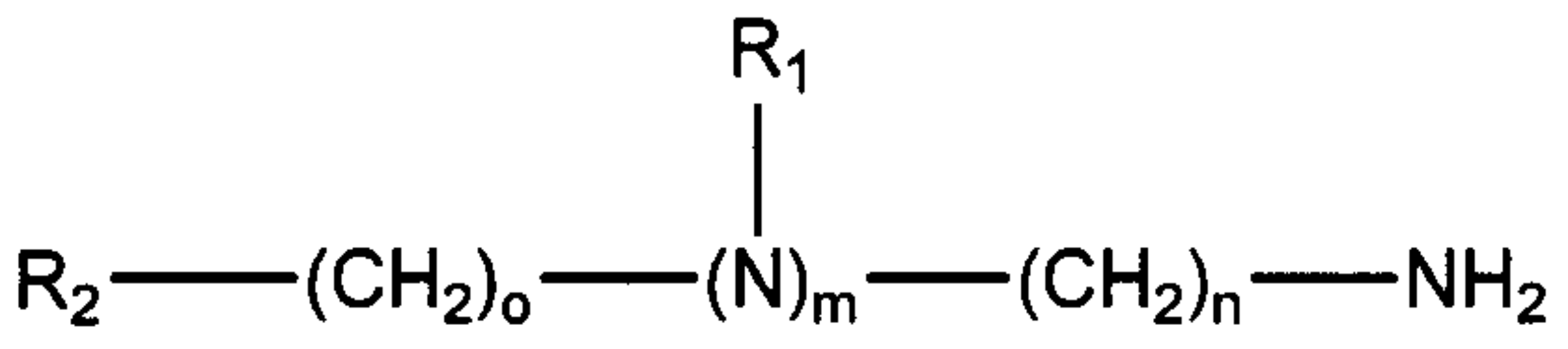


(III)

wherein:

k and l are the same or different and are either 0 or 1, R_3 is either H or CH_3, and R_4 and R_5 are the same or different and selected from H and CH_3, as a biocidal activity enhancing compound in an aqueous mineral preparation comprising at least one of aqueous ground natural calcium carbonate, precipitated calcium carbonate, dolomite, surface-reacted calcium carbonate, clay, talc, TiO_2, kaolin, kaolinitic clay, calcined kaolinitic clay, calcium sulfate, quartz, attapulgite, montmorillonite, diatomaceous earth, finely divided silica, aluminium oxide, aluminium hydroxide, silicates, and comprising at least one aldehyde-containing, aldehyde-releasing, phenolic and/or isothiazoline biocide, where the total amount of said biocide(s) in the aqueous preparation is from 90 ppm to 1 350 ppm, calculated relative to the weight of the aqueous phase of said preparation, and the total amount of said linear or cyclic diamine or triamine compound(s) in the aqueous preparation is from 600 to 1 200 ppm, calculated relative to the weight of the aqueous phase of said preparation.

Another aspect of the present invention resides in the use of at least one linear diamine, linear triamine or cyclic diamine compound, the linear or cyclic diamine or triamine compound having at least one primary amine group, and where the linear diamine or linear triamine compound has the following formula (I):



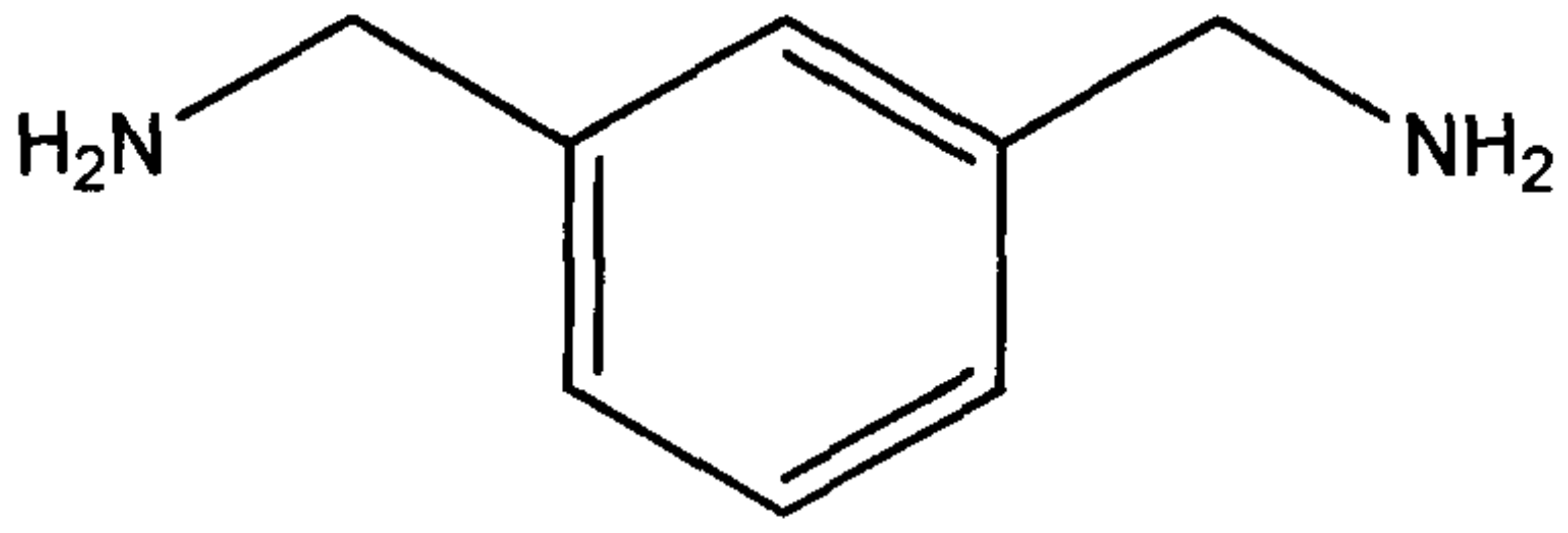
$$R_2-(CH_2)_o-\overset{\displaystyle R_1}{\overset{|}{(N)_m}}-(CH_2)_n-NH_2$$

(I)

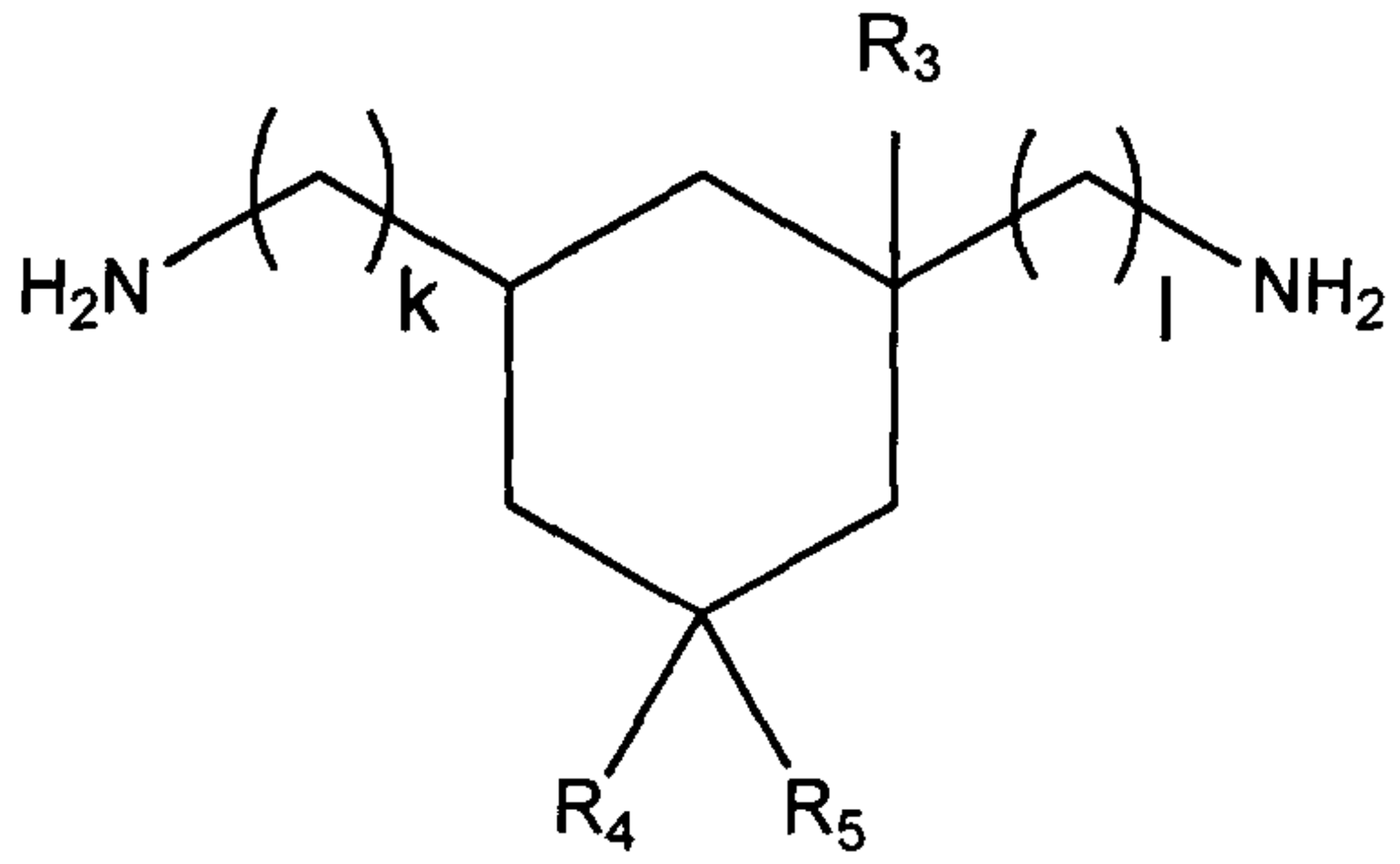
wherein:

m is an integer and is either 0 or 1, n is an integer and is from 2 to 8, o is an integer and is from 0 to 3, R_1 is a C_1 to C_{12} alkyl group, and R_2 is CH_3 or NH_2, and with the proviso that when m = 0, then o = 0 and R_2 is NH_2;

and where the cyclic diamine compound has one of the following formulas (II) and (III):



(II)



(III)

wherein:

k and l are the same or different and are either 0 or 1, R_3 is either H or CH_3, and R_4 and R_5 are the same or different are H or CH_3, as a biocidal activity enhancing compound in an aqueous mineral preparation comprising at least one of aqueous ground natural calcium carbonate, precipitated calcium carbonate, dolomite, surface-reacted calcium carbonate, clay, talc, TiO_2, kaolin, kaolinitic clay, calcined kaolinitic clay, calcium sulfate, quartz, attapulgite, montmorillonite, diatomaceous earth, finely divided silica, aluminium oxide, aluminium hydroxide or silicates, and comprising at least one aldehyde-containing, aldehyde-releasing, phenolic and/or isothiazoline biocide, where the total amount of said biocide(s) in the aqueous preparation is from 90 ppm to 1 350 ppm, calculated relative to the weight of the aqueous phase of said preparation, and the total amount of said linear diamine, linear triamine or cyclic diamine compound(s) in the aqueous preparation is from 600 to 1 200 ppm, calculated relative to the weight of the aqueous phase of said preparation.

Another aspect of the present invention resides in the use of an aqueous preparation as defined in the invention in paper making, paints, detergents or cosmetics.

An “aqueous mineral preparation” in the meaning of the present invention is a suspension comprising ground natural calcium carbonate and/or precipitated calcium carbonate and/or dolomite and/or surface-reacted calcium carbonate-comprising minerals and water and optionally further additives. Preparations having the required solids content may be viscous and require the implementation of dispersing agents or other rheology modifying agents.

The solids content in the meaning of the present application corresponds to the residual weight of the aqueous preparation following evaporation of the aqueous phase and is determined according to the measurement method described in the Examples section herebelow.

The weight of the aqueous phase is determined by subtracting the residual weight of the aqueous preparation following evaporation of the aqueous phase (determined according to the measurement method described in the Examples section herebelow) from the total weight of the aqueous preparation.

In accordance with the present invention, an “aldehyde-releasing biocide” refers to a compound which is able to release mono- di-, and/or tri-aldehyde. Aldehyde-releasing biocides include, for example, (ethylenedioxy)dimethanol, which releases formaldehyde.

In accordance with the present invention, an “aldehyde-based biocide” refers to a biocide which has one or more aldehyde-groups. Aldehyde-based biocides include, for example, formaldehyde, acetaldehyde, propionaldehyde, glutardialdehyde and glyoxal.

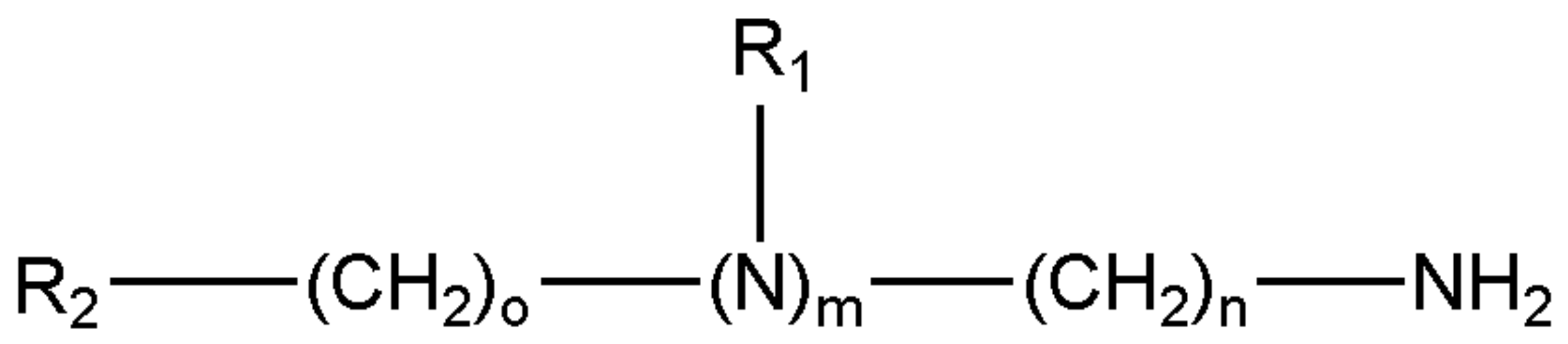
In accordance with the present invention, a “phenolic biocide” refers to a biocide which comprises at least one phenol functional group.

In accordance with the present invention, an "isothiazoline biocide" refers to a biocide which comprises at least one isothiazoline group.

According to the present invention, the content of the aldehyde-releasing and/or aldehyde-based and/or phenolic and/or isothiazoline biocides in water can be evaluated by HPLC (high pressure liquid chromatography). If necessary, the corresponding aldehyde-releasing and/or aldehyde-based and/or phenolic and/or isothiazoline biocide may be converted into a derivative before evaluation with HPLC.

The term "mineral" in the meaning of the present invention encompasses not only natural occurring pigments, fillers and minerals, such as marble, talc, chalk, dolomite, limestone and the like, but also synthetic compounds that are man-made and that show the same or similar properties, for example in an X-ray diffraction spectrum, like naturally occurring pigments, fillers and minerals. One example for such a synthetic compound is precipitated calcium carbonate (PCC) that is generally obtained by precipitation following the reaction of carbon dioxide and lime in an aqueous environment or by precipitation of a calcium and carbonate source in water or by precipitation of calcium and carbonate ions, for example $CaCl_2$ and Na_2CO_3, out of solution. Precipitated calcium carbonate exists in three primary crystalline forms: calcite, aragonite and vaterite, and there are many different polymorphs (crystal habits) for each of these crystalline forms. The three primary crystalline forms of PCC are similar to or the same as those of the natural occurring minerals calcite, aragonite and vaterite.

Furthermore, the present invention refers to the use of at least one linear or cyclic diamine or triamine compound, the linear or cyclic diamine or triamine compound having at least one primary amine group, and where the linear diamine or triamine compound has the following formula (I):



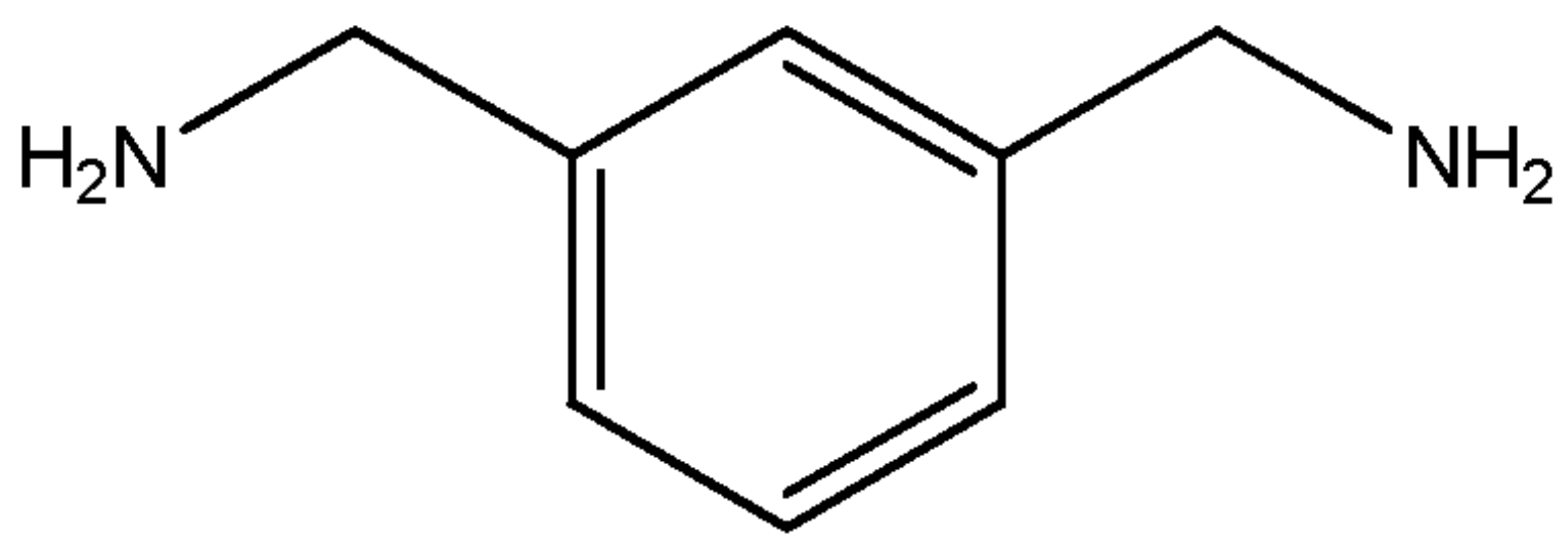
$$R_2—(CH_2)_o—\overset{\displaystyle R_1 \atop |}{(N)_m}—(CH_2)_n—NH_2$$

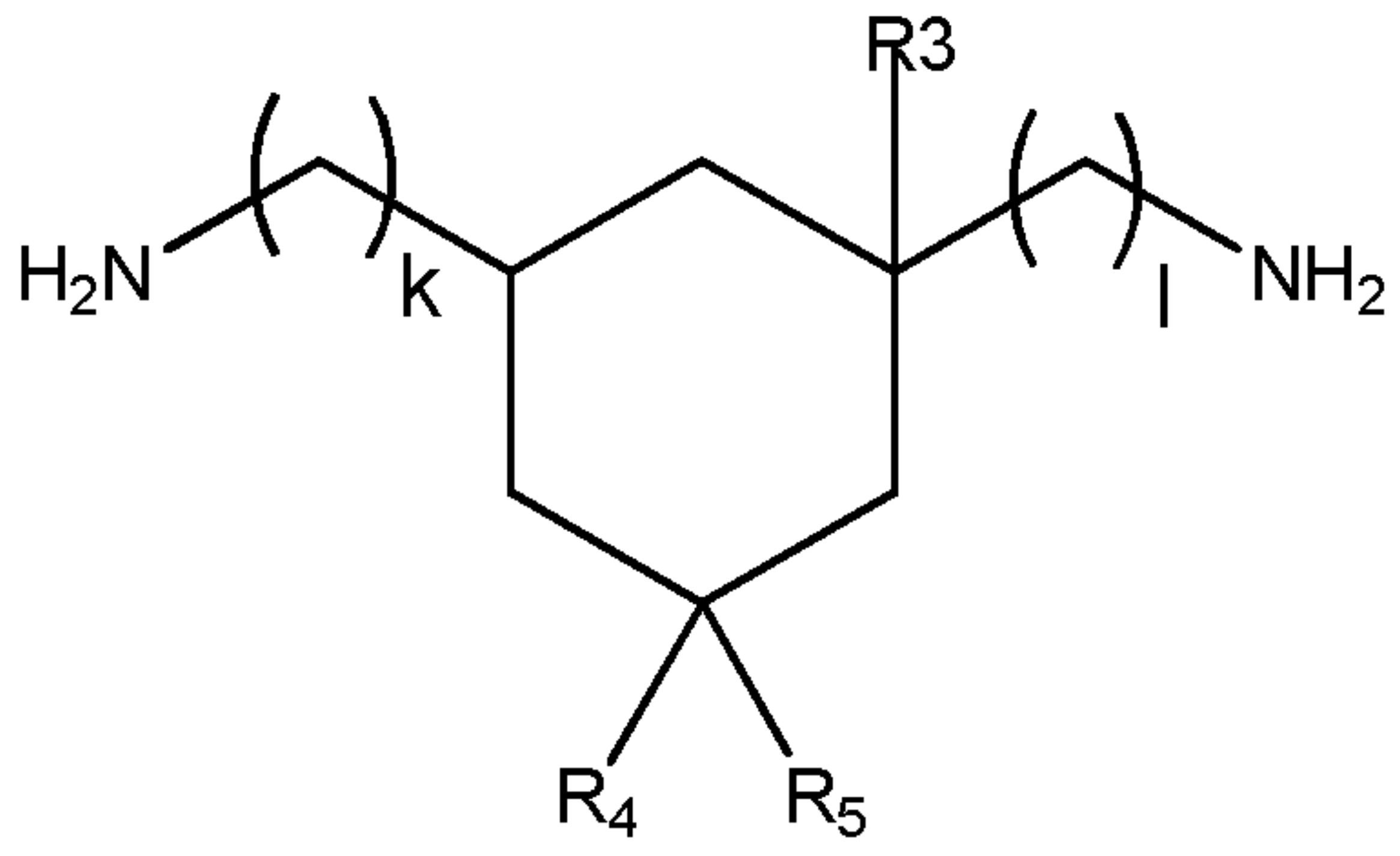
(I)

wherein:

m is an integer and is either 0 or 1, n is an integer and is from 2 to 8, o is an integer and is from 0 to 3, R_1 is a C_1 to C_{12} alkyl group, and in particular a linear $C_{12}H_{25}$ alkyl group, and R_2 is CH_3 or NH_2, and with the proviso that when m = 0, then o = 0 and R_2 is NH_2;

and where the cyclic diamine or triamine compound has one of the following formulas (II) and (III):





(II) **(III)**

wherein:

k and l are the same or different and are either 0 or 1, R_3 is either H or CH_3, and R_4 and R_5 are the same or different and selected from H and CH_3, as a biocidal activity enhancing compound in an aqueous mineral preparation comprising at least one of ground natural calcium carbonate, precipitated calcium carbonate, dolomite, surface-reacted calcium carbonate, clay, talc, TiO_2, kaolin, kaolinitic clay, calcined kaolinitic clay, calcium sulfate, quartz, attapulgite, montmorillonite, diatomaceous earth, finely divided silica, aluminium oxide, aluminium hydroxide, silicates such as aluminium silicate, pumice and sepiolite, or a mixture thereof, and comprising at least one aldehyde-containing and/or aldehyde-releasing and/or phenolic and/or isothiazoline biocide, where the total amount of said biocide(s) in the aqueous preparation is from 90 ppm to 1 350 ppm, calculated relative to the weight of the aqueous phase of said preparation, and the total amount of said linear or cyclic diamine or triamine compound(s) in the aqueous preparation is from 600 to 1 200 ppm, calculated relative to the weight of the aqueous phase of said preparation.

A biocidal activity enhancing compound referred to herein is a compound which is capable of increasing or inducing the biocidal activity of one or more biocides in comparison with a preparation having no such biocidal activity enhancing compound but, e.g. only one or more biocides in an amount such that the total amount of biocides in the aqueous preparation is from 90 to 1 350 ppm, calculated relative to the water in the preparation.

Notably, the biocidal activity enhancing compound may be capable of inducing the biocidal activity of one or more biocides when these biocides are dosed in an amount that is less than their Minimum Inhibition Concentration (MIC), the MIC being defined as the lowest concentration needed to reduce the TVC to the order of 10^2 cfu/ml.

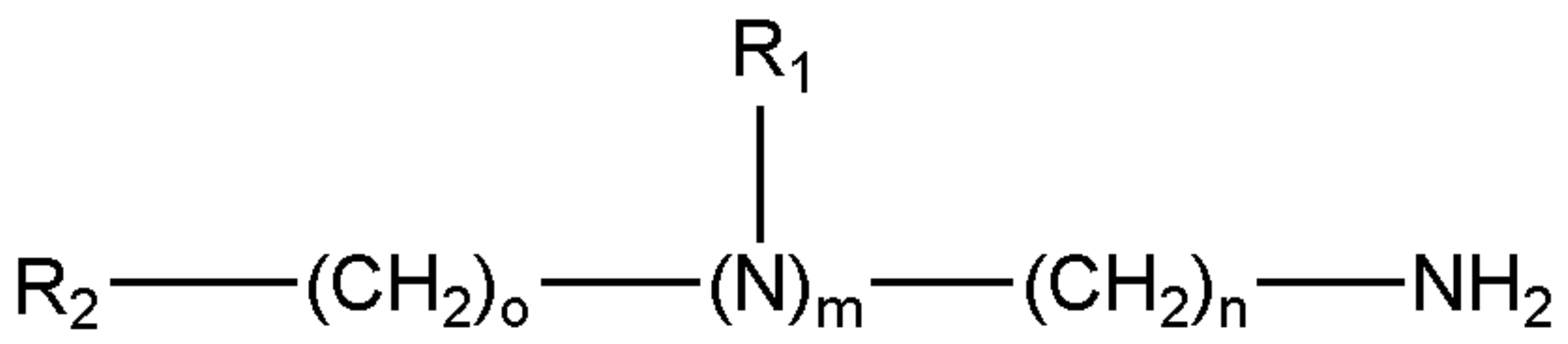
A first aspect of the present application resides in a process for stabilising an aqueous mineral preparation comprising a step of:

(a) adding at least one aldehyde-containing and/or aldehyde-releasing and/or phenolic and/or isothiazoline biocide to said aqueous mineral preparation;

characterised in that:

- said mineral comprises at least one of: a ground natural calcium carbonate, a precipitated calcium carbonate, a dolomite, a surface-reacted calcium carbonate, clay, talc, TiO_2, kaolin, kaolinitic clay, calcined kaolinitic clay, calcium sulfate, quartz, attapulgite, montmorillonite, diatomaceous earth, finely divided silica, aluminium oxide, aluminium hydroxide, silicates such as aluminium silicate, pumice and sepiolite, or a mixture thereof;

- said process comprises a step (b), which may be simultaneous and/or distinct relative to step (a), of adding at least one to linear or cyclic diamine or triamine compound said aqueous mineral preparation, the linear or cyclic diamine or triamine compound having at least one primary amine group, and where the linear diamine or triamine compound has the following formula (I):



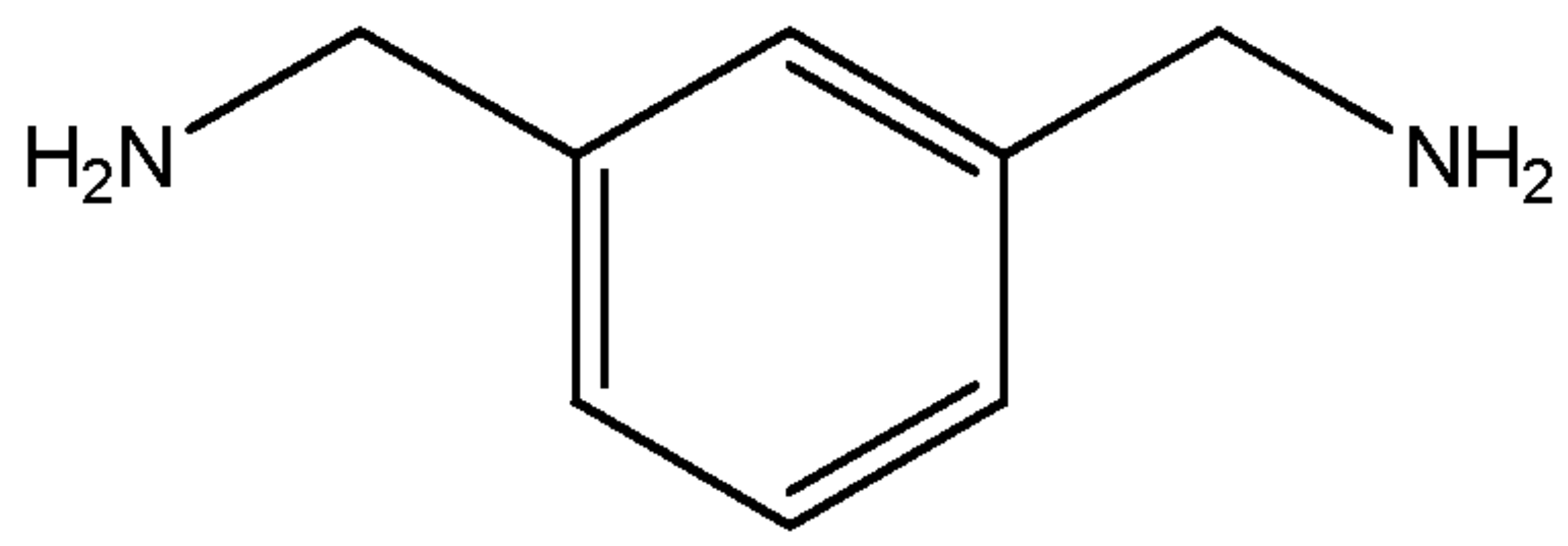
$$R_2-(CH_2)_o-\underset{}{\overset{R_1}{\overset{|}{(N)_m}}}-(CH_2)_n-NH_2$$

(I)

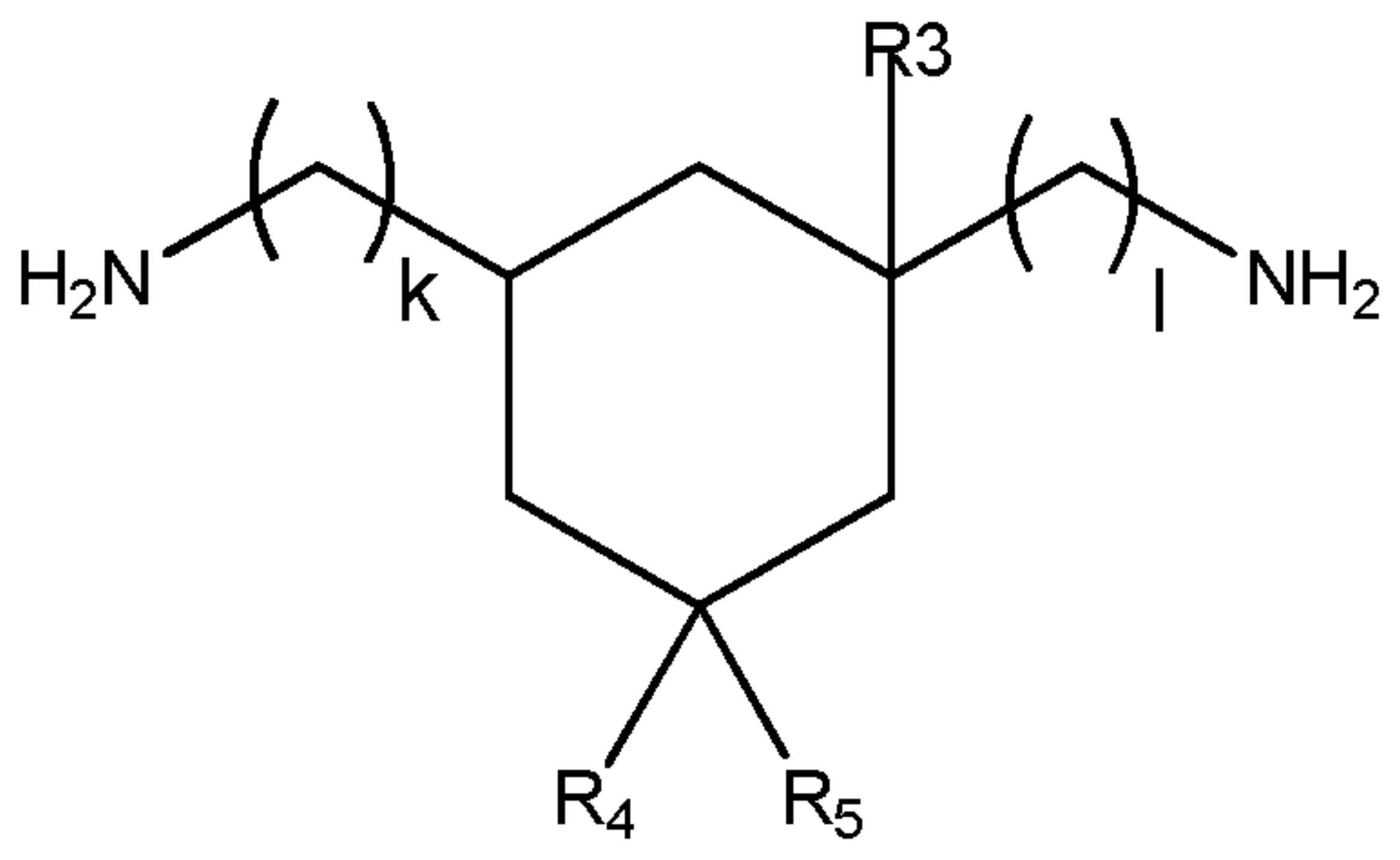
wherein:

m is an integer and is either 0 or 1, n is an integer and is from 2 to 8, o is an integer and is from 0 to 3, R_1 is a C_1 to C_{12} alkyl group, and is in particular CH_3, CH_2CH_3 or a linear $C_{12}H_{25}$ alkyl group, and R_2 is CH_3 or NH_2, and with the proviso that when m = 0, then o = 0 and R_2 is NH_2;

and where the cyclic diamine or triamine compound has one of the following formulas (II) and (III):



(II)



(III)

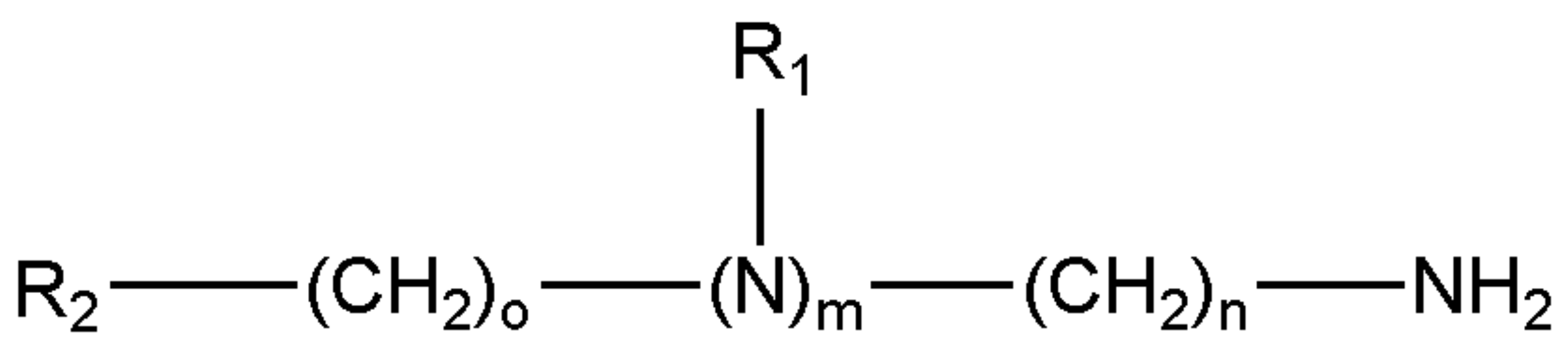
wherein:

k and l are the same or different and are either 0 or 1, R_3 is either H or CH_3, and R_4 and R_5 are the same or different and selected from H and CH_3;

- said biocide(s) are added to said aqueous preparation in an amount corresponding to from 90 to 1 350 ppm, based on the weight of the aqueous phase of said aqueous preparation; and

- said linear or cyclic diamine or triamine compound(s) are added to said aqueous preparation in an amount corresponding to from 600 to 1 200 ppm based on the weight of the aqueous phase of said aqueous preparation.

A second aspect of the present invention resides in the use of at least one linear or cyclic diamine or triamine compound, the linear or cyclic diamine or triamine compound having at least one primary amine group, and where the linear diamine or triamine compound has the following formula (I):



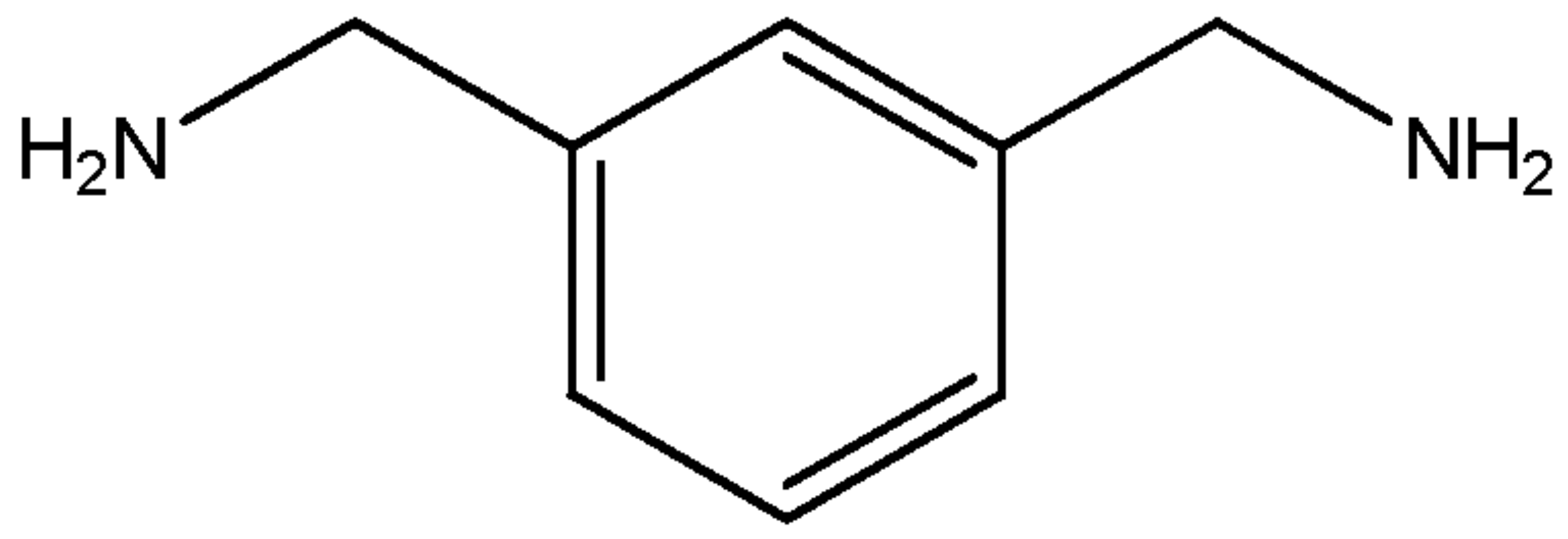
$$R_2 - (CH_2)_o - \overset{\overset{R_1}{|}}{(N)_m} - (CH_2)_n - NH_2$$

(I)

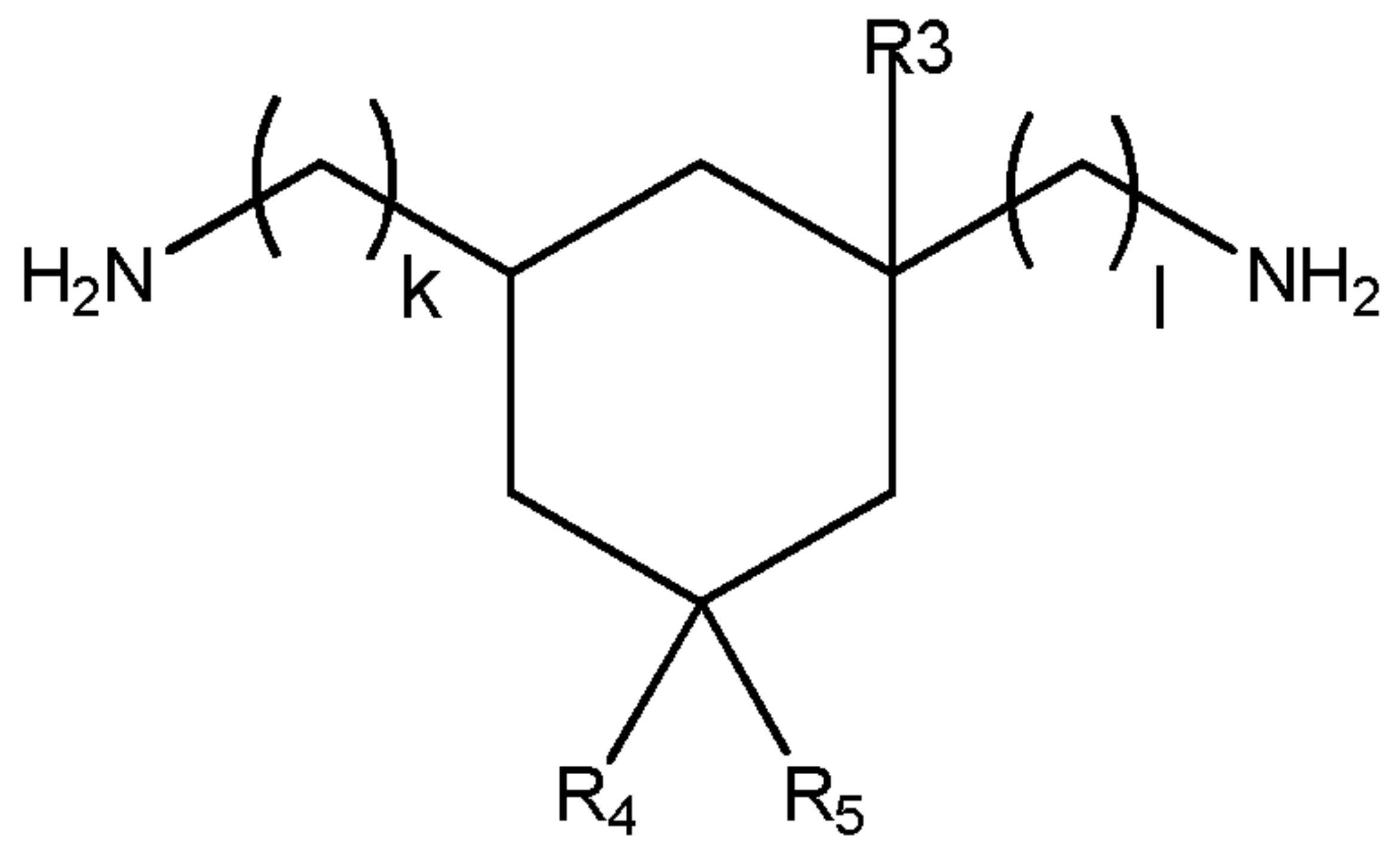
wherein:

m is an integer and is either 0 or 1, n is an integer and is from 2 to 8, o is an integer and is from 0 to 3, R_1 is a C_1 to C_{12} alkyl group, and in particular a linear $C_{12}H_{25}$ alkyl group, and R_2 is CH_3 or NH_2, and with the proviso that when m = 0, then o = 0 and R_2 is NH_2;

and where the cyclic diamine or triamine compound has one of the following formulas (II) and (III):



(II)



(III)

wherein:

k and l are the same or different and are either 0 or 1, R_3 is either H or CH_3, and R_4 and R_5 are the same or different and selected from H and CH_3, as a biocidal activity enhancing compound in an aqueous mineral preparation comprising at least one of ground natural calcium carbonate, precipitated calcium carbonate, dolomite, surface-reacted calcium carbonate, clay, talc, TiO_2, kaolin, kaolinitic clay, calcined kaolinitic clay, calcium sulfate, quartz, attapulgite, montmorillonite, diatomaceous earth, finely divided silica, aluminium oxide, aluminium hydroxide, silicates such as aluminium silicate, pumice and sepiolite, or a mixture thereof, and comprising at least one aldehyde-containing and/or aldehyde-releasing and/or phenolic and/or isothiazoline biocide, where the total amount of said biocide(s) in the aqueous preparation is from 90 ppm to 1 350 ppm, calculated relative to the weight of the aqueous phase of said preparation, and the total amount of said linear or cyclic diamine or triamine compound(s) in the aqueous preparation is from 600 to 1 200 ppm, calculated relative to the weight of the aqueous phase of said preparation.

Biocides

According to a preferred embodiment of the inventive process or use, said aldehyde-containing and/or aldehyde-releasing and/or phenolic and/or isothiazoline biocide(s) are added to the aqueous preparation in a total amount of from 100 ppm to 1 000 ppm, preferably in amount of from 150 ppm to 800 ppm, calculated relative to the water in the preparation.

In one embodiment of the present invention, said biocide(s) are in an undiluted, i.e. concentrated form. In another embodiment, the biocide(s) are diluted to a suitable concentration before being added to the aqueous preparation. In the diluted form, the biocide(s) are preferably dissolved in water, wherein the corresponding diluted composition comprises preferably up to 99 wt.-% of biocide, based on the total weight of the composition. More preferably, the composition in water comprises 50 to 95 wt.-% of biocide and most preferably 60 to 90 wt.-% of biocide, based on the total weight of the composition, whereby the composition may further comprise suitable stabilizers.

The aldehyde-based biocide of the present invention is preferably selected from the group consisting of formaldehyde, acetaldehyde, glyoxal, succinaldehyde, glutaraldehyde, 2-propenal, phthalic dialdehyde and mixtures thereof, and preferably is formaldehyde, glutaraldehyde and mixtures thereof.

In this application glutaraldehyde and glutardialdehyde (GDA) are identical. Both names are widely used in the industry.

Preferred aldehyde-releasing biocides according to the present invention include formaldehyde-releasing biocides, acetaldehyde-releasing biocides, succinaldehyde-releasing biocides, 2-propenal-releasing biocides and mixtures thereof.

According to another embodiment, the aldehyde-releasing compound is selected from the group consisting of benzyl alcoholmono(poly)-hemiformal, ethyleneglycolhemiformal (EGHF), [1,2-Ethanediylbis(oxy)]-bis-methanol, tetrahydro-1,3,4,6-tetrakis(hydroxylmethyl)imidazo[4,5-d]imidazole-2,5(1H,3H)-dione (also commonly referred to as TetraMethylolAcetyleneDiurea TMAD) and mixtures thereof.

Other preferred compounds are those having activated halogen atoms and liberating formaldehyde.

A preferred phenolic biocide is orthophenylphenol (OPP).

A preferred isothiazoline biocide is 2-methyl-4-isothiazoline-3-one (MIT), 5-chloro-2-methyl-2H-isothiazolin-3-one (CIT), 1,2-benzisothiazoline-3-one (BIT), or mixtures thereof.

According to another preferred embodiment of the present invention, the aldehyde-releasing and/or aldehyde-based biocide is used together with biocides selected from the group consisting of 5-chloro-2-methyl-2H-isothiazolin-3-one (CIT), 2-methyl-2H-isothiazolin-3-one (MIT) and mixtures thereof.

The mixtures of biocides which may be used according to the present invention are preferably dissolved in water.

An especially preferred biocide mixture comprises glutaraldehyde, 5-chloro-2-methyl-2H-isothiazolin-3-one (CIT) and 2-methyl-2H-isothiazolin-3-one (MIT).

Another especially preferred biocide mixture comprises ethyleneglycolhemiformal, 5-chloro-2-methyl-2H-isothiazolin-3-one (CIT) and 2-methyl-2H-isothiazolin-3-one (MIT).

Solids of the aqueous mineral preparation

The water-insoluble solids of the aqueous mineral preparation comprise at least one of: a ground natural calcium carbonate, a precipitated calcium carbonate, a dolomite, a surface-reacted calcium carbonate, clay, talc, TiO_2, kaolin, kaolinitic clay, calcined kaolinitic clay, calcium sulfate, quartz, attapulgite, montmorillonite, diatomaceous earth, finely divided silica, aluminium oxide, aluminium hydroxide, silicates such as aluminium silicate, pumice and sepiolite, or a mixture thereof. In a preferred embodiment of the present invention, said water-insoluble solids of the aqueous mineral preparation comprise at least one ground natural calcium carbonate, a precipitated calcium carbonate, a dolomite, a surface-reacted calcium carbonate.

“Ground natural calcium carbonate” (GNCC) in the meaning of the present invention is a calcium carbonate obtained from natural sources, such as limestone, marble or chalk, and processed through a treatment such as grinding, screening and/or fractionizing by wet and/or dry, for example by a cyclone or classifier.

“Precipitated calcium carbonate” (PCC) in the meaning of the present invention is a synthesized material, generally obtained by precipitation following reaction of carbon dioxide and lime in an aqueous environment or by precipitation of a calcium and carbonate ion source, for example $CaCl_2$ and Na_2CO_3, in water. Precipitated calcium carbonate exists in three primary crystalline forms: calcite, aragonite and vaterite, and there are many different polymorphs (crystal habits) for each of these crystalline forms. Calcite has a trigonal structure with typical crystal habits such as scalenohedral (S-PCC), rhombohedral (R-PCC), hexagonal prismatic, pinacoidal, colloidal (C-PCC), cubic, and prismatic (P-PCC). Aragonite is an orthorhombic structure with typical crystal habits of twinned hexagonal prismatic crystals, as well as a diverse assortment of thin elongated prismatic, curved bladed, steep pyramidal, chisel shaped crystals, branching tree, and coral or worm-like form.

Said GNCC or PCC may be surface reacted to form a surface-reacted calcium carbonate, which are materials comprising GNCC and/or PCC and an insoluble, at least partially crystalline, non-carbonate calcium salt extending from the surface of at least part of the calcium carbonate. Such surface-reacted products may, for example, be prepared according to WO 00/39222, WO 2004/083316, WO 2005/121257, WO 2009/074492, EP 2 264 108, and EP 2 264 109.

Said GNCC or PCC may additionally be surface treated, for example with fatty acids such as stearic acid and corresponding calcium salts.

In a preferred embodiment of the present invention, said mineral comprises one or more of: ground natural calcium carbonate, precipitated calcium carbonate, dolomite and surface-reacted calcium carbonate, and one or more of: kaolin, kaolinitic clay, calcined kaolinitic clay, talc, calcium sulfate, quartz, attapulgite, montmorillonite, diatomaceous earth, finely divided silica, aluminium oxide, aluminium hydroxide, silicates such as aluminium silicate, pumice and sepiolite, wherein said ground natural calcium carbonate and/or precipitated calcium carbonate and/or dolomite and/or surface-reacted calcium carbonate preferably is present in an amount of greater than or equal to 50 % by weight, more preferably greater than or equal to 60 % by weight, even more preferably greater than or equal to 70 % by weight, even more preferably greater than or equal to 80 % by weight, and most preferably greater than or equal to 90 % by weight, relative to the total weight of the mineral solids.

Clay refers to crystalline small particles of mainly hydrous silicates of aluminium, sometimes with magnesium and/or iron substitution for all or a part of the aluminium. The main groups of clay minerals are: kaolinite, the main constituent of kaolin; halloysite; illite; montmorillonite and vermiculite. The term “kaolinitic clay” used herein refers to a soft white clay that is composed of mainly the mineral kaolinite.

Kaolin is especially used in the paper industry, which uses it to coat and fill papers and boards and improves some of the optical properties of the final product, such as gloss, opacity or brightness. However, kaolin based products include paints, agricultural compositions, fibre glass products, polymers and rubber compositions, ceramic applications, catalyst supports, pharmaceuticals, cosmetics, adhesives, filter aids, and many more.

More preferably, said mineral consists essentially of only ground natural calcium carbonate, precipitated calcium carbonate, dolomite, surface-reacted calcium carbonate or mixture thereof, and most preferably consists essentially only of ground natural calcium carbonate.

Minerals having a positive surface charge at a pH of between 8 and 10 may be particularly advantageous according to the present invention.

In a preferred embodiment, the aqueous mineral preparation has a solids content of from 40 to 82 % by weight, as measured according to the measurement method provided in the Examples section hereafter. More preferably, the solids content is from 50 to 80 % by weight, and even more preferably from 60 to 80 % by weight.

The water-insoluble solid in the preparation may have a particle size distribution as conventionally employed for the material(s) involved in the type of product to be produced. In general, 90 % of the particles will have an esd (equivalent spherical diameter as measured by the well known technique of sedimentation using Sedigraph 5100 series, Micrometrics) of less than 5 µm. Coarse minerals, filler or pigment materials may have a particle esd generally (i.e. at least 90 wt.-%) in the range of 1 to 5 µm. Fine minerals materials may have a particle esd generally less than 2 µm, e.g. 50 to 99 wt.-% less than 2 µm and preferably 60 to 90 wt.-% less than 2 µm. It is preferred that the solid particles in the preparation have a d_{50} value (median esd defined in terms of 50 weight percent of particles being finer than esd, d_{50}) of from 0.1 to 5 µm, preferably from 0.2 to 2 µm and most preferably from 0.35 to 1 µm, for example 0.7 µm as measured using a Sedigraph^{TM} 5100 of Micromeritics Instrument Corporation. The method and the instrument are known to the skilled person and are commonly used to determine grain size of fillers. The measurement is carried out in an aqueous solution of 0.1 wt.-% $Na_4P_2O_7$. The samples are dispersed using a high speed stirrer and supersonics.

For keeping mineral particles in such an aqueous preparation and thus ensuring that the viscosity of the preparation remains substantially the same over time, additives such as dispersing agents, thickeners or anti-settling agents are used. A suitable dispersing agent is preferably made of monomers and/or co-monomers selected from the group consisting of acrylic acid, methacrylic acid, itaconic acid, crotonic acid, fumaric acid, maleic acid, isocrotonic acid, aconitic acid (cis or trans), mesaconic acid, sinapinic acid, undecylenic acid, angelic acid, canellic acid, hydroxyacrylic acid, acrolein, acrylamide, acrylonitrile, dimethylaminoethyl methacrylate, vinylpyrrolidone, vinylcaprolactam, ethylene, propylene, isobutylene, diisobutylene, vinyl acetate, styrene, α-methyl styrene, methyl vinyl ketone, the esters of acrylic and methacrylic acids, such as the acrylates and methacrylates of alkyl, of aryl, of alkylaryl, of arylalkyl, and in particular ethyl acrylate, butyl acrylate, methyl methacrylate, acrylamido methyl propane sulphonic acid, acrylamide and/or methacrylamide, acrylate phosphate of ethylene glycol, methacrylate phosphate of ethylene glycol, acrylate phosphate of propylene glycol acrylate, methacrylate phosphate of propylene glycol, methacrylamido propyl trimethyl ammonium chloride or sulphate, ethyl chloride or ammonium trimethyl methacrylate sulphate, together with their acrylate and acrylamide counterparts, whether or not quaternised, and/or dimethyldiallyl chloride, sodium sulfonate styrene, and mixtures thereof, wherein poly(acrylic acid) and/or poly (methacrylic acid) are preferred as dispersing agent. In addition, dispersing agents based on cellulose or starch can also be used. The skilled man will know how to correctly dose such dispersants to reach an optimal resting and process dispersion viscosity.

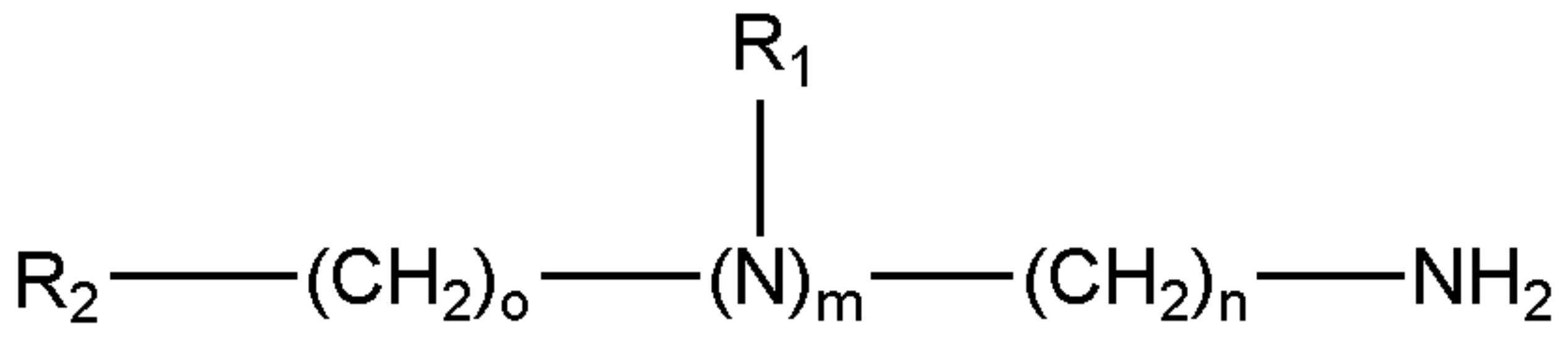
pH of the aqueous mineral preparation

According to a preferred embodiment of the process or the use of the present invention, said aqueous mineral preparation has a pH of between 8 and 10 prior to the addition of any biocide and/or linear or cyclic diamine or triamine compound(s) having at least one primary amine group.

In such a case, the biocides implemented according to the present invention are preferably stable, i.e. not degraded, at a pH of between 8 and 10, at least for a time sufficient to function as a biocide when in combination with the linear or cyclic diamine or triamine compound(s) having at least one primary amine group.

Linear or cyclic diamine or triamine compound

The linear or cyclic diamine or triamine compound(s) employed in the present invention have at least one primary amine group (NH_2) and are selected from a linear or cyclic diamine or triamine compound, where the linear diamine or triamine compound has the following formula (I):



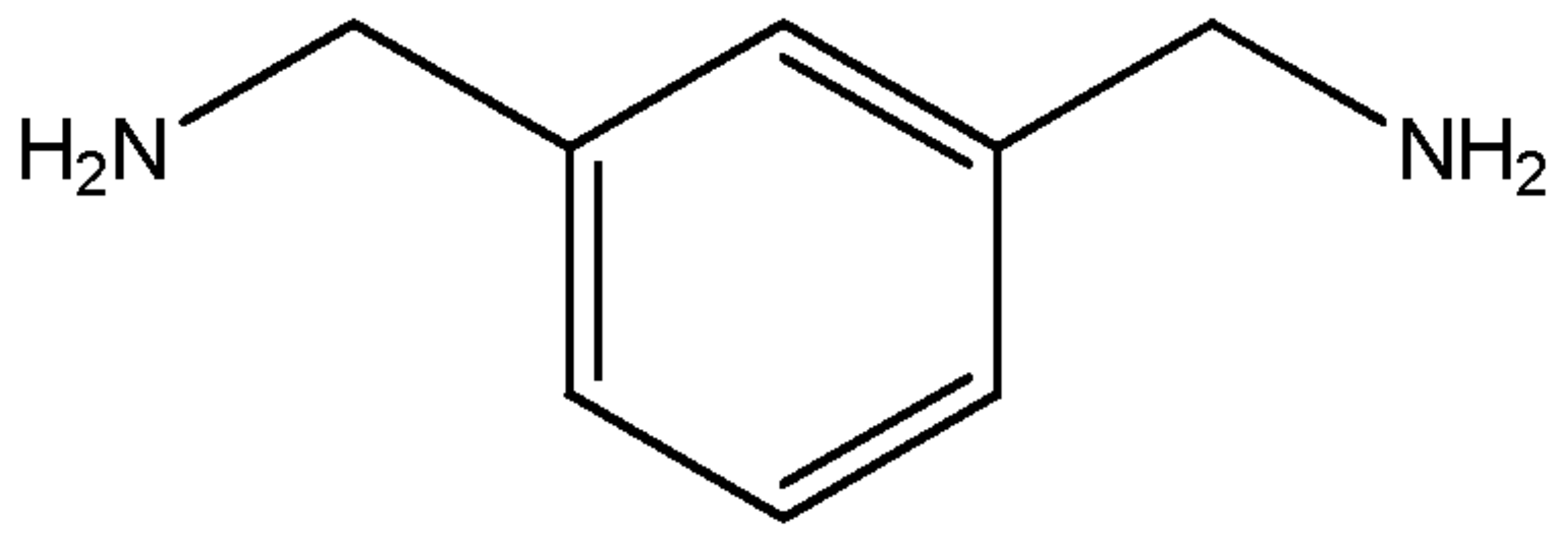
$$R_2—(CH_2)_o—\overset{\displaystyle R_1}{\overset{|}{(N)_m}}—(CH_2)_n—NH_2$$

(I)

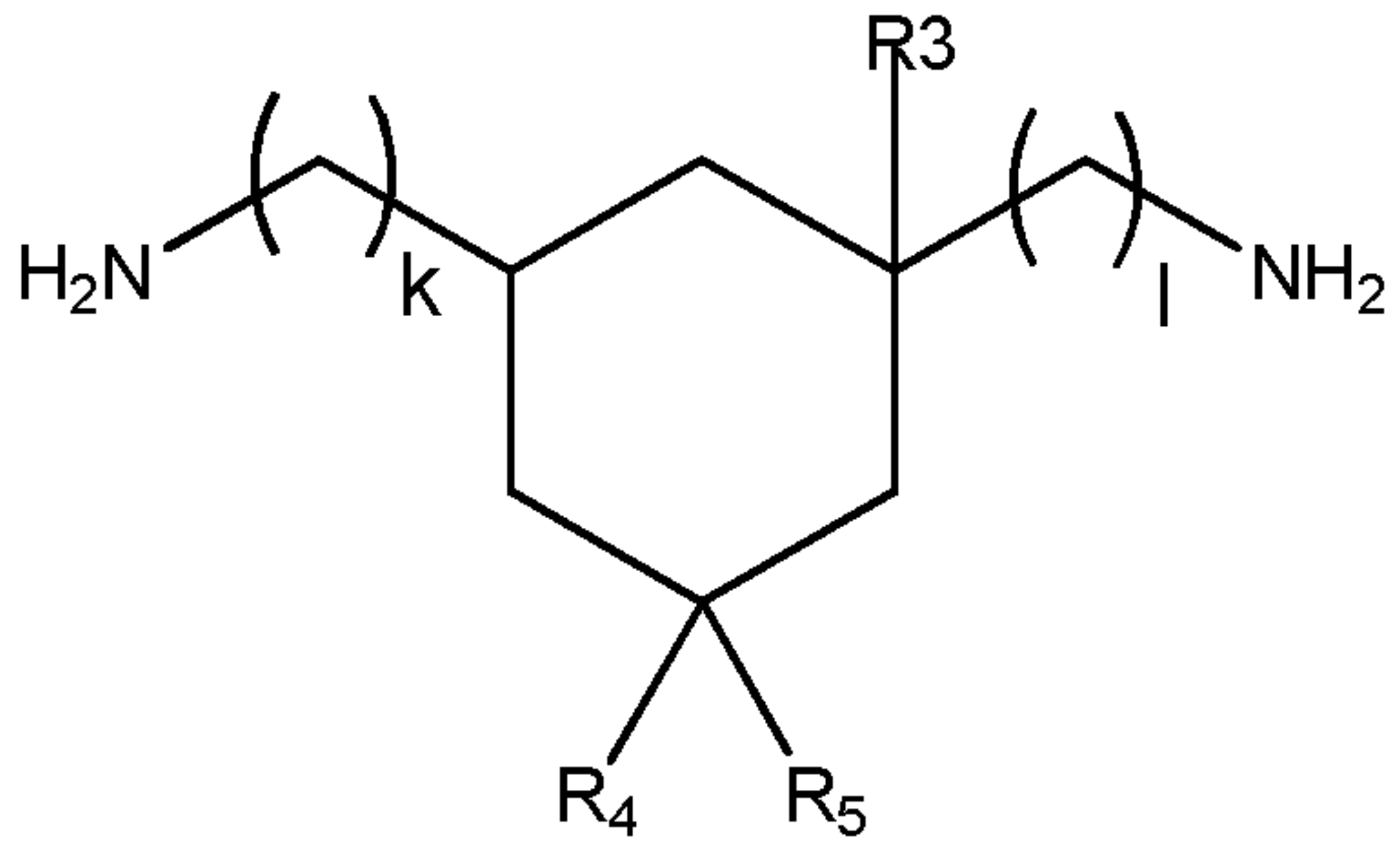
wherein:

m is an integer and is either 0 or 1, n is an integer and is from 2 to 8, o is an integer and is from 0 to 3, R_1 is a C_1 to C_{12} alkyl group, and is in particular CH_3, CH_2CH_3 or a linear $C_{12}H_{25}$ alkyl group, and R_2 is CH_3 or NH_2, and with the proviso that when m = 0, then o = 0 and R_2 is NH_2;

and where the cyclic diamine or triamine compound has one of the following formulas (II) and (III):



(II)



(III)

wherein:

k and l are the same or different and are either 0 or 1, R_3 is either H or CH_3, and R_4 and R_5 are the same or different and selected from H and CH_3.

It has to be noted that when in formula (I) m is equal 0, then R_1 is also not present in the linear diamine or triamine compound, in other words, group R_2 is directly attached to the $(CH_2)_n$-unit of the $(CH_2)_n$-NH_2 residue.

As regards formula (III), it has to be noted that when any one of k and/or l is equal to 0, then the NH_2 group is directly attached to the cyclohexane ring.

In a preferred embodiment of the present invention, said linear or cyclic diamine or triamine compound having at least one primary amine group is selected from the group comprising 1,3-bis(aminomethyl)cyclohexane, 1,3-bis(aminomethyl)benzene, 1,7-diaminoheptane, 1,8-diaminooctane, diethylaminoethylamine, ethylenediamine, N,N-bis-(3-aminopropyl)methylamine, isophorondiamine, and N-(3-aminopropyl)-N-dodecylpropane-1,3-diamine.

1,3-Bis(aminomethyl)benzene is represented by formula (II).

1,3-Bis(aminomethyl)cyclohexane is represented by formula (III), wherein $k = l = 1$, and $R_3 = R_4 = R_5 = H$; 1,7-diaminoheptane is represented by formula (I), wherein $o = m = 0$, $R_2 = NH_2$, and $n = 7$; 1,8-diaminooctane is represented by formula (I), wherein $o = m = 0$, $R_2 = NH_2$, and $n = 8$; diethylaminoethylamine is represented by formula (I), wherein $m = 1$, $o = 0$; $R_1 = CH_2CH_3$, $R_2 = CH_3$, and $n = 2$; ethylenediamine (also known as “en”) is represented by formula (I), wherein $o = m = 0$, $R_2 = NH_2$, and $n = 2$; N,N-bis-(3-aminopropyl)methylamine is represented by formula (I), wherein $m = 1$, $o = 3$, $R_1 = CH_3$, $R_2 = NH_2$, and $n = 3$; isophorondiamine is represented by formula (III), wherein $k = 0$, $l = 1$, and $R_3 = R_4 = R_5 = CH_3$; and N-(3-aminopropyl)-N-dodecylpropane-1,3-diamine is represented by formula (I), wherein $m = 1$, $n = o = 3$, R_1 = linear $C_{12}H_{25}$ alkyl, and $R_2 = NH_2$.

In a more preferred embodiment of the present invention said linear or cyclic diamine or triamine compound is selected from the group consisting of 1,3-bis(aminomethyl)cyclohexane, 1,3-bis(aminomethyl)benzene, 1,7-diaminoheptane, 1,8-diaminooctane, diethylaminoethylamine, and ethylenediamine.

The ratios of said biocide(s) to said linear or cyclic diamine or triamine compound(s) having at least one primary amine group may vary over a wide range.

The concentrations of the biocide(s) and the linear or cyclic diamine or triamine compound(s) having at least one primary amine group to be used in the aqueous preparation depend on the nature and the occurrence of the microorganisms to be controlled, the initial microbial load, and on the expected storage time of the aqueous preparations of minerals, fillers or pigments to be protected. The optimum amount to be employed within the defined ranges can be determined by preliminary tests and test series on a laboratory scale and by supplementary operational tests.

In the case where said biocide is an aldehyde-based biocide, such as glutaraldehyde, it is preferred to add said linear or cyclic diamine or triamine compound(s) having at least one primary amine group in an amount such that the weight ratio biocide : linear or cyclic diamine or triamine compound(s) is from 1 : 4 to 1: 1.

In the case where said biocide is a phenolic biocide, such as OPP, it is preferred to add said linear or cyclic diamine or triamine compound(s) having at least one primary amine group in an amount such that the weight ratio biocide : linear or cyclic diamine or triamine compound(s) is from 1 : 4 to 1: 2.

Order of addition

According to one preferred embodiment of the inventive process said biocide(s) and said linear or cyclic diamine or triamine compound(s) having at least one primary amine group are added separately to the aqueous preparation.

According to another preferred embodiment of the inventive process, said linear or cyclic diamine or triamine compound(s) having at least one primary amine group is added before all or part of said biocide(s). In the alternative, it may especially be preferred according to the inventive process that said biocide(s) are added before all or part of said linear or cyclic diamine or triamine compound(s) having at least one primary amine group.

It is especially preferred to add all of said linear or cyclic diamine or triamine compound(s) having at least one primary amine group before any of said biocide(s).

According to another preferred embodiment of the inventive process, said biocide(s) and said linear or cyclic diamine or triamine compound(s) having at least one primary amine group are added simultaneously. In this embodiment, it is possible that all or part of said biocide(s) are mixed with all or part of said linear or cyclic diamine or triamine compound(s) having at least one primary amine group before addition to the aqueous preparation.

Furthermore, said biocide(s) and/or the linear or cyclic diamine or triamine compound(s) having at least one primary amine group can be added once, e.g. before, during or after the manufacture of the preparation, or several times e.g. in specific time intervals.

Targeted bacteria

According to the present invention, it is especially preferred that prior to addition of any of said linear or cyclic diamine or triamine compound(s) having at least one primary amine group or said biocide, said aqueous preparation contains bacteria selected from the group consisting of *Thermus sp., Propionibacterium sp., Rhodococcus sp., Panninobacter sp., Caulobacter sp., Brevundimonas sp., Asticcacaulis sp., Sphingomonas sp., Rhizobium sp., Ensifer sp., Bradyrhizobium sp., Tepidimonas sp., Tepidicella sp., Aquabacterium sp., Pelomonas sp., Alcaligenis sp., Achromobacter sp., Ralstonia sp., Limnobacter sp., Massilia sp., Hydrogenophaga sp., Acidovorax sp., Curvibacter sp., Delftia sp., Rhodoferax sp., Alishewanella sp., Stenotrophomonas sp., Dokdonella sp., Methylosinus sp., Hyphomicrobium sp., Methylosulfomonas sp., Methylobacteria sp., Pseudomonas sp.* and mixtures thereof, and more preferably contains bacteria selected from the group consisting of *Pseudomonas putida, Pseudomonas mendocina, Pseudomonas fluorescens, Pseudomonas alcaligenes, Pseudomonas pseudoalcaligenes, Pseudomonas alcaliphila, Pseudomonas entomophila, Pseudomonas syringae, Methylobacterium extorquens, Methylobacterium radiotolerans, Methylobacterium dichloromethanicum, Methylobacterium organophilu, Hyphomicrobium zavarzini* and mixtures thereof.

In one embodiment, the aqueous preparation may further or alternatively contain strains of the above bacteria which are resistant to, tolerant to and/or degrade said biocides in absence of said linear or cyclic diamine or triamine compound(s) having at least one primary amine group.

In the embodiment where the aqueous preparation comprises strains of the above bacteria which are resistant to, tolerant to and/or degrade said biocides in absence of said linear or cyclic diamine or triamine compound(s) having at least one primary amine group, said linear or cyclic diamine or triamine compound(s) having at least one primary amine group in the aqueous preparation is preferably employed in an amount of from 600 to 1 200 ppm, calculated relative to the weight of the aqueous phase of said preparation

In the meaning of the present invention, bacteria which are “resistant” refer to bacteria having the ability to withstand the effects of said biocides when these are dosed in a total amount of from 90 to 1 350 ppm, calculated relative to the amount of water in the preparation. Such resistance evolves naturally via natural selection acting upon random mutation, but it can also be engineered by applying an evolutionary stress on a population.

In the meaning of the present invention, bacteria which are “tolerant” refer to bacteria having the ability to survive in the presence of said biocides without evolving a random mutation.

Bacteria which “degrade” said biocides in the meaning of the present invention correspond to bacteria having the ability to convert said biocides into inactive forms and/or smaller molecules, e.g. by utilizing these substrates as intermediates in their pathways.

Preferably, the inventive process and use provide biocidal activity (stabilization, preservation and/or control of the microbial contamination) of aqueous preparations for a time period of at least 2 days, more preferably for at least 4 days, still more preferably for at least 6 days and most preferably for a minimum of 8 days.

Applications

According to the present invention, resulting aqueous preparations may be used in many applications, for example, in the field of paper making, paints, detergents and cosmetics.

The following examples may additionally illustrate the invention, but are not meant to restrict the invention to the exemplified embodiments.

EXAMPLES

Particle size distribution (mass % particles with a diameter <X) and weight median diameter (d_{50}) of mineral material (i.e. GNCC)

In all of the following examples, the weight median diameter and the particle size distribution characteristics of the mineral material, such as GNCC, are determined via the sedimentation method, i.e. an analysis of sedimentation behavior in a gravimetric field. The measurement is made using a Sedigraph™ 5100 of Micromeritics Instrument Corporation.

The method and the instrument are known to the skilled person and are commonly used to determine grain size of fillers and pigments. The measurement is carried out in an aqueous solution of 0.1 wt% $Na_4P_2O_7$. The samples are dispersed using a high speed stirrer and supersonics.

Specific Surface Area (SSA) of a material

The specific surface area is measured via the BET (Brunauer, Emmett, Teller) method according to ISO 9277 using nitrogen, following conditioning of the sample by heating at 250°C for a period of 30 minutes. Prior to such measurements, the sample is filtered, rinsed and dried at 90 to 100°C in an oven for at least 12 hours before being broken down in a mortar with a pestle, and then placed in a weighing balance at 130°C until a constant weight is observed.

Viscosity measurement

All Brookfield-viscosities are measured with a Brookfield DV-II Viscometer equipped with a LV-3 spindle at a speed of 100 rpm and room temperature (20 ± 3°C).

Solids content of an aqueous slurry

All mineral preparation solids content (also known as "dry weight") was measured using a Mettler Toledo^{TM} MJ33 Moisture Analyser.

Biocide amount and amount of linear or cyclic diamine or triamine compound(s) having at least one primary amine group

All biocide amounts and the amounts of linear or cyclic diamine or triamine compound(s) having at least one primary amine group quoted in ppm represent mg values of active content per kilogram of water in the aqueous preparation.

Total Viable Count (TVC)

All quoted bacterial counts (Total Viable Count (TVC) values are in cfu/ml) in the Tables herebelow are determined after **48 hours** following plate-out and in accordance with the counting method described in "Bestimmung von aeroben mesophilen Keimen", Schweizerisches Lebensmittelbuch, chapter 56, section 7.01, edition of 1985, revised version of 1988.

Ground Natural Calcium Carbonate Slurry (GNCCS)

The GNCCS used is a slurry of natural ground carbonate (marble). The product is commercialized by Omya, Switzerland, under the trade name Hydrocarb® 90 GU 76.5 %.

The Brookfield-viscosity of the slurry was determined as 350 mPa·s and the pH as 10.

Biocidal activity in slurry

Example 1: Ethylene diamine (EDA)

Aldehyde-based biocide and Isothiazoline biocide mixture (BM1)

Biocide mixture 1 (BM1) is an aqueous solution containing 24 % by weight of GDA (glutaraldehyde /glutardialdehyde) and 1.5 % by weight of a combination of CIT and MIT (5-chloro-2-methyl-2H-isothiazolin-3-one (CIT) and 2-methyl-2H-isothiazolin-3-one (MIT); in a weight ratio CIT : MIT of 3:1), relative to the total solution weight.

BM1 and ethylene diamine (hereafter “EDA”) were introduced into 50 g samples of each of the slurries indicated in Table 1 in the listed amounts (quoted in ppm based on the weight of the aqueous phase in the slurry). The samples were then stored at 30°C for 72 hours. References were prepared according to the same protocol but in absence of EDA and in absence of EDA and BM1.

The slurry samples were then inoculated with 1 ml of a mixture of rGDA/IT bacteria culture. Each of the samples was incubated at 30°C for 24 hours. Thereafter, a 1:10 dilution in phosphate buffered saline (PBS) was plated on plate count agar (PCA). These plates were incubated at 30°C and analysed after 48 hours.

The biocide-resistant calcium carbonate slurry culture rGDA/IT is GDA/CIT/MIT-resistant and was obtained from product storage tanks located at white mineral dispersion (WMD) manufacturing plants that used the related biocide to preserve the products. Sequence analysis of the isolated strains revealed that the resistant culture rGDA/IT contained bacteria belonging to the genus *Pseudomonas*. The closest relatives based on the similarity of the 16S rRNA gene sequence were the species *Pseudomonas pseudoalcaligenes*, *Pseudomonas mendocina* and *Pseudomonas alcaliphila.*

Table 1

Test	Invention (IN) Comparison (CO)	Slurry	Bacteria culture	BM1 (ppm on aqueous phase)	EDA (ppm on aqueous phase)	TVC (cfu/ml)
1	CO	GNCCS	rGDA/IT	--	--	$1x10^6$
2	CO	GNCCS	rGDA/IT	1350	--	$1x10^6$
3	CO	GNCCS	rGDA/IT	--	1050	$1x10^6$
4	CO	GNCCS	rGDA/IT	1350	450	$1x10^6$
5	IN	GNCCS	rGDA/IT	1350	750	**$1x10^2$**
6	IN	GNCCS	rGDA/IT	675	750	**$1x10^2$**
7	CO	GNCCS	rGDA/IT	675	450	$1x10^4$

Test 1 shows that there is a growth of the bacterial culture in the slurry in the absence of any one of the biocide BM1 and EDA. Although the biocide BM1 is present in a rather high amount, namely in an amount of 1 350 ppm, Test 2 shows that there is still a significant growth of bacteria in the slurry. This clearly indicates that the biocide BM1 cannot effectively used as a biocide for inhibiting the growth of the rGDA/IT bacteria culture. Test 3 shows that EDA does not provide bacteria inhibiting properties to the slurry. Tests 4 and 7 show the bacterial growth in slurries that were treated with a mixture of the biocide BM1 and EDA. However, it is apparent from these tests, namely a TVC of $1x10^6$ cfu/ml, that the amount of EDA is insufficient to enhance the biocide function of BM1. Finally, Tests 5 and 6 show the bacterial growth in slurries that were treated with a mixture of the biocide BM1 and EDA according to the present invention. From these test results it is evident that an EDA amount of 750 ppm is sufficient to enhance the biocide function of BM1. In summary, the results of the above table confirm that EDA enhances the biocide function of BM1, allowing BM1 to be employed in quantities far below its MIC. Further increasing the amount of EDA allowed the amount of BM1 to be reduced even further relative to its minimum inhibition concentration (MIC).

The above results clearly demonstrate that the biocide enhancer according to the invention provides the necessary enhancement.

Tests 8 and 9 below represent the same slurry as Tests 5 and 6, respectively, but following a second inoculation of 1 ml of a mixture of *Pseudomonas* species.

Table 2

Test	Invention (IN) Comparison (CO)	Slurry	Bacteria culture	BM1 (ppm on aqueous phase)	EDA (ppm on aqueous phase)	TVC (cfu/ml)
8	IN	GNCCS	rGDA/IT	1350	750	**$1x10^2$**
9	IN	GNCCS	rGDA/IT	675	750	**$1x10^2$**

The results of the above table confirm that EDA enhances the biocide function of BM1, allowing BM1 to be employed in quantities below its MIC. The biocide function of EDA is still present after a total of two inoculations of the slurry with the bacteria culture.

Tests 10 and 11 below represent the same slurry as Tests 5 and 6, but following two additional inoculations of each 1 ml of a mixture of *Pseudomonas* species.

Table 3

Test	Invention (IN) Comparison (CO)	Slurry	Bacteria culture	BM1 (ppm on aqueous phase)	EDA (ppm on aqueous phase)	TVC (cfu/ml)
10	IN	GNCCS	rGDA/IT	1350	750	**$5.5x10^2$**
11	IN	GNCCS	rGDA/IT	675	750	**$1x10^2$**

The results of the above table confirm that EDA enhances the biocide function of BM1, allowing BM1 to be employed in quantities below its MIC. The biocide function of EDA is still present after a total of three inoculations of the slurry with the bacteria culture.

Example 2: Other Diamines

Aldehyde-based biocide and Isothiazoline biocide mixture (BM1)

Biocide mixture 1 (BM1) is an aqueous solution containing 24 % by weight of (glutaraldehyde /glutardialdehyde) and 1.5 % by weight of a combination of CIT and MIT (in a weight ratio CIT : MIT of 3:1), relative to the total solution weight.

BM1 and a diamine selected from 1,3-bis(aminomethyl)cyclohexane (hereinafter “AMC”), 1,3-bis(aminomethyl)benzene (hereinafter “AMB”), 1,7-diaminoheptane (hereinafter “DAH”), and 1,8-diamionoocatane (hereinafter “DAO”) were introduced into 50 g samples of each of the slurries indicated in Table 4 in the listed amounts (quoted in ppm based on the weight of the aqueous phase in the slurry). The samples were then stored at 30°C for 72 hours. References were prepared according to the same protocol but in absence of the respective diamine used and in the absence of the respective diamine and BM1.

The slurry samples were then inoculated with 1 ml of a mixture of rGDA/IT bacteria culture. Each of the samples was incubated at 30°C for 24 hours. Thereafter, a 1:10 dilution in phosphate buffered saline (PBS) was plated on plate count agar (PCA). These plates were incubated at 30°C and analysed after 48 hours.

The biocide-resistant calcium carbonate slurry culture rGDA/IT is GDA/CIT/MIT-resistant and was obtained from product storage tanks located at white mineral dispersion (WMD) manufacturing plants that used the related biocide to preserve the products. Sequence analysis of the isolated strains revealed that the resistant culture rGDA/IT contained bacteria belonging to the genus *Pseudomonas*. The closest relatives based on the similarity of the 16S rRNA gene sequence were the species *Pseudomonas pseudoalcaligenes*, *Pseudomonas mendocina* and *Pseudomonas alcaliphila*.

Table 4

Test	(IN) / (CO)	Slurry	Bacteria culture	BM1 (ppm)	AMC (ppm)	AMB (ppm)	DAH (ppm)	DAO (ppm)	TVC (cfu/ml)
12	CO	GNCCS	rGDA/IT	--	--	--	--	--	$1x10^6$
13	CO	GNCCS	rGDA/IT	1350	--	--	--	--	$1x10^6$
14	CO	GNCCS	rGDA/IT	--	750	--	--	--	$1x10^6$

15	CO	GNCCS	rGDA/IT	--	--	750	--	--	$1x10^6$
16	CO	GNCCS	rGDA/IT	--	--	--	750	--	$1x10^6$
17	CO	GNCCS	rGDA/IT	--	--	--	--	750	$1x10^6$
18	CO	GNCCS	rGDA/IT	1350	375	--	--	--	$1x10^6$
19	CO	GNCCS	rGDA/IT	1350	--	375	--	--	$1x10^6$
20	CO	GNCCS	rGDA/IT	1350	--	--	375	--	$1x10^6$
21	CO	GNCCS	rGDA/IT	1350	--	--	--	375	$1x10^6$
22	IN	GNCCS	rGDA/IT	1350	750	--	--	--	**$1x10^2$**
23	IN	GNCCS	rGDA/IT	1350	--	750	--	--	**$1x10^2$**
24	IN	GNCCS	rGDA/IT	1350	--	--	750	--	**$1x10^2$**
25	IN	GNCCS	rGDA/IT	1350	--	--	--	750	**$1x10^2$**

Tests 12 to 17 demonstrate the bacterial growth in slurries which have been treated with no biocide (Test 12), only the biocide BM1 (Test 13), and no biocide and only 1,3-bis(aminomethyl)cyclohexane (AMC; Test 14), 1,3-bis(aminomethyl)benzene (AMB; Test 15), 1,7-diaminoheptane (DAH, Test 16), or 1,8-diamionoocatane (DAO; Test 17). From these tests it is apparent that neither one of the aforementioned compounds shows biocide functions with regard to the rGDA/IT bacteria culture in the slurries.

Tests 18 to 21show the bacteria growth in slurries that were treated with a mixture of the biocide BM1 and EDA. However, it is apparent from these tests, namely a TVC of $1x10^6$ cfu/ml, that the amount of any one of AMC, AMB, DAH, or DAO used (i.e. 375 ppm) is insufficient to enhance the biocide function of BM1.

Finally, Tests 22 to 25 demonstrate the bacterial growth in slurries that were treated with a mixture of the biocide BM1 and any one of AMC, AMB, DAH, or DAO according to the present invention. From these test results it is evident that an AMC, AMB, DAH, or DAO amount of 750 ppm is sufficient to enhance the biocide function of BM1. In summary, the results of the above table confirm that each one of 1,3-bis(aminomethyl)cyclohexane, 1,3-bis(aminomethyl)benzene, 1,7-diaminoheptane, and 1,8-diamionoocatane enhances the biocide function of BM1, allowing BM1 to be employed in quantities far below its minimum inhibition concentration (MIC).

The above results clearly demonstrate that the biocide enhancer according to the invention provides the necessary enhancement.

Tests 25, 26, 27 and 28 below represent the same slurry as Tests 22, 23, 24 and 25, respectively, but following a second inoculation of 1 ml of a mixture of *Pseudomonas* species.

Table 5

Test	(IN) / (CO)	Slurry	Bacteria culture	BM1 (ppm)	AMC (ppm)	AMB (ppm)	DAH (ppm)	DAO (ppm)	TVC (cfu/ml)
13	CO	GNCCS	rGDA/IT	1350	--	--	--	--	**$1x10^6$**
25	IN	GNCCS	rGDA/IT	1350	750	--	--	--	**$1x10^2$**
26	IN	GNCCS	rGDA/IT	1350	--	750	--	--	**$1x10^2$**
27	IN	GNCCS	rGDA/IT	1350	--	--	750	--	**$1x10^2$**
28	IN	GNCCS	rGDA/IT	1350	--	--	--	750	**$1x10^2$**

The results of the above table confirm that any one of AMC, AMB, DAH, or DAO enhances the biocide function of BM1, allowing BM1 to be employed in quantities below its MIC. The biocide function of any one of AMC, AMB, DAH, and DOH is still present after a total of two inoculations of the slurry with the bacteria culture.

Example 3: AMC, AMB, DAH, and DAO

Orthophenylphenol (OPP)

OPP, in the form of an aqueous solution having a concentration of 45 %, and one of **AMC, AMB, DAH, and DAO** were introduced into 50 g samples of each of the slurries indicated in Table 6 in the listed amounts (quoted in ppm active content based on the weight of the aqueous phase in the slurry). References were prepared according to the same protocol but in absence of any one of **AMC, AMB, DAH, and DAO**. A reference was prepared according to the same protocol but in absence of **AMC, AMB, DAH, and DAO** and in absence of any biocide.

The slurry samples were then inoculated with 1 ml of a mixture of *Pseudomonas* species containing predominantly *Pseudomonas putida* and *Pseudomonas stutzeri* that are resistant to OPP. Each of the samples was incubated at 30 °C for 72 hours. Thereafter, a 1:10 dilution in phosphate buffered saline (PBS) was plated on plate count agar (PCA). These plates were incubated at 30 °C and analysed after 24 hours.

The biocide-resistant calcium carbonate slurry culture rOPP is resistant toward OPP and was obtained from product storage tanks located at calcium carbonate slurry manufacturing plants that used the related biocide to preserve the products.

Tests 41, 42, 43, 44 and 45 below represent the same slurry as Tests 36, 37, 38, 39 and 40, respectively, but following a second inoculation of 1 ml of a mixture of *Pseudomonas* species. Tests 46, 47, 48, 49 and 50 below represents the same slurry as Tests 36, 37, 38, 39 and 40, respectively, but following two additional inoculations of each 1 ml of a mixture of *Pseudomonas* species.

Table 6

Test	(IN) / (CO)	Slurry	Bacteria culture	OPP (ppm)	AMC (ppm)	AMB (ppm)	DAH (ppm)	DAO (ppm)	TVC (cfu/ml)
29	CO	GNCCS	rOPP	--	--	--	--	--	$1x10^6$
30	CO	GNCCS	rOPP	250	--	--	--	--	$1x10^6$
31	CO	GNCCS	rOPP	--	750	--	--	--	$1x10^6$
32	CO	GNCCS	rOPP	--	--	750	--	--	$1x10^6$
33	CO	GNCCS	rOPP	--	--	--	750	--	$1x10^6$
34	CO	GNCCS	rOPP	--	--	--	--	750	$1x10^6$
35	IN	GNCCS	rOPP	250	750	--	--	--	**$1x10^2$**
36	IN	GNCCS	rOPP	250	--	750	--	--	**$1x10^2$**
37	IN	GNCCS	rOPP	250	--	--	750	--	**$1x10^2$**
38	IN	GNCCS	rOPP	250	--	--	--	750	**$1x10^2$**

Tests 29 to 34 demonstrate the bacterial growth in slurries which have been treated with no biocide (Test 29), only the biocide BM1 (Test 30), and no biocide and only 1,3-bis(aminomethyl)cyclohexane (AMC; Test 31), 1,3-bis(aminomethyl)benzene (AMB; Test 32), 1,7-diaminoheptane (DAH, Test 33), or 1,8-diamionoocatane (DAO; Test 34). From these tests it is apparent that neither one of the aforementioned compounds shows biocide functions with regard to the rOPP bacteria culture in the slurries.

Tests 35 to 38 demonstrate the bacterial growth in slurries that were treated with a mixture of the biocide BM1 and any one of AMC, AMB, DAH, or DAO according to the present invention. From these test results it is evident that an AMC, AMB, DAH, or DAO amount of 750 ppm is sufficient to enhance the biocide function of BM1. In summary, the results of the above table confirm that each one of 1,3-bis(aminomethyl)cyclohexane, 1,3-bis(aminomethyl)benzene, 1,7-diaminoheptane, and 1,8-diamionoocatane enhances the biocide function of BM1, allowing BM1 to be employed in quantities far below its MIC.

Also, the results of the above table confirm that every one of ethylene diamine (EDA), 1,3-bis(aminomethyl)cyclohexane (AMC), 1,3-bis(aminomethyl)benzene (AMB), 1,7-diaminoheptane (DAH), and 1,8-diamionoocatane (DAO) enhances the biocide function of OPP.

Tests 39, 40, 41, and 42 below represent the same slurry as Tests 35, 36, 37, and 38, respectively, but following a second inoculation of 1 ml of a mixture of *Pseudomonas* species.

Table 7

Test	(IN) / (CO)	Slurry	Bacteria culture	OPP (ppm)	AMC (ppm)	AMB (ppm)	DAH (ppm)	DAO (ppm)	TVC (cfu/ml)
29	CO	GNCCS	rOPP	--	--	--	--	--	$1x10^6$
39	IN	GNCCS	rOPP	250	750	--	--	--	**$1x10^2$**
40	IN	GNCCS	rOPP	250	--	750	--	--	**$1x10^2$**
41	IN	GNCCS	rOPP	250	--	--	750	--	**$1x10^2$**
42	IN	GNCCS	rOPP	250	--	--	--	750	**$1x10^2$**

The results of the above table confirm that any one of AMC, AMB, DAH, or DAO enhances the biocide function of BM1, allowing BM1 to be employed in quantities below its MIC. The biocide function of any one of AMC, AMB, DAH, and DOH is still present after a total of two inoculations of the slurry with the bacteria culture rOPP.

Tests 43, 44, 45, and 46 below represent the same slurry as Tests 35, 36, 37, and 38, respectively, but following two additional inoculations of each 1 ml of a mixture of *Pseudomonas* species.

Table 8

Test	(IN) / (CO)	Slurry	Bacteria culture	OPP (ppm)	AMC (ppm)	AMB (ppm)	DAH (ppm)	DAO (ppm)	TVC (cfu/ml)
29	CO	GNCCS	rOPP	--	--	--	--	--	$1x10^6$
43	IN	GNCCS	rOPP	250	750	--	--	--	**$1x10^2$**
44	IN	GNCCS	rOPP	250	--	750	--	--	**$1x10^2$**
45	IN	GNCCS	rOPP	250	--	--	750	--	**$1x10^2$**
46	IN	GNCCS	rOPP	250	--	--	--	750	**$1x10^2$**

The results of the above table confirm that any one of AMC, AMB, DAH, or DAO enhances the biocide function of BM1, allowing BM1 to be employed in quantities below its MIC. The biocide function of any one of AMC, AMB, DAH, and DOH is still present after a total of three inoculations of the slurry with the bacteria culture rOPP.

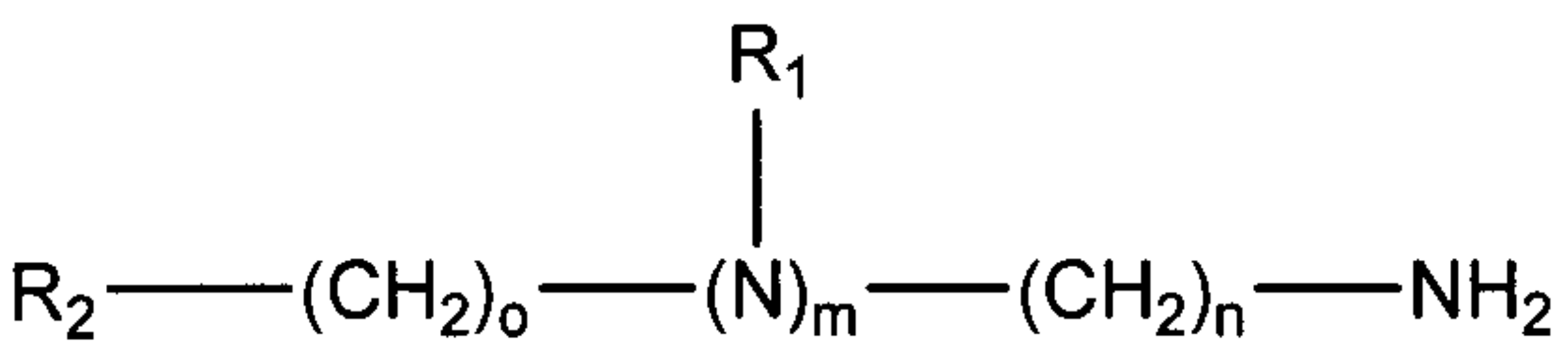
CLAIMS

1. Process for bacterial stabilization of an aqueous mineral preparation, comprising a step of:

(a) adding at least one aldehyde-containing, aldehyde-releasing, phenolic and/or isothiazoline biocide to said aqueous mineral preparation;

characterised in that:
- the bacterial stabilization entails a lack of significant growth of bacteria, with a reduction and/or maintenance of the Total Viable Count of bacteria of less than 10^4 cfu/ml;
- said mineral comprises at least one of: a ground natural calcium carbonate, a precipitated calcium carbonate, a dolomite, a surface-reacted calcium carbonate, clay, talc, TiO_2, kaolin, kaolinitic clay, calcined kaolinitic clay, calcium sulfate, quartz, attapulgite, montmorillonite, diatomaceous earth, finely divided silica, aluminium oxide, aluminium hydroxide, silicates, or a mixture thereof;

- said process comprises a step (b), which is simultaneous and/or distinct relative to step (a), of adding at least one linear diamine, linear triamine or cyclic diamine compound to said aqueous mineral preparation, the linear diamine, linear triamine or cyclic diamine compound having at least one primary amine group, and where the linear diamine or linear triamine compound has the following formula (I):



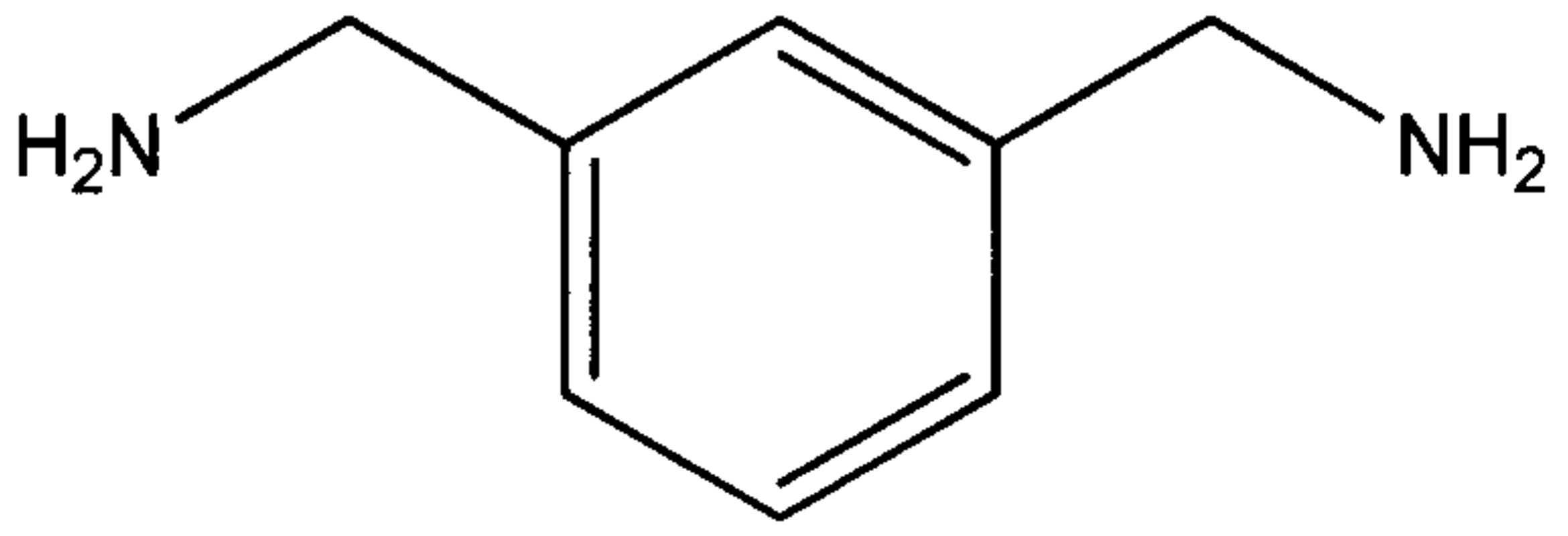
$$R_2 - (CH_2)_o - \overset{\overset{\displaystyle R_1}{|}}{(N)_m} - (CH_2)_n - NH_2$$

(I)

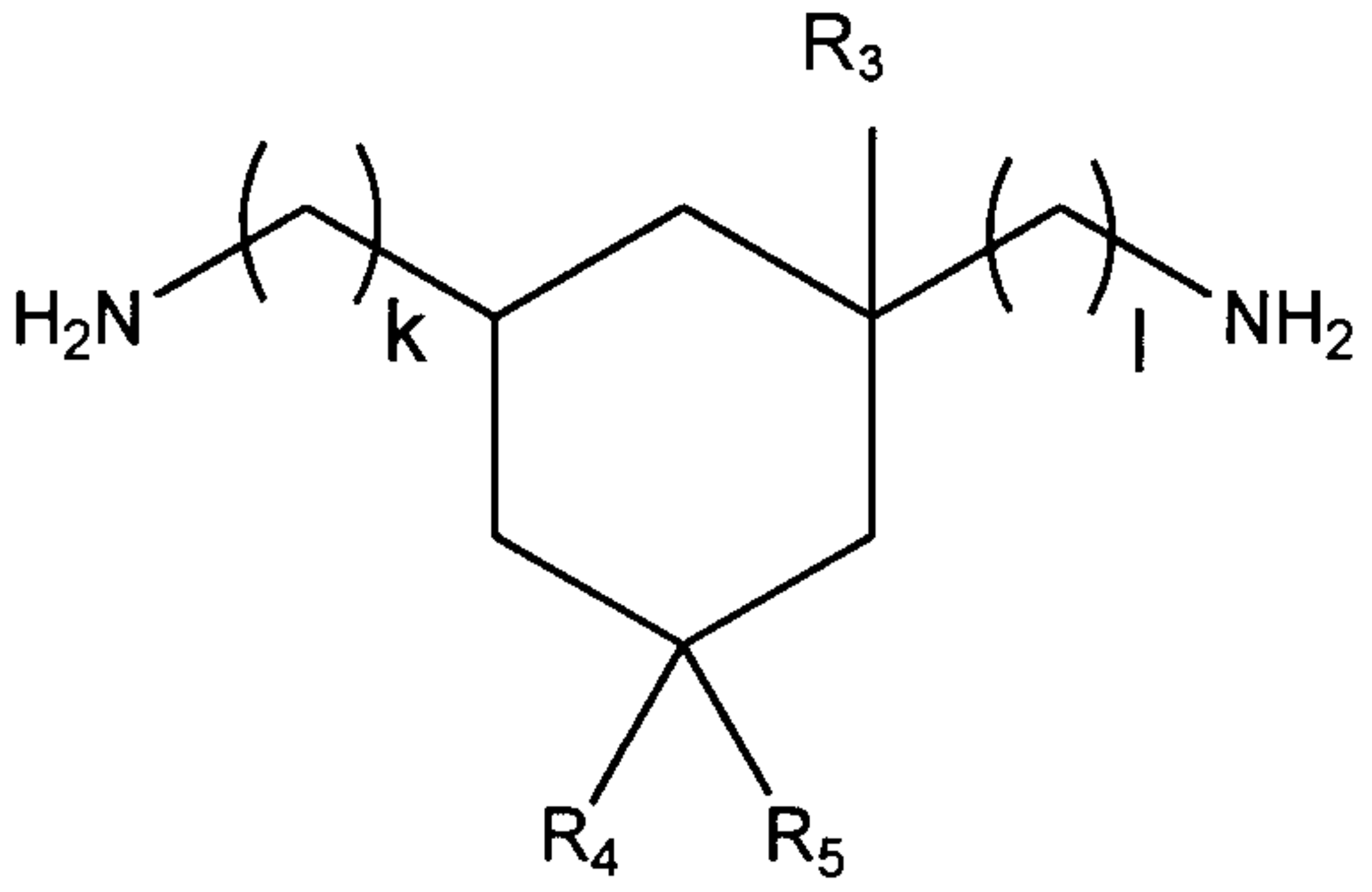
wherein:

m is an integer and is either 0 or 1, n is an integer and is from 2 to 8, o is an integer and is from 0 to 3, R_1 is a C_1 to C_{12} alkyl group, and R_2 is CH_3 or NH_2, and with the proviso that when m = 0, then o = 0 and R_2 is NH_2;

and where the cyclic diamine compound has one of the following formulas (II) and (III):



(II)



(III)

wherein:

k and l are the same or different and are either 0 or 1, R_3 is either H or CH_3, and R_4 and R_5 are the same or different and selected from H and CH_3,

- said biocide(s) are added to said aqueous preparation in an amount corresponding to from 90 to 1 350 ppm based on the weight of the aqueous phase of said aqueous preparation; and
- said linear diamine, linear triamine or cyclic diamine compound(s) are added to said aqueous preparation in an amount corresponding to from 600 to 1 200 ppm, based on the weight of the aqueous phase of said aqueous preparation.

2. The process according to claim 1, characterized in that the mineral comprises at least one of: a ground natural calcium carbonate, a precipitated calcium carbonate, a dolomite or a surface-reacted calcium carbonate.

3. The process according to claim 1 or 2, characterized in that the silicate is aluminium silicate, pumice, sepiolite or a mixture thereof.

4. The process according to any one of claims 1 to 3, characterized in that the C_1 to C_{12} alkyl group of R_1 is CH_3, CH_2CH_3 or a linear $C_{12}H_{25}$ alkyl group.

5. The process according to any one of claims 1 to 4, characterised in that said aldehyde-containing, aldehyde-releasing, phenolic and/or isothiazoline biocide(s) are added to the aqueous preparation in a total amount of from 100 ppm to 1 000 ppm, calculated relative to the water in the preparation.

6. The process according to any one of claims 1 to 5, wherein said aldehyde-containing, aldehyde-releasing, phenolic and/or isothiazoline biocide(s) are added to the aqueous preparation in a total amount of from 150 ppm to 800 ppm, calculated relative to the water in the preparation.

7. The process according to any one of claims 1 to 6, characterised in that said aldehyde-containing biocide is formaldehyde, acetaldehyde, glyoxal, succinaldehyde, glutaraldehyde, 2-propenal, phthalic dialdehyde or a mixture thereof, and/or characterised in that said aldehyde-releasing biocide is a formaldehyde-releasing biocide, an acetaldehyde-releasing biocide, a succinaldehyde-releasing biocide, a 2-propenal-releasing biocide or a mixture thereof.

8. The process according to any one of claims 1 to 7, characterised in that said aldehyde-containing biocide is formaldehyde, glutaraldehyde or a mixture thereof.

9. The process according to claim 7, wherein said aldehyde-releasing biocide is benzyl alcoholmono(poly)-hemiformal, ethyleneglycolhemiformal (EGHF), [1,2-Ethanediylbis(oxy)]-bis-methanol, tetrahydro-1,3,4,6-

tetrakis(hydroxylmethyl)imidazo[4,5-d]imidazole-2,5(1H,3H)-dione (also commonly referred to as TetraMethylolAcetyleneDiurea TMAD) or a mixture thereof.

10. The process according to any one of claims 1 to 9, characterised in that said phenolic biocide is orthophenylphenol (OPP), and/or characterised in that said isothiazoline biocide is 2-methyl-4-isothiazoline-3-one (MIT), 5-chloro-2-methyl-2H-isothiazolin-3-one (CIT), 1,2-benzisothiazoline-3-one (BIT), or a mixture thereof.

11. The process according to any one of claims 1 to 10, characterised in that said aldehyde-releasing and/or aldehyde-containing biocide is used together with a biocide being 5-chloro-2-methyl-2H-isothiazolin-3-one (CIT), 2-methyl-2H-isothiazolin-3-one (MIT) or a mixture thereof.

12. The process according to any one of claims 1 to 6, characterised in that said biocide is a combination of glutaraldehyde, 5-chloro-2-methyl-2H-isothiazolin-3-one (CIT) and 2-methyl-2H-isothiazolin-3-one (MIT), or a combination of ethyleneglycol-hemiformal, 5-chloro-2-methyl-2H-isothiazolin-3-one (CIT) and 2-methyl-2H-isothiazolin-3-one (MIT).

13. The process according to any one of claims 1 to 12, characterised in that said mineral comprises one or more of: ground natural calcium carbonate, precipitated calcium carbonate, dolomite and surface-reacted calcium carbonate, and one or more of: kaolin, kaolinitic clay, calcined kaolinitic clay, talc, calcium sulfate, quartz, attapulgite, montmorillonite, diatomaceous earth, finely divided silica, aluminium oxide, aluminium hydroxide, or silicates.

14. The process according to any one of claims 1 to 13, wherein said ground natural calcium carbonate, precipitated calcium carbonate, dolomite and/or surface-reacted calcium carbonate is present in an amount of greater than or equal to 50 % by weight.

15. The process according to any one of claims 1 to 14, wherein said ground natural calcium carbonate, precipitated calcium carbonate, dolomite and/or surface-reacted calcium carbonate is present in an amount of greater than or equal to 60 % by weight.

16. The process according to any one of claims 1 to 14, wherein said ground natural calcium carbonate, precipitated calcium carbonate, dolomite and/or surface-reacted calcium carbonate is present in an amount of greater than or equal to 70 % by weight.

17. The process according to any one of claims 1 to 14, wherein said ground natural calcium carbonate, precipitated calcium carbonate, dolomite and/or surface-reacted calcium carbonate is present in an amount of greater than or equal to 80 % by weight.

18. The process according to any one of claims 1 to 14, wherein said ground natural calcium carbonate, precipitated calcium carbonate, dolomite and/or surface-reacted calcium carbonate is present in an amount of greater than or equal to 90 % by weight.

19. The process according to any one of claims 1, 2, 4 to 12, or 14 to 18, characterised in that said mineral consists essentially of only ground natural calcium carbonate, precipitated calcium carbonate, dolomite, surface-reacted calcium carbonate or mixtures thereof.

20. The process according to any one of claims 1, 2, 4 to 12, or 14 to 18, characterised in that said mineral consists essentially only of ground natural calcium carbonate.

21. The process according to any one of claims 1 to 20, characterised in that said aqueous mineral preparation has a solids content of from 40 to 82 % by weight, and/or characterised in that said aqueous mineral preparation has a pH of between 8 and 10, prior to the addition of any biocide and/or linear diamine, linear triamine or cyclic diamine compound having at least one primary amine group.

22. The process according to any one of claims 1 to 21, characterised in that said aqueous mineral preparation has a solids content of from 50 to 80 % by weight.

23. The process according to any one of claims 1 to 21, characterised in that said aqueous mineral preparation has a solids content of from 60 to 80 % by weight.

24. The process according to any one of claims 1 to 23, characterised in that said linear diamine, linear triamine or cyclic diamine compound having at least one primary amine group is 1,3-bis(aminomethyl)cyclohexane, 1,3-bis(aminomethyl)benzene, 1,7-diaminoheptane, 1,8-diaminooctane, diethylaminoethylamine, ethylenediamine, N,N-bis-(3-aminopropyl)methylamine, isophorondiamine, or N-(3-aminopropyl)-N-dodecylpropane-1,3-diamine.

25. The process according to any one of claims 1 to 23, characterised in that said linear diamine, linear triamine or cyclic diamine compound having at least one primary amine group is 1,3-bis(aminomethyl)cyclohexane, 1,3-bis(aminomethyl)benzene, 1,7-diaminoheptane, 1,8-diaminooctane, diethylaminoethylamine, or ethylenediamine.

26. The process according to any one of claims 1 to 6, characterised in that in the case where said biocide is an aldehyde-containing biocide, said linear diamine, linear triamine or cyclic diamine compound having at least one primary amine group is added in an amount such that the weight ratio biocide : linear diamine, linear triamine or cyclic diamine compound is from 1 : 4 to 1 : 1, or

characterised in that in the case where said biocide is a phenolic biocide, said linear diamine, linear triamine or cyclic diamine compound having at least one primary amine group is added in an amount such that the weight ratio biocide : linear diamine, linear triamine or cyclic diamine compound is from 1 : 4 to 1 : 2.

27. The process according to any one of claims 1 to 26, characterised in that said biocide(s) and said linear diamine, linear triamine or cyclic diamine compound having at least one primary amine group are added separately to the aqueous preparation.

28. The process according to any one of claims 1 to 26, wherein all of said linear diamine, linear triamine or cyclic diamine compound having at least one primary amine group are added before any of said biocide(s).

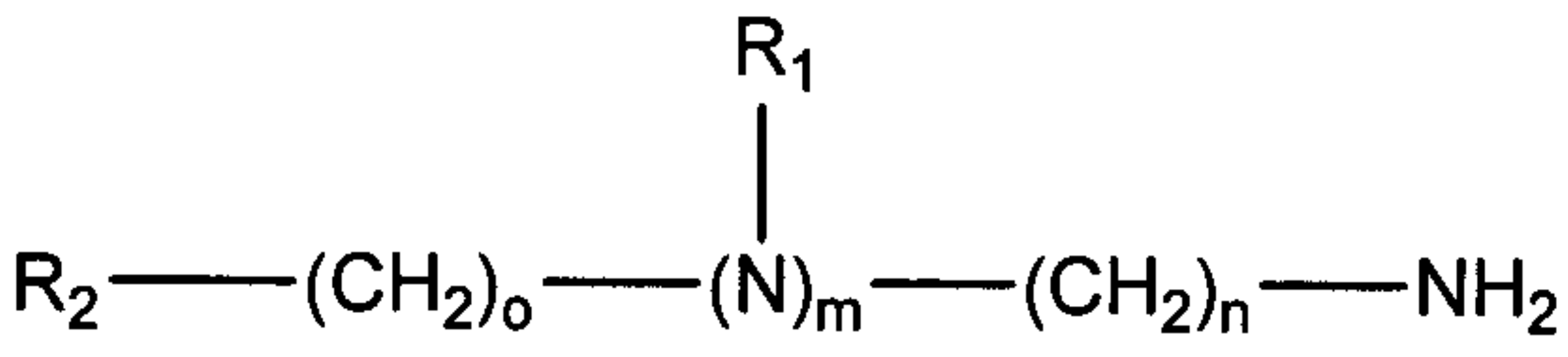
29. The process according to any one of claims 1 to 28, characterised in that prior to addition of any of said linear diamine, linear triamine or cyclic diamine compound having at least one primary amine group or said biocide, said aqueous preparation contains bacteria being *Thermus sp., Propionibacterium sp., Rhodococcus sp., Panninobacter sp., Caulobacter sp., Brevundimonas sp., Asticcacaulis sp., Sphingomonas sp., Rhizobium sp., Ensifer sp., Bradyrhizobium sp., Tepidimonas sp., Tepidicella sp., Aquabacterium sp., Pelomonas sp., Alcaligenis sp., Achromobacter sp., Ralstonia sp., Limnobacter sp., Massilia sp., Hydrogenophaga sp., Acidovorax sp., Curvibacter sp., Delftia sp., Rhodoferax sp., Alishewanella sp., Stenotrophomonas sp., Dokdonella sp., Methylosinus sp., Hyphomicrobium sp., Methylosulfomonas sp., Methylobacteria sp., Pseudomonas sp.* or a mixture thereof.

30. The process according to any one of claims 1 to 29, characterised in that prior to addition of any of said linear diamine, linear triamine or cyclic diamine compound having at least one primary amine group or said biocide, said aqueous preparation contains bacteria being *Pseudomonas putida, Pseudomonas mendocina, Pseudomonas fluorescens, Pseudomonas alcaligenes, Pseudomonas pseudoalcaligenes, Pseudomonas alcaliphila, Pseudomonas entomophila, Pseudomonas syringae, Methylobacterium extorquens, Methylobacterium radiotolerans, Methylobacterium dichloromethanicum, Methylobacterium organophilu, Hyphomicrobium zavarzini* or a mixture thereof.

31. The process according to claim 29 or 30, characterised in that all or part of said bacteria are resistant to, tolerant to and/or degrade said biocides in absence of said linear diamine, linear triamine or cyclic diamine compound(s) having at least one primary amine group.

32. Aqueous preparation obtained by the process as defined in any one of claims 1 to 31.

33. Use of at least one linear diamine, linear triamine or cyclic diamine compound, the linear or cyclic diamine or triamine compound having at least one primary amine group, and where the linear diamine or linear triamine compound has the following formula (I):



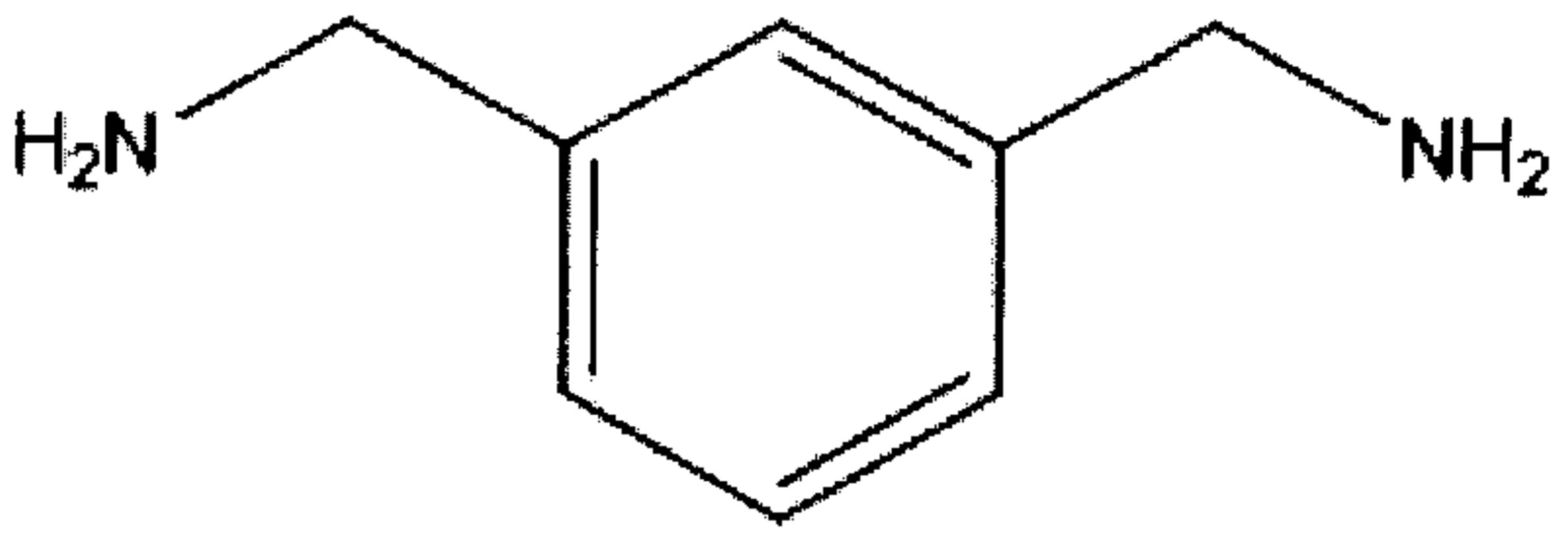
$$R_2-(CH_2)_o-\overset{\overset{R_1}{|}}{(N)_m}-(CH_2)_n-NH_2$$

(I)

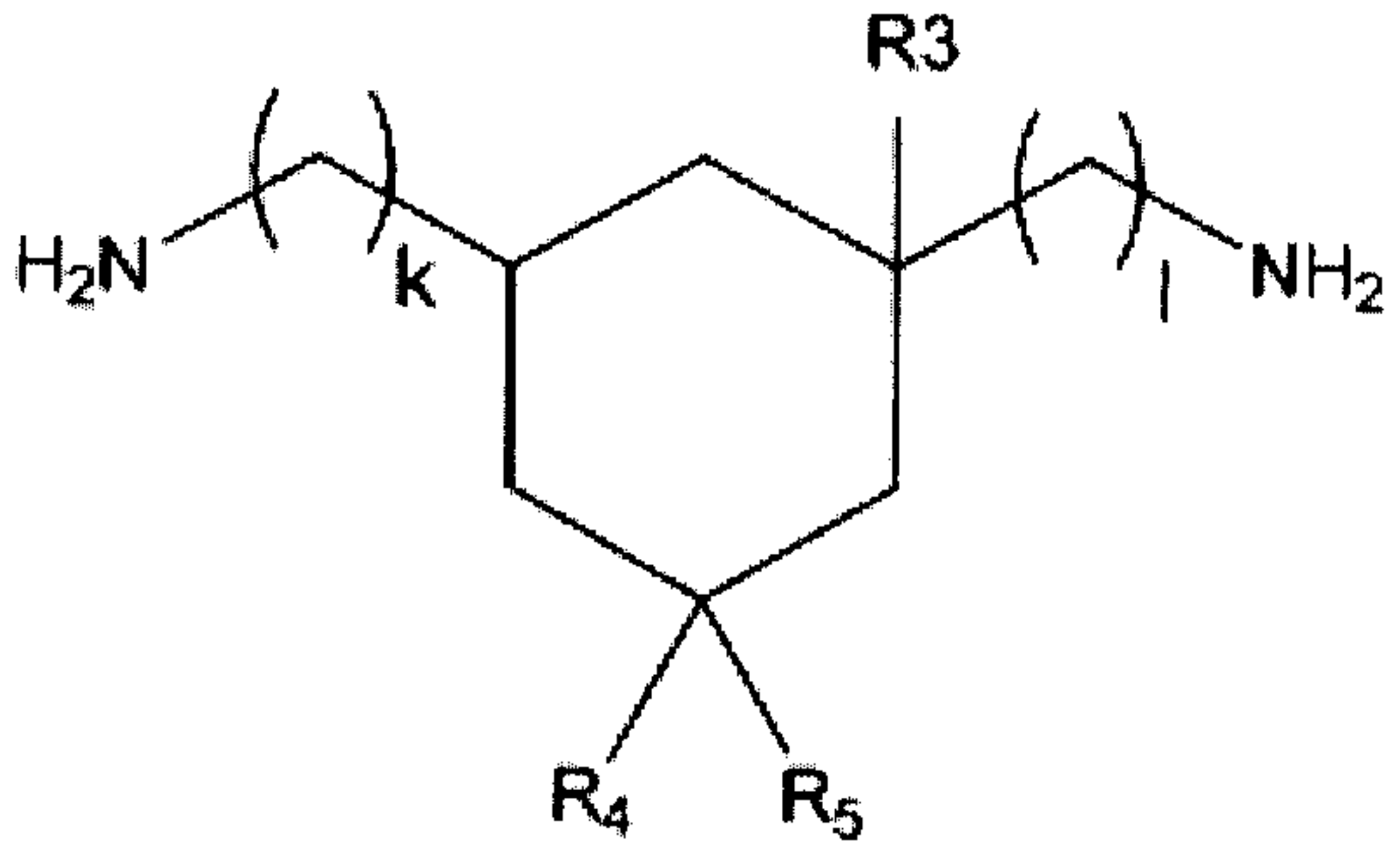
wherein:

m is an integer and is either 0 or 1, n is an integer and is from 2 to 8, o is an integer and is from 0 to 3, R_1 is a C_1 to C_{12} alkyl group, and R_2 is CH_3 or NH_2, and with the proviso that when m = 0, then o = 0 and R_2 is NH_2;

and where the cyclic diamine compound has one of the following formulas (II) and (III):



(II)



(III)

wherein:

k and l are the same or different and are either 0 or 1, R_3 is either H or CH_3, and R_4 and R_5 are the same or different are H or CH_3, as a biocidal activity enhancing compound in an aqueous mineral preparation comprising at least one of aqueous ground natural calcium carbonate, precipitated calcium carbonate, dolomite, surface-reacted calcium carbonate, clay, talc, TiO_2, kaolin, kaolinitic clay, calcined kaolinitic clay, calcium sulfate, quartz, attapulgite, montmorillonite, diatomaceous earth, finely divided silica, aluminium oxide, aluminium hydroxide or silicates, and comprising at least one aldehyde-containing, aldehyde-releasing, phenolic and/or isothiazoline biocide, where the total amount of said biocide(s) in the aqueous preparation is from 90 ppm to 1 350 ppm, calculated relative to the weight of the aqueous phase of said preparation, and the total amount of said linear diamine, linear triamine or cyclic diamine compound(s) in the aqueous preparation is from 600 to 1 200 ppm, calculated relative to the weight of the aqueous phase of said preparation.

34. The use according to claim 33, characterized in that the C_1 to C_{12} alkyl group of R_1 is a linear $C_{12}H_{25}$ alkyl group.

35. The use according to claim 33 or 34, characterized in that the silicate is aluminium silicate, pumice, sepolite or a mixture thereof.

36. The use according to claim 33, characterized in that the aqueous mineral preparation comprises at least one of: a ground natural calcium carbonate, a precipitated calcium carbonate, a dolomite, or a surface-reacted calcium carbonate.

37. The use according to any one of claims 33 to 36, characterized in that the linear diamine, linear triamine or cyclic diamine compound having at least one primary amine group is 1,3-bis(aminomethyl)cyclohexane, 1,3-bis(aminomethyl)benzene, 1,7-diaminoheptane, 1,8-diaminooctane, diethylaminoethylamine, ethylenediamine, N,N-bis-

(3-aminopropyl)methylamine, isophorondiamine, or N-(3-aminopropyl)-N-dodecylpropane-1,3-diamine.

38. The use according to any one of claims 33 to 36, characterized in that the linear diamine, linear triamine or cyclic diamine compound having at least one primary amine group is 1,3-bis(aminomethyl)cyclohexane, 1,3-bis(aminomethyl)benzene, 1,7-diaminoheptane, 1,8-diaminooctane, diethylaminoethylamine, or ethylenediamine.

39. Use of the aqueous preparation as defined in claim 32 in paper making, paints, detergents or cosmetics.