

COMPOSITION FOR FINE BUBBLE PRODUCTION, AND GENERATION APPARATUS

CROSS-REFERENCE TO RELATED APPLICATIONS

5 [0001]

This application claims the benefits of priorities based on Japanese Patent Application Nos. 2017-015846 and 2017-015863, filed on January 31, 2017; the entire contents of which are incorporated herein by reference.

10

BACKGROUND OF THE INVENTION

Field of the Invention

[0002]

15 The present invention relates to an aqueous composition for production of fine bubbles having desired properties, and a fine bubble generation apparatus. More specifically, the present invention relates to an aqueous composition for production of fine bubbles having properties suitable for use in washing, and a fine bubble generation apparatus which does not
20 need any facilities such as a large pump and which is small in size and low in cost. Furthermore, the present invention also relates to a method of washing with fine bubbles produced by use of the aqueous composition and/or the fine bubble generation apparatus.

25

Background Art

[0003]

Rental clothing and linens for use in care homes, hospitals, and the like, and uniforms for use in security
30 companies and the like are demanded to have cleanliness for the reason of sanitary management. Therefore, such clothing, linens and uniforms are frequently laundered, and there are concerns about the influence of cleaning discharge water on the environment. Furthermore, wear of objects to be washed, such
35 as clothing, is also caused by such frequent laundering, and cannot be avoided (Fundamental properties involved in the

washing for the micro/nano-bubble water: Bulletin of the Department of Home Economics, Kyoritsu Women's Junior College).

[0004]

5 While inpatients and elderly people have a bath or a bed-bath in care homes, hospitals, and the like in order to keep cleanliness of the bodies thereof, it is not preferable to apply a load to the skin in many cases. In particular, patients and elderly people with dermatosis are needed to keep cleanliness
10 because dirt on the skin causes symptoms to be worsened, but irritation to the skin must be avoided. Thus, there is a need for a washing method which less apply physical irritation to the skin.

[0005]

15 In recent years, minute bubbles called fine bubbles are utilized in various fields, for example, environmental fields including water clarification, industrial fields including washing and combustion improvement, food fields including sterilization and washing, and daily fields including bathing and health
20 promotion. In addition, washing by means of such fine bubbles is expected as an art which less has an effect on objects to be washed and the environment. For example, JP-A No. 2005-118462 discloses, as a method for washing with fine bubbles, a cleaning apparatus where microbubbles are used in a
25 rinsing step in cleaning. JP-A No. 2007-83142 discloses a washing method by a combination of a washing liquid including a surfactant with microbubbles, and JP-A No. 2016-132712 describes an enhancement in the effect of washing a contact lens with fine bubbles by addition of a disinfectant and a
30 surfactant.

[0006]

 Fine bubbles refer to bubbles having a diameter of 100 μm or less, and in particular, visible cloudy bubbles having a diameter of 1 to 100 μm are referred to as microbubbles and
35 invisible clear and colorless bubbles having a diameter of 1 μm or less are referred to as ultrafine bubbles (HP of The Union of

Fine Bubbles Scientists and Engineers:
<http://www.fb-union.org/index.html>).

[0007]

5 Fine bubbles are very minute and thus have various
 distinctive properties as compared with usual bubbles. In
 particular, fine bubbles have a larger specific surface area at the
 same volume than usual bubbles, and thus are very large in
 physical adsorption force on the action surface at the gas-liquid
 interface. Such an adsorption action of bubbles is important
 10 for all applied fields, and it is thus preferable to impart a small
 bubble diameter whenever possible and a high bubble density
 whenever possible in order to allow bubbles to have a large
 surface area whenever possible at the same volume.

[0008]

15 As a fine bubble generation apparatus currently known,
 for example, JP-A No. 2006-289183 describes a method and an
 apparatus for producing nanobubbles in a liquid, by feeding
 liquid including microbubbles to a storage tank and applying an
 ultrasonic vibration to the liquid to thereby break the
 20 microbubbles in the liquid with pressure. JP-A No.
 2012-250138 describes an apparatus for rapidly shrinking
 microbubbles, by applying a high pressure to microbubbles
 included in a liquid and thus applying physical irritation thereto.

25 Citation List

Patent Literature

[0009]

Patent Literature 1: JP-A No. 2005-118462

Patent Literature 2: JP-A No. 2007-83142

30 Patent Literature 3: JP-A No. 2016-132712

Patent Literature 4: JP-A No. 2006-289183

Patent Literature 5: JP-A No. 2012-250138

Non-Patent Literature

[0010]

35 Non-Patent Literature 1: Fundamental properties involved
 in the washing for the micro/nano-bubble water: Bulletin of the

Department of Home Economics, Kyoritsu Women's Junior
College

Non-Patent Literature 2: HP of The Union of Fine Bubbles
Scientists and Engineers, <http://www.fb-union.org/index.html>

5

SUMMARY

[0011]

However, it cannot be said that such washing is
sufficiently studied, and it cannot also be said with respect to
10 the field where high sanitary conditions are demanded that a
sufficient effect is obtained by washing with only fine bubbles.
For example, the cleaning apparatus described in JP-A No.
2005-118462 performs laundering by a conventional laundry
with a conventional washing liquid including a detergent in a
15 washing step before rinsing. JP-A No. 2007-83142 and JP-A No.
2016-132712 describe use of a surfactant for an enhancement
in wettability to a washing object, and do not propose any
synergetic effect between the type of the surfactant to be
selected and the effect of washing with fine bubbles.

20 [0012]

Thus, all such literature do not sufficiently dissolve any
mechanisms for an enhancement in the effect of washing with
fine bubbles, and cannot also be said to sufficiently dissolve
various conditions for an enhancement in the effect of washing,
25 for example, for an enhancement in the effect of washing due to
a combination of fine bubbles with any additive.

[0013]

As described above, a method for washing with fine
bubbles, which is a washing method less causing the burden of
30 discharge water to the environment and less applying physical
irritation to a washing object, needs an aqueous composition
having a washing ability comparable to or more than that of a
detergent without use of any detergent and the like in
combination.

35 [0014]

Accordingly, the present disclosure provides an aqueous

composition for use in production of fine bubbles having desired properties suitable for washing, and furthermore, an object thereof is to provide a washing method which uses the fine bubbles to thereby less apply a load to not only the environment, but also an object to be washed.

[0015]

Such an apparatus for generation of fine bubbles has the problems of needing a high pressure pump and a large apparatus and thus being increased in installation space and introduction cost. Such an apparatus also has the problem of not sufficiently obtaining generation of fine bubbles because the amount and the pressure of water are restricted in the case of use of a small pump small in footprint and low in cost as in a conventional apparatus.

[0016]

Accordingly, there is a need for a fine bubble generation apparatus small in size and low in cost, which can generate a desired amount of fine bubbles even at a lower pressure of water and in a smaller amount of water than those of a conventional apparatus.

[0017]

The present inventors have made intensive studies in order to solve the above problems, and as a result, have led to completion of an aqueous composition for generation of microbubbles for washing, such microbubbles having a smaller particle size in bubble generation than in use of usual water and then having a larger particle size after being left for a while than in use of usual water. The present inventors also have led to completion of an effective washing method with microbubbles thus obtained.

[0018]

The present inventors further have led to completion of an apparatus small in size and low in cost without use of any large pump, which enables fine bubbles sufficiently small in bubble diameter and high in bubble density to be generated. The present inventors also have led to completion of a method

for producing fine bubbles by use of such an apparatus.

[0019]

Accordingly, the present disclosure provides the following aqueous composition and washing method.

5 (i) An aqueous composition for fine bubble production, the composition including one or more components selected from the group consisting of an alkali metal salt of casein, polyoxyethylene dodecyl ether, soybean lecithin, sodium 1-octanesulfonate, saponin and trimethyl stearyl ammonium
10 chloride, and water.

(ia) In one aspect, the present disclosure provides the use of an aqueous composition comprising:

one or more components selected from the group consisting of an alkali metal salt of casein, polyoxyethylene
15 dodecyl ether, soybean lecithin, sodium 1-octanesulfonate, saponin and trimethyl stearyl ammonium chloride; and water, for the production of fine bubbles in a fine bubble generation apparatus comprising a fine bubble generation mechanism wherein the fine bubble generation mechanism generates a fine
20 bubble-containing fluid from a mixed fluid of a liquid and air;

the fine bubble generation apparatus comprising:

the fine bubble generation mechanism that generates a fine bubble-containing fluid from a mixed fluid of a liquid and air;

25 a gas-liquid inflow pipe that allows for introduction of the mixed fluid;

a cylindrical gas-liquid mixed phase generation mechanism where the gas-liquid inflow pipe is provided at the center of a cylinder;

30 an eddy-current generation mechanism which is provided so as to divide the interior of the gas-liquid mixed phase generation mechanism into two sections, which comprises an upper surface having 2 to 4 holes and a lower surface having 2 to 4 holes disposed with being shifted from the holes of the
35 upper surface, and in which the holes of the upper surface and

the holes of the lower surface are pierced so as to correspond to each other; and

a discharge pipe provided on a side surface of the gas-liquid mixed phase generation mechanism,

5 wherein said fine bubble generation mechanism comprises a wall that partitions the mixed fluid to be introduced and the fine bubble-containing fluid to be discharged,

the wall has a cone shape opened at a bottom,

10 a through-hole for introduction of the mixed fluid into the interior of the wall is formed on at least a part of a side surface of a shape partitioned by the wall, and

the mixed fluid is introduced through the through-hole into the interior of the wall and discharged as the fine bubble-containing fluid from the opening,

15 the bubble generation mechanism is provided on an end of the gas-liquid inflow pipe, through which the mixed fluid is discharged, and

the gas-liquid inflow pipe is centrally pierced from an upper surface of the cylinder, and an end thereof, through which the mixed fluid is discharged, is placed with a gap from a bottom section of the main body of the cylinder, and

the fine bubbles have a diameter of 100 μm or less.

(ii) The aqueous composition for fine bubble production according to (i), wherein the alkali metal salt of casein is casein sodium.

(iii) A washing method including

(1) a step of generating fine bubbles by use of the aqueous composition for fine bubble production according to (i) or (ii),

30 (2) a step of allowing fine bubbles generated in step (1) to penetrate into fouling of a washing object,

(3) a step of allowing fine bubbles penetrating into the fouling in step (2) to be aggregated, and

(4) a step of allowing fine bubbles aggregated in step (3) to ascend, thereby peeling the fouling from the washing object.

(iiia) In another aspect, the present disclosure provides a

washing method comprising:

- (1) a step of generating fine bubbles by use of a fine bubble generation apparatus as defined herein and an aqueous composition for fine bubble production as defined herein;
- 5 (2) a step of allowing fine bubbles generated in step (1) to penetrate into fouling of a washing object;
- (3) a step of allowing fine bubbles penetrating into the fouling in step (2) to be aggregated; and
- (4) a step of allowing fine bubbles aggregated in step (3)
- 10 to ascend, thereby peeling the fouling from the washing object, wherein the fine bubbles have a diameter of 100 μm or less.

[0020]

The present disclosure also provides the following fine bubble generation apparatus and production method.

- 15 (iv) A fine bubble generation apparatus including a fine bubble generation mechanism that generates a fine bubble-containing fluid from a mixed fluid of a liquid and air, wherein

20 the fine bubble generation mechanism includes a wall that partitions the mixed fluid to be introduced and a fine bubble-containing fluid to be discharged,

 the wall has a shape opened at a bottom section and selected from the group consisting of a cone, a frustum and a column,

25

a through-hole for introduction of the mixed fluid into the interior of the wall is formed on at least a part of a side surface of a shape partitioned by the wall, and

the mixed fluid is introduced through the through-hole
5 into the interior of the wall and discharged as a fine bubble-containing fluid from the opening.

(v) The fine bubble generation apparatus according to (iv), further including

a gas-liquid inflow pipe that allows for introduction of the
10 mixed fluid,

a cylindrical gas-liquid mixed phase generation mechanism where the gas-liquid inflow pipe is provided at the center of a cylinder,

an eddy-current generation mechanism which is provided
15 so as to divide the interior of the gas-liquid mixed phase generation mechanism into two sections, which includes an upper surface having 2 to 4 holes and a lower surface having 2 to 4 holes disposed with being shifted from the holes on the upper surface, and in which the holes on the upper surface and
20 the holes on the lower surface are pierced so as to correspond to each other, and

a discharge pipe provided on a side surface of the gas-liquid mixed phase generation mechanism, wherein

the bubble generation mechanism is provided on an end
25 of the gas-liquid inflow pipe, through which the mixed fluid is discharged, and

the gas-liquid inflow pipe is centrally pierced from an upper surface of the cylinder, and an end thereof, through which the mixed fluid is discharged, is placed with a gap from a
30 bottom section of the main body of the cylinder.

(vi) The fine bubble generation apparatus according to (iv), further including

a gas-liquid inflow pipe that allows for introduction of the mixed fluid,

a large-size-bubble removal mechanism that separates
35 bubbles having a particle size of 1 mm or more,

a first partition section having 2 to 8 communication holes provided between the large-size-bubble removal mechanism and a middle tank section adjacent thereto,

5 a middle tank section to which the mixed fluid flows from the large-size-bubble removal mechanism via the communication holes,

a cylindrical skirt section provided in the middle tank section with a lower section being opened,

10 a cylindrical eddy-current generation mechanism which is provided in the skirt section with an upper section being opened and which generates an eddy-current by an inner spiral structure,

15 a bubble shredding mechanism that shreds bubbles, disposed in a lower tank section adjacent to the middle tank section, and

a discharge pipe provided on a side surface of the lower tank section, wherein

the bubble generation mechanism is provided downstream of the eddy-current generation mechanism.

20 (vii) A fine bubble generation method, wherein the aqueous composition for fine bubble production according to (i) or (ii) is used for the fine bubble generation apparatus according to any one of (iv) to (vi).

[0021]

25 Fine bubbles produced by use of the aqueous composition according to the present disclosure can be used for washing, thereby not only suppressing a load on the ambient environment and relieving physical irritation to clothing and the human skin as washing objects, but also realizing desired
30 cleanliness depending on such washing objects.

[0022]

The fine bubble generation apparatus according to the present disclosure can generate fine bubbles having a desired particle size and concentration by use of the bubble generation
35 mechanism provided by the present inventors, even at a relatively low pressure and in a small amount of water as

compared with a conventional apparatus, and therefore a fine bubble generation apparatus small in size and low in cost can be provided.

[0023]

5 The present inventors have also found that fine bubbles can be further efficiently generated by combining the bubble generation mechanism provided by the present inventors with an eddy-current generation mechanism and a large-size-bubble separation mechanism.

10

BRIEF DESCRIPTION OF THE DRAWINGS

[0024]

15 FIG. 1 includes photographs for comparison before and after a washing test with fine bubbles in addition of casein sodium (0.01% by mass, 0.005% by mass, 0.002% by mass) and in no addition of any composition, and before and after a washing test with no fine bubbles in no addition of the composition according to the present invention.

20 FIG. 2 includes a photograph of fine bubbles penetrating into greasy dirt.

 FIG. 3 includes schematic views of peeling of fouling with fine bubbles generated according to the present invention.

25 FIG. 4 includes respective schematic views of a fine bubble generation apparatus according to one aspect of the present invention and an eddy-current generation mechanism of the apparatus.

 FIG. 5 includes a schematic view of a fine bubble generation apparatus according to another aspect of the present invention.

30 FIG. 6 includes examples of preferable modes of a bubble generation mechanism of the fine bubble generation apparatus of the present invention.

 FIG. 7 includes a schematic view of the bubble generation mechanism in the present invention.

35

DETAILED DESCRIPTION OF THE INVENTION

[0025]

Fine bubbles

Fine bubbles refer to bubbles having a diameter of 100 μm or less, and in particular, visible cloudy bubbles having a diameter of 1 to 100 μm are referred to as microbubbles and invisible clear and colorless bubbles having a diameter of 1 μm or less are referred to as ultrafine bubbles. A distinct difference between microbubbles and ultrafine bubbles is in that ultrafine bubbles cannot be directly observed with the naked eye because of no scattering of visible light and microbubbles can be confirmed in terms of the presence thereof because of clouding. In the present invention, confirmation of generation of fine bubbles including microbubbles is performed by visually confirming such clouding. The presence of ultrafine bubbles is confirmed by measuring the particle size distribution by number distribution with laser diffraction described below in detail.

[0026]

Method for measuring particle size distribution of ultrafine bubbles

The particle size distribution by number distribution of ultrafine bubbles is measured in the following conditions.

Analysis apparatus: measurement instrument Microtrack Series (microtrac version 10.5.3-22tR) (MicrotracBEL Corp.)

Bubble generation apparatus: apparatus illustrated in FIG.

25 4

Bubble generation solvent: tap water (room temperature)

[0027]

Millibubbles/sub-millibubbles

In the present invention, millibubbles refer to bubbles of 1 to 100 μm , and sub-millibubbles refer to bubbles of 100 μm to 1 mm. In the present invention, confirmation of generation of such bubbles is performed by visual confirmation.

[0028]

Thus, minute fine bubbles have various distinctive properties as compared with usual bubbles, in particular, fine bubbles have a large specific surface area at the same volume

as compared with usual bubbles, and thus a physical adsorption force on the action surface at the gas-liquid interface is very large.

[0029]

5 One feature of fine bubbles is a self-pressurizing effect. That is, fine bubbles are bubbles having a substantially spherical shape in a liquid, and surface tension acts on the gas-liquid interface. Thus, it is known that a smaller bubble diameter leads to a higher inner pressure of each bubble to allow bubbles
10 to disappear in a liquid with time. It has been found in the present invention that, when fine bubbles are generated in an aqueous composition including any additive as described below, bubbles have a small particle size immediately after generation and then aggregate and have a larger particle size. It has been
15 surprisingly found that the aqueous composition is brought into contact with a washing object in the state where such fine bubbles are present in the aqueous composition for a long time, thereby allowing a washing effect to be exerted at the same level or more than that in use of a detergent, without use of any
20 detergent and the like. Hereinafter, the additive to be added to the aqueous composition will be described.

[0030]

Additive

25 An additive refers to any agent which is to be added as a component in a predetermined amount to a certain material to thereby serve to improve stability, physical properties, and the like of the material. The additive in the present invention is not limited to such an additive, and may include one or more selected from the group consisting of a surfactant, an emulsifier,
30 a thickener and a stabilizer. The additive may include, if desired, in addition to one or more of such additives, but not limited to the following, a PH adjuster, a moisturizer, and the like.

[0031]

35 The additive for use in the present invention can be one or more selected from the group consisting of an alkali metal

salt of casein, serving as a thickener, polyoxyethylene dodecyl ether, sodium 1-octanesulfonate, saponin and trimethyl stearyl ammonium chloride serving as surfactants, and soybean lecithin serving as an emulsifier. The additive in the present invention is preferably casein sodium, polyoxyethylene dodecyl ether, trimethyl stearyl ammonium chloride, or sodium 1-octanesulfonate, most preferably casein sodium. Fine bubbles can be generated in an aqueous composition where such an additive is added to water, thereby resulting in a dramatic enhancement in the washing effect of the aqueous composition.

[0032]

Aqueous composition

An aqueous composition refers to an aqueous solution composition which is a composition having an aqueous phase being a continuous phase and including a water-soluble component. The aqueous phase in the present invention is a phase containing water.

[0033]

Method for producing fine bubbles

The additive for fine bubbles in the present invention can be used in any fine bubble production method known in the art, and enables fine bubbles having desired properties suitable for a washing application to be produced even in the case of use of any fine bubble production method. Methods for generating fine bubbles, known in the art, are mainly an ejector method, a cavitation method, a gas-liquid shear (swirling flow) method, a pressurized dissolution method, and the like.

[0034]

An ejector method is a method involving feeding a liquid pressurized by an ejector and atomizing a gas self-absorbed by countless "separated flows" generated in the ejector to thereby produce bubbles. In the method, air self-absorbed is formed into bubbles by allowing water to flow from a broad passage to a narrow passage and thereafter again allowing the water to flow to the broad passage, thereby rapidly releasing the

pressure and thus crushing air self-absorbed, and rapidly increasing the flow rate in the narrow passage and thus crushing air self-absorbed, due to the flow rate increased.

[0035]

5 A cavitation method is a method involving feeding a pressurized liquid to a generator having a cavitation structure and precipitating a dissolved gas contained in the liquid by means of a cavitation phenomenon (cavitation) occurring in a structure section, thereby producing bubbles.

10 [0036]

 A gas-liquid shear (swirling flow) method is a method involving feeding a pressurized liquid to a generator having a cylindrical structure, in an eccentric direction, to induce swirling in the cylinder and thus cut air by the shear stress, thereby
15 producing bubbles.

[0037]

 A pressurized dissolution method is a method involving forcibly dissolving gas under pressure and performing pressure reduction (atmospheric relief), thereby precipitating bubbles.
20 That is, the method is a method involving applying pressure to thereby excessively dissolve gas in an amount more than a saturation value, in a liquid, according to the Henry's law and then relieve the pressure, thereby again forming the gas dissolved in an amount more than a saturation value, into
25 bubbles.

[0038]

 In the present invention, any of the methods enables fine bubbles having desired properties to be produced by use of the aqueous composition according to the present invention, and
30 also enables a high washing force to be exhibited by use of the fine bubbles thus produced, without application of any physical irritation to an object to be washed.

[0039]

Embodiments

35 The fine bubble generation apparatus according to the present invention is described with reference to the drawings.

[0040]

One embodiment of the fine bubble generation apparatus for use in the present invention is described with reference to FIG. 4(a). A fine bubble generation apparatus 20 includes a gas-liquid inflow pipe 21 that allows a mixed fluid of an aqueous composition and air to be introduced, a bubble generation mechanism 22 provided on an end of the gas-liquid inflow pipe 21, through which the mixed fluid is discharged, a cylindrical gas-liquid mixed phase generation mechanism 25 disposed so that the gas-liquid inflow pipe 21 is located at the center of a cylinder, and a discharge pipe 26 provided on the side surface of the gas-liquid mixed phase generation mechanism 25, through which an aqueous composition including fine bubbles is discharged. The gas-liquid mixed phase generation mechanism 25 has a cylindrical shape, in which the gas-liquid inflow pipe 21 is pierced from the upper surface of the main body of the cylinder to the center of the cylinder and an end of the gas-liquid inflow pipe 21, through which the mixed fluid is discharged, is disposed with a gap from the bottom section of the main body of the cylinder. The interior of the main body of the cylinder is divided by an eddy-current generation mechanism 24 into two sections of a lower tank section 23a closer to the bottom section of the main body of the cylinder and an upper tank section 23b closer to the upper section of the main body of the cylinder. The eddy-current generation mechanism 24 includes an upper surface 27a having 2 to 4 holes and a lower surface 27b having 2 to 4 holes disposed with being shifted from the holes on the upper surface 27a, and the holes on the upper surface 27a and the holes on the lower surface 27b are pierced so as to correspond to each other. That is, each through-hole 28 is disposed on the cross section of the eddy-current generation mechanism 24 with being inclined at a certain angle relative to the upper surface 27a or the lower surface 27b, as illustrated in FIG. 4(b).

[0041]

First, a mixed fluid of an aqueous composition and air,

introduced into the gas-liquid inflow pipe 21, is introduced into the bubble generation mechanism 22, and is formed into a mixed fluid including bubbles. The bubble generation mechanism 22 includes a hollow member having a conical shape, and has a structure where one or more through-holes 29 are provided on a part of the conical face. The mixed fluid introduced into the gas-liquid inflow pipe 21 passes through the through-hole(s) 29 from the outside of the bubble generation mechanism 22 and is introduced into the bubble generation mechanism 22, and bubbles are here generated. The bubble generation mechanism 22 is provided, thereby enabling fine bubbles to be sufficiently produced even at a relatively low pressure of water and in a small amount of water.

[0042]

An aqueous composition formed as a mixed fluid including bubbles, by the bubble generation mechanism 22, is discharged through an end of the gas-liquid inflow pipe 21, introduced into the lower tank section 23a of the gas-liquid mixed phase generation mechanism 25, subsequently passes through the through-hole 28 of the eddy-current generation mechanism 24 and is introduced into the upper tank section 23b of the gas-liquid mixed phase generation mechanism 25. The through-hole 28 is provided with being inclined in the cross-sectional direction as described above, and thus an aqueous composition including bubbles passes through the through-hole 28 to thereby allow the aqueous composition including bubbles to be in the form of an eddy-current in the upper tank section 23b. Such eddy-current is made around the pipe of the gas-liquid inflow pipe 21 in the upper tank section 23b, and here, whereas an aqueous composition including large-size-bubbles light in specific gravity is collected in the inside of the upper tank section 23b (the center of the cylinder shape) and separated toward the upper section of the upper tank section 23b, an aqueous composition including small-size bubbles is pushed to the outside of the upper tank section 23b (the periphery of the cylinder shape) by a centrifugal force.

Thus, an aqueous composition including many small-size bubbles is produced and discharged through the discharge pipe 26 provided on the side surface of the gas-liquid mixed phase generation mechanism 25.

5 [0043]

The discharge pipe 26 can be, if desired, provided with the bubble generation mechanism 22 in the pipe thereof, as in the gas-liquid inflow pipe 21, and the mechanism can allow an aqueous composition having small-size bubbles to pass through
10 to thereby provide an aqueous composition having much smaller-size bubbles. If desired, two or more of the bubble generation mechanisms 22 may be disposed in parallel in the discharge pipe 26, and three or more of the bubble generation mechanisms can be provided in the entire apparatus 20 to
15 thereby result in an enhancement in generation efficiency of fine bubbles. It is preferable to provide, if desired, one of the bubble generation mechanism 22 in the gas-liquid inflow pipe 21 and one to four of the bubble generation mechanisms 22 in the discharge pipe 26.

20 [0044]

A fine bubble generation apparatus 30 according to another aspect is described with reference to FIG. 5. The fine bubble generation apparatus 30 includes a gas-liquid inflow pipe 37 that allows a mixed fluid of an aqueous composition and air
25 to be introduced, a large-size-bubble removal mechanism 31 that separates relatively large-size bubbles, a first partition section 32 provided with a through-hole 32a, which partitions the large-size-bubble removal mechanism 31 and a middle tank section 33 located thereunder, the middle tank section 33 into
30 which a gas-liquid mixed phase from the large-size-bubble removal mechanism 31 flows, a skirt section 34 disposed in the middle tank section 33 with a lower section being opened, an eddy-current generation section 35 that generates an eddy-current by a spiral structure, a bubble generation
35 mechanism 36 disposed in the eddy-current generation section and provided with a through-hole 36a, a bubble shredding

mechanism 38 disposed in a lower tank section 40, a through-hole 38a provided on the bubble shredding mechanism 38, and a discharge pipe 39 provided on the side surface of the lower tank section 40, through which an aqueous composition including fine bubbles is discharged. All the large-size-bubble removal mechanism 31, the middle tank section 33, the lower tank section 40, the skirt section 34, the eddy-current generation section 35 and the bubble shredding mechanism 38 have a cylinder shape. In another embodiment, these may have a tubular shape whose cross section has a polygonal shape, other than a circular shape.

[0045]

First, air and an aqueous composition are sent using a pump from the gas-liquid inflow pipe 37 to the fine bubble generation apparatus 30, thereby allowing a mixed fluid of the air and the aqueous composition to remain in a small-diameter cylinder mechanism 31a disposed on the center section of the large-size-bubble removal mechanism 31, with bubbles being generated in corrosion to the bottom surface of the large-size-bubble removal mechanism 31. Thereafter, when a mixed fluid including bubbles overflows from the cylinder mechanism 31a, relatively large-size bubbles are separated toward the upper section of the large-size-bubble removal mechanism 31. The mixed fluid overflowing from the cylinder mechanism 31a enters the middle tank section 33 through the through-hole 32a provided on the first partition section 32, and then travels between the skirt section 34 and an eddy-current generation mechanism 35 having a spiral structure therein. A gas-liquid mixed fluid reaches an upper end of the eddy-current generation mechanism 35, and then relatively large-size bubbles are trapped in a void in the upper section of the eddy-current generation mechanism 35. The bubbles trapped are cut by and taken in a gas-liquid mixed phase flowing in the eddy-current generation mechanism 35, and a mixed phase flow is induced by the spiral structure formed in the eddy-current generation mechanism 35, resulting in generation of an

eddy-current. The eddy-current passes through the through-hole 36a from the outside of the bubble generation mechanism 36 having a conical shape and is introduced into the bubble generation mechanism 36, and here bubbles are generated. Such a bubble generation mechanism 36 can be provided to thereby sufficiently produce fine bubbles even at a relatively low pressure of water and in a small amount of water. Thereafter, fine bubbles are further minutely shredded in a cylindrical bubble shredding mechanism 38 disposed perpendicularly to the traveling direction of a water flow. An aqueous composition including many fine bubbles thus generated is discharged from the cylindrical bubble shredding mechanism 38 through the through-hole 38a to the lower tank section 40, and thereafter discharged through a discharge water pipe 39 disposed on the side surface of the lower tank section 40. In another embodiment according to the present invention, a plurality of the bubble generation mechanisms 36 each having a conical shape can be, if desired, disposed.

[0046]

As illustrated in FIG. 6, the bubble generation mechanism according to the present invention includes a wall that partitions a mixed fluid of a liquid and air to be introduced and a bubble-containing fluid to be discharged, in which the wall has a shape opened at the bottom section and selected from the group consisting of a cone, a frustum and a column, and a through-hole for introduction of the mixed fluid into the interior of the wall is formed on at least a part of a side surface of a shape partitioned by the wall. The mixed fluid is introduced through the through-hole into the interior of the wall and discharged as a bubble-containing fluid from the opening of the bottom section.

[0047]

The number of such through-holes provided in the wall of the bubble generation mechanism according to the present invention is preferably 3 to 6, and such through-holes are preferably provided at an equal interval around the wall section.

The shape of each of the holes can be any shape, is not limited, and is preferably a circle. In the case where such each through-hole has a circular shape, the inner diameter thereof is 2 mm to 10 mm, preferably 2 mm to 6 mm.

5 [0048]

In the case where the bubble generation mechanism has a conical shape, the height thereof can be 8 mm to 50 mm, preferably 10 mm to 30 mm, most preferably 12 mm to 25 mm, and the inner diameter of the bottom section can be 6 mm to 20
10 mm, preferably 8 mm to 18 mm, most preferably 10 mm to 16 mm.

[0049]

In the case where the bubble generation mechanism has a truncated cone shape, the height of the truncated cone
15 section can be 8 mm to 50 mm, preferably 10 mm to 30 mm, most preferably 12 mm to 25 mm, the inner diameter of the upper bottom section can be 5 mm to 10 mm, preferably 6 mm to 9 mm, most preferably 7 mm to 8 mm, and the inner diameter of the lower bottom section can be 6 mm to 20 mm,
20 preferably 8 mm to 18 mm, most preferably 10 mm to 16 mm.

[0050]

In the case where the bubble generation mechanism has a columnar shape, the height can be 8 mm to 50 mm, preferably 10 mm to 30 mm, most preferably 12 mm to 25 mm,
25 and the inner diameter of the bottom section can be 6 mm to 20 mm, preferably 8 mm to 18 mm, most preferably 10 mm to 16 mm.

[0051]

The thickness of the wall forming the bubble generation
30 mechanism is 0.5 mm to 8 mm, preferably 1 mm to 5 mm, most preferably 2 mm to 3 mm, and the wall is preferably made by a metal such as an aluminum alloy, stainless steel or brass, a resin, or the like.

[0052]

35 The number of such through-holes can be 2 to 8, preferably 2 to 6, most preferably 2 to 4, and in the case where

a plurality of such through-holes is disposed, the through-holes are preferably disposed at an interval of a uniform angle. For example, in the case where the number of such through-holes is 2, the through-holes are disposed at an angle of 180°. In the case where the bubble generation mechanism has a conical shape, such each hole can be disposed at a position of 2 mm to 18 mm, preferably 3 mm to 15 mm, most preferably 5 mm to 10 mm from the conical top downward in the axial direction. In the case where the bubble generation mechanism has any of a frustum and a column, such each hole can be disposed at a position of 1 mm to 18 mm, preferably 2 mm to 15 mm, most preferably 2 mm to 10 mm from the upper bottom section downward in the axial direction.

[0053]

The hole diameter is 1 mm to 4 mm, preferably 1 mm to 3 mm, most preferably 2 mm to 3 mm in the case of use of a pump having an output of 8.9 L/min. The hole diameter is preferably appropriately changed depending on the performance and the like of a pump to be used.

[0054]

In the case where the skirt section and the spiral structure are used in the eddy-current generation mechanism, the inner diameter of the outer pipe of two pipes in the eddy-current generation mechanism can be 10 mm to 30 mm, preferably 15 mm to 25 mm, most preferably 17 mm to 20 mm, and the inner diameter of the inner pipe thereof can be 6 mm to 24 mm, preferably 11 mm to 21 mm, most preferably 13 mm to 16 mm.

[0055]

The length of the outer pipe in the eddy-current generation mechanism can be 25 mm to 95 mm, preferably 30 mm to 85 mm, most preferably 35 mm to 75 mm, and the length of the inner pipe therein can be 35 mm to 95 mm, preferably 45 mm to 85 mm, most preferably 55 mm to 75 mm.

[0056]

The spiral pitch of a spiral member formed in the interior

of the inner pipe can be 1 mm to 30 mm, preferably 5 mm to 20 mm, most preferably 10 mm to 15 mm. The groove width of the spiral member can be 2 mm to 20 mm, preferably 3 mm to 15 mm, most preferably 5 mm to 10 mm. The length of a
5 section with a groove provided therein can be 10 mm to 85 mm, preferably 20 mm to 75 mm, most preferably 30 mm to 60 mm.
[0057]

According to another embodiment of the present invention, a plurality of the bubble generation mechanisms 36
10 may be disposed in parallel in the middle tank section 33 of the fine bubble generation apparatus 30 illustrated in FIG. 5. For example, two of the bubble generation mechanisms 36 can be disposed in parallel. The influence by the output performance of a pump is hardly exhibited in the case of disposing in parallel
15 as compared with the case of disposing in series.
[0058]

According to still another embodiment of the present invention, the bubble generation mechanism can be used in combination with other bubble generation mechanism in the
20 middle tank section 33 of the fine bubble generation apparatus 30 illustrated in FIG. 5. Such a mechanism which can be used is, for example, a pressurized dissolution mechanism (not illustrated). Such a pressurized dissolution mechanism can be provided upstream of the bubble generation mechanism
25 according to the present invention to thereby further enhance the concentration of bubbles to be generated. The pressurized dissolution mechanism is here provided to thereby increase the pressure (required pressure of a pump) of the entire apparatus, and thus the pressure of the pressurized dissolution mechanism
30 is preferably low for a reduction in size, and is preferably, for example, 0.2 MPa to 0.15 MPa.
[0059]

According to still another embodiment of the present invention, a plurality of the eddy-current generation
35 mechanisms 35 and a plurality of the bubble generation mechanisms 36 may be disposed, respectively (not illustrated),

in series in the middle tank section 33 of the fine bubble generation apparatus 30 illustrated in FIG. 5. For example, these can be alternately disposed in the order of a first eddy-current generation mechanism, a first bubble generation
5 mechanism, a second eddy-current generation mechanism, and a second bubble generation mechanism. In the case where a plurality of the bubble generation mechanisms 36 is provided, the number thereof can be two or more depending on the desired conditions, and is preferably 2 to 4.

10 [0060]

According to still another embodiment of the present invention, a mechanism that roughly pulverizes bubbles may also be further provided upstream of the eddy-current generation mechanism 35 and the bubble generation mechanism
15 36 in the middle tank section 33 of the fine bubble generation apparatus 30 illustrated in FIG. 5. Such a mechanism can be, for example, but not limited to, a venture tube, or a lateral cylinder disposed in a direction perpendicular to the axial direction, in communication with mechanisms located before
20 and after such a mechanism. Such a mechanism can be further disposed to thereby efficiently more finely generate bubbles.

[0061]

As illustrated in FIG. 5, the lower tank section 40 includes a bubble-pulverizing section 38 that further pulverizes
25 and grows fine bubbles generated in the middle tank section 33, and a discharge pipe 39 that discharges fine bubbles generated. The bubbles generated in the middle tank section 33 are supplied through the opening of the lower section of the bubble generation mechanism 36 to the bubble-pulverizing section 38,
30 and further finely pulverized in the pulverizing section 38.

[0062]

The bubble-pulverizing section 38 has a hollow cylinder shape disposed perpendicularly to the axial direction, in the fine bubble generation apparatus 30 illustrated in FIG. 5. The
35 cylinder is closed on the upper base and the lower base thereof, and is provided with a plurality of holes 38a on the

circumference of each of both ends thereof. Swirling flow including bubbles, flowing in the axial direction of the middle tank section toward the pulverizing section 38, can be changed in the direction to a direction perpendicular to the axial direction, thereby further finely pulverizing bubbles. Bubbles finely pulverized are discharged through a plurality of holes 38a on the cylinder, grown in the lower tank section 40 including the cylinder, and thereafter discharged from the fine bubble generation apparatus 30 via the discharge pipe 39.

10 [0063]

The cylinder has a length of 20 mm to 50 mm, preferably 25 mm to 45 mm, most preferably 30 mm to 40 mm, and has an inner diameter of 5 mm to 30 mm, preferably 10 mm to 25 mm, most preferably 15 mm to 20 mm.

15 [0064]

The number of holes on the cylinder can be 2 to 10, preferably 2 to 8, most preferably 4 to 8. The size of each of the holes is 1 mm to 6 mm, preferably 2 mm to 5 mm, most preferably 3 mm to 4 mm. The holes are preferably disposed on the circumference at an equal interval. The shape of each of the holes can be any shape, is not limited, and is preferably a circle.

20 [0065]

The thickness of the wall of the cylinder can be 1 mm to 5 mm, preferably 1 mm to 4 mm, most preferably 2 mm to 3 mm, and the wall is preferably made by a metal such as an aluminum alloy, stainless steel or brass, a resin, or the like.

[0066]

According to another embodiment of the present invention, a mechanism (not illustrated) that adjusts the particle size of bubbles may be further provided downstream of the bubble generation mechanism in the fine bubble generation apparatus 30 illustrated in FIG. 5. Such a mechanism can be, for example, but not limited to, a venture tube or an ultrasonic pulverizer. More specifically, for example, water flowing from the bubble generation mechanism can be ejected opposite to

30
35

the discharge port 39, and changed in direction in the lower tank section 40, thereby pulverizing a large mass of bubbles, or further pulverizing it by corrosion to a wall section. Such a mechanism can be disposed to thereby further pulverize fine
5 bubbles generated in the previous step.

[0067]

According to still another embodiment of the present invention, a bubble generation mechanism can be further disposed in the discharge pipe 39 of the lower tank section 40 in
10 the fine bubble generation apparatus 30 illustrated in FIG. 5. Such a bubble generation mechanism preferably has the same structure as that disposed in the middle tank section 33. Preferably, the number of such bubble generation mechanism(s) to be disposed in the discharge pipe 39 is 1 to 4.

15 [0068]

The upper tank section 31, the middle tank section 33 and the lower tank section 40 can be connected in any form in the fine bubble generation apparatus 30 illustrated in FIG. 5 in all the above embodiments as long as these sections are
20 disposed in the listed order. For example, only the upper tank section 31 can be independently disposed, and the middle tank section 33 and the lower tank section 40 can be disposed vertically in a continuous manner. Alternatively, for example, the middle tank section 33 can be disposed beneath the upper
25 tank section 31 and the lower tank section 40 can be disposed beneath the middle tank section 33, in line vertically in a continuous manner.

[0069]

The fine bubble generation apparatus according to the
30 present invention is not limited to these combinations, and can be disposed by any combination so that the effects of the present invention can be exerted, depending on the desired size of the apparatus, and the concentration and the amount of bubbles generated.

35 [0070]

Method for measuring particle size of fine bubbles

The particle size of fine bubbles is measured in the following conditions.

Apparatus: measurement instrument Microtrack Series (microtrac version 10.5.3-225R) (MicrotracBEL Corp.)

5 Optical bench: MT3000II

A measurement method using the present measurement instrument can measure a particle size of sub-micrometers or less, and there is no influence of the environmental factor of a sample on the measurement value.

10 [0071]

The 50% cumulative particle size, the average particle size and the mode particle size are used as indexes of the particle size in the present invention. The definitions of such particle sizes are described below.

15 50% cumulative particle size

The 50% cumulative particle size means a particle size (μm) where, when a cumulative curve is determined under the assumption that the entire volume of an aggregation of fine bubble particles is 100%, the cumulative curve reaches 50%.

20 The relevant index is commonly used as one parameter for evaluation of the particle size distribution as a cumulative median point (Median diameter).

Average particle size

25 The average particle size means an average size determined from a theoretical number distribution determined from calculation. In this case, all particles are assumed to be spherical.

Mode particle size

30 The mode particle size refers to a particle size at the highest frequency of presence in an aggregation of fine bubble particles.

[0072]

Washing method

35 The washing method with fine bubbles produced by the aqueous composition according to the present invention involves washing by allowing fine bubbles produced by use of the

additive in the present invention to act on a surface of a washing object, the surface being a treatment surface to be washed. Specifically, a washing object is washed by immersing the washing object in water including fine bubbles produced by use of the aqueous composition according to the present invention, for a predetermined time, without application of any physical irritations such as friction.

[0073]

Fine bubbles produced by any known method may be used in the present invention, and are preferably fine bubbles produced by the apparatus 20 illustrated in FIG. 4.

[0074]

The fine bubbles produced by use of the aqueous composition according to the present invention have a small particle size immediately after generation and thereafter have a larger particle size due to aggregation, as compared with bubbles produced in water including no additive.

[0075]

In the case where the washing object is a part of a human body or an animal body, casein sodium less irritating the body, among the above additives, is preferably used. Any water such as tap water, well water, or hot spring water can be used for such washing.

[0076]

25 Method for evaluating washing effect

The washing effect of each sample is evaluated based on a washing effect value. The washing effect value is calculated by quantifying the degree of dirt, based on the image data of the sample (gray scale).

30 [0077]

Object to be washed

The object to be washed (washing object) with fine bubbles generated according to the present invention is not particularly limited as long as it may be wetted by water, and examples thereof can include an article to which dirt such as skin oil is attached due to contact with a human body. In one

aspect of the present invention, examples of such an article include clothing such as a uniform and a snowsuit, and linens such as a sheet and a pillowcase.

[0078]

5 Examples of the object to be washed with fine bubbles generated according to the present invention can include the skin of a human or an animal, and a part of a human or animal body, such as hairs. In a preferable aspect of the present invention, fine bubbles, which are produced in warm water
10 stored in a bathtub or warm water for use in a shower during bathing, are used for washing a part of a human or animal body.

EXAMPLES

[0079]

15 The present invention is specifically described based on the following Examples, but the present invention is not intended to be limited to such Examples.

[0080]

Example 1: Washing ability test 1 of fine bubbles

20 The washing ability test of fine bubbles produced by use of the aqueous composition for fine bubble production according to the present invention was performed using a pig skin specimen as the washing object, as follows.

[0081]

25 Test conditions

(1) Specimen

Pig skin: cut leather, Craft Flower (Juton), plain, cut to 2 cm × 2 cm

Artificial dirt: color for chocolate, 10% by weight,
30 sorbitan monopalmitate 25% by weight

Edible soybean oil 65% by weight

(2) Washing test conditions

Volume of water tank: 4 L

Temperature of warm water: 40°C

35 Number of specimens: in triplicate with respect to each specimen

Respective specimens where casein sodium was added in concentrations of 0.01% by mass, 0.005% by mass, and 0.002% by mass to tap water were prepared in triplicate. One where fine bubbles were generated in tap water, and one where no bubbles were generated in tap water were prepared as controls.

[0082]

Test procedure

(1) The surface of the pig skin was photographed with a microscope.

(2) The artificial dirt in an amount of 3.5 mg/cm^2 was spread on and attached to the surface of the pig skin with scoopula, and the surface was photographed with a microscope.

(3) The resultant was immersed in a solution of bubbles produced by use of the fine bubble generation apparatus including one bubble generation mechanism having a conical shape, according to the invention of the present inventors, illustrated in FIG. 4, for a predetermined time (5 minutes).

The resultants were immersed in tap water as a control where fine bubbles were generated and tap water as a control where no fine bubbles were generated, respectively, for 5 minutes. The tap water where no fine bubbles were generated was circulated by a pump during the test.

(4) Moisture on the surface was lightly blotted by a paper towel.

(5) After the pig skin was confirmed to be completely dried, the surface was photographed with a microscope.

[0083]

Washing effect

FIG. 1 includes photographs of each of the specimens before washing and after washing. As clear from the photographs, the washing effect was almost not exerted by both control samples including no casein sodium, one where fine bubbles were generated and one where no fine bubbles were generated.

On the other hand, the washing effect was exerted by all specimens washed by fine bubbles generated in water including

casein sodium. In particular, a higher washing effect was exerted due to a higher concentration of casein sodium.

[0084]

Example 2: Washing ability test 2 of fine bubbles

5 Test conditions

The test was performed in the same manner as in Example 1 except that the skin of the back of the human hand (the area attached was 5 cm × 5 cm) was used as a specimen and 96.8% by mass of oleic acid having a concentration of 10 mg/cm³ and 2.2% by mass of sudan IV (oil red) were used in the artificial dirt.

[0085]

Evaluation index of washing effect

A washing effect value was used as the evaluation index of the washing effect in the case of addition of each additive. The washing effect value was calculated as follows.

Formula: (Gray scale value before washing) - (Gray scale value after washing)

The gray scale value was automatically calculated using image processing software. Specifically, the procedure was made as follows.

1. The specimen with the dirt attached thereto was placed in a box which was sealed so that no light of the external environment was admitted and in which a light was installed to allow the brightness to be constant.

2. The specimen prepared in 1 was photographed. The test was performed using six specimens with respect to one washing condition, and the same specimen was photographed reciprocatingly three times (18 images in total).

3. The specimens after washing were also photographed according to the procedures of 1 and 2.

4. Each of the resulting images was subjected to gray scale measurement with image processing software GIMP.

5. The resulting gray scales with such reciprocation three times were averaged with respect to each of the specimens, and the average values of the six specimens before and after washing

were compared. The difference in gray scale value before and after washing was defined as the washing effect value. A case where the washing evaluation value was 3 or more and the significance level calculated according to the T-test was $p < 0.05$ in comparison of the average values of the gray scales of each of the specimens in the reciprocation three times, before and after washing, was determined as having a significant difference.

[0086]

A case where the washing effect value thus calculated was less than 4 was determined as exerting no washing effect, a case where the washing effect value was 4 to 7 was determined as exerting the washing effect, and in particular, a case where the washing effect value was 7.1 or more was determined as favorably exerting the washing effect. Herein, a case where the significance level was $p > 0.05$ in comparison of the average values of the gray scales of each of the specimens in the reciprocation three times, before and after washing, even if the washing effect value was less than 3 or 3 or more was determined as exerting no washing effect.

[0087]

Test results

(1) Washing effect

The results of the washing test are described in Table 1 below. The minimum value of the concentration of addition, at which the washing effect was exerted, was studied with respect to each additive. The washing effect could be confirmed in respective concentrations of 0.008% or more of casein sodium, 0.003% or more of polyoxyethylene dodecyl ether, 0.01% or more of soybean lecithin, 0.01% or more of saponin, and 0.01% or more of trimethyl stearyl ammonium.

[0088]

[Table 1]

Table 1: Washing effect in addition of additive in present invention

Sample name	Washing effect value	Viscosity (mPa·s)	Temperature (°c)	Surface tension (mN/m)	Standard deviation
Casein sodium 0.008%	5.4	0.82	20.9	69.2	3
Casein sodium 0.005%	-	0.80	20.8	70.3	4
Polyoxyethylene dodecyl ether 0.003%	4.7	0.78	20.5	53.2	2.5
Polyoxyethylene dodecyl ether 0.001%	-	0.75	19.8	51.9	2.2
Soybean lecithin 0.01%	4.3	0.94	18.9	65.7	5.4
Soybean lecithin 0.008%	-	0.79	20.7	59.9	4.7
Sodium 1-octanesulfonate 0.01%	6.2	0.93	18.9	69.5	6.9
Sodium 1-octanesulfonate 0.008%	-	0.77	20.8	65.5	5.9
Saponin 0.01%	4.8	1.03	18.9	69.9	5.3
Saponin 0.008%	-	0.49	20.7	62.9	3.7
Trimethyl stearyl ammonium 0.01%	7.9	0.93	18.6	49.8	4.1
Trimethyl stearyl ammonium 0.008%	-	0.78	20.2	51.3	3.4

In Table, “-” indicates no effect.

[0089]

Example 3: Washing ability test 3 of fine bubbles

The washing ability test of fine bubbles was performed by the same method as in Example 1 except that two bubble
 5 generation mechanisms 22 having a conical shape were included.

As a result, only a case where casein sodium was used as the additive was decreased in the minimum value of the concentration of the additive, at which the washing ability was
 10 exhibited, as compared with the case of Example 1 where fine bubbles produced by the apparatus having one cone were used.

Specifically, the minimum amount where the effect was exerted was 0.004% (washing value = 5.8), and no washing effect was exerted at a value equal to or less than such a
 15 washing value. In the case of the present Example, the washing value was 8.5 in a concentration of 0.008% of casein sodium, and was increased as compared with Example 1.

The reason for this is considered because the conical mechanism was increased to two of the mechanisms to thereby
 20 result in an increase in the amount of fine bubbles generated.

[0090]

Example 4: Measurement of particle size of fine bubbles

(1) Measurement conditions of particle size

Measurement instrument

25 Microtrack Series (microtrac version 10.5.3-225R)

Optical bench: MT3000II

[0091]

(2) Measurement method of particle size

Fine bubbles were generated in water to which 0.01% of casein sodium as one additive in the present invention was
 30 added, by the above fine bubble generation apparatus 20 according to the invention of the present inventors. The particle size of the sample was measured in the above measurement conditions after operation of the apparatus for 5
 35 minutes and after 5 minutes from the stop of the operation.

[0092]

(3) Measurement results of particle size

Table 2 below describes the measurement values of the mode particle sizes, the average particle sizes and the 50% cumulative particle sizes, of fine bubbles generated by adding casein sodium among the additives in the present invention and of fine bubbles generated in tap water with no addition of any additive, after 5 minutes from the start of operation of the fine bubble generation apparatus and after 5 minutes from the stop of the operation of the apparatus.

10 [0093]
[Table 2]

Table 2: Comparison in particle size between addition of casein sodium and no addition thereof

Sample name	Mode particle size (μm)	Average particle size (μm)	50% cumulative particle size (μm)
Solution in tap water immediately after operation with fine bubbles for 5 minutes	37	72	59.77
Solution in tap water left for 5 minutes after generation of fine bubbles	37	70.38	54.96
Solution with 0.01% casein sodium added, immediately after operation for 5 minutes	31.11	62.75	49.85
Solution with 0.01% casein sodium added, left for 5 minutes after operation	44	91.4	79.13

[0094]

The mode particle size was not changed and the average particle size and the 50% cumulative particle size were decreased with respect to no addition of casein sodium, during a period from after operation of the fine bubble generation apparatus for 5 minutes to after leaving for 5 minutes after fine bubble generation. On the other hand, all the mode particle size, the average particle size and the 50% cumulative particle size were increased with respect to addition of casein sodium, during a period after operation of the fine bubble generation apparatus for 5 minutes to after leaving for 5 minutes after fine bubble generation.

It could also be confirmed that bubbles were shrunk with time with respect to no addition of casein sodium. On the other hand, the particle size after 5 minutes from the generation was decreased with respect to addition of casein sodium as compared with no addition of casein sodium. On the other hand, the particle size after leaving for 5 minutes after the operation was increased.

[0095]

Example 5: Change in particle size of fine bubbles over time

In order that the relationship between the washing effect of each additive and the particle size over time was examined, fine bubbles were generated in water to which each additive was added in a concentration of 0.01%, on another day than that in Example 1, and the 50% cumulative particle size was measured after 5 minutes from the start of operation of the fine bubble generation apparatus and after 5 minutes from the stop of the operation of the apparatus. These results are described in Table 3 below.

[0096]

[Table 3]

Table 3: Change in particle size of fine bubbles over time with respect to addition of each additive in present invention

Group	Additive name	50% cumulative particle size (μm) in operation for 5 minutes	50% cumulative particle size (μm) after stop for 5 minutes	Washing evaluation value
1	Casein sodium	20.74	63.14	11.3
	Soybean lecithin	26.69	48.31	4.3
2	Polyoxyethylene dodecyl ether	0.544	58.99	10.1
	Trimethyl stearyl ammonium chloride	0.561	54.14	7.9
3	Saponin	71	64.48	4.8
	Sodium 1-octanesulfonate	108.5	104	6.2
Control	Bubble generation in tap water without any additive	69.53	51.44	2.8

[0097]

Fine bubbles in the case of casein sodium included as the additive had a 50% cumulative particle size of about 10 μm to 65 μm and fine bubbles in the case of polyoxyethylene dodecyl ether or trimethyl stearyl ammonium included as the additive had a 50% cumulative particle size of about 0.5 μm to 65 μm , after 5 minutes from the start. Fine bubbles had a 50% cumulative particle size of about 40 μm to 90 μm after 5 minutes from the stop. All the particle sizes were smaller than those in Example 3, and the reason for this was because many bubbles having a smaller particle size were generated by an increase in the amount of water in the pump used.

The particle size of fine bubbles generated in tap water with no addition of any additive was shrunk over time. The reason for this is considered because of self-shrinkage (self-pressurizing effect) of fine bubbles as known in the art.

The particle size after 5 minutes from the start of operation of the bubble generation apparatus was smaller in the cases of casein sodium and soybean lecithin in group 1 and polyoxyethylene dodecyl ether and trimethyl stearyl ammonium chloride in group 2, than the case of no addition. However, the particle size was increased over time in the cases of such additives unlike the case of no addition.

The particle size was decreased over time in the cases of saponin and sodium 1-octanesulfonate in group 3, like the case of no addition.

[0098]

Conclusion

It is presumed that an increase in average particle size over time in the case of addition of casein sodium is affected by the property of aggregation of casein by itself.

Without being bound to the following theory, in the case where an acrylic plate to which oils and fats are attached is placed in a solution of fine bubbles, penetration of the bubbles into the oils and fats is observed (FIG. 2), and thus it is presumed that bubbles penetrate into oils and fats and

aggregate therein and thus are expanded, resulting in an increase in ascending force to allow the oils and fats to be peeled from the pig skin. In particular, the particle size immediately after fine bubble generation is smaller in the
5 respective cases of addition of the additives in group 1 with shrinkage of the particle size to a micrometer level and the additives in group 2 with shrinkage of the particle size to a nanometer level, than the case of no addition, and thus it is presumed that an increase in washing force is achieved because
10 bubbles more easily penetrate into oils and fats and thereafter aggregate and are increased in particle size, resulting in an increase in ascending force to allow any dirt to be peeled. In other words, it is presumed that a washing object 10 having fouling 11 is immersed in water including fine bubbles 13
15 generated in a water tank 12, thereby allowing small-size fine bubbles to penetrate into the fouling 11 and aggregate in the fouling 11 and thus imparting an ascending force 15 due to fine bubbles aggregated 14 to allow the fouling 11 to ascend, thereby peeling the fouling from the washing object 11 (FIG. 3).
20 Accordingly, it is considered that dirt is peeled from a washing object according to an action completely different from that according to a conventional washing method with a surfactant.

[0099]

The reason for a high washing value of sodium
25 1-octanesulfonate among additives in group 3 with a tendency of shrinkage of the particle size over time as in the case of no addition of any additive is considered because sodium 1-octanesulfonate has a high washing force even in no use in combination with fine bubbles and thus a composition thereof
30 originally has a high washing force.

[0100]

It has been thus found that fine bubbles produced by use of the aqueous additive in the present invention is excellent in washing force as compared with fine bubbles produced by use of
35 no additive.

[0101]

Example 6: Difference in bubble generation due to difference in structure between bubble generation mechanism and eddy-current generation mechanism

5 The effects of the shapes and the presences of the bubble generation mechanism and the eddy-current generation mechanism on the bubble generation state were tested.

(1) Bubble generation mechanism

10 The bubble generation mechanism for use in the fine bubble generation apparatus of the present invention was one having a conical shape, in which two holes were provided at an angle of 180° (namely, such holes being located oppositely with the center interposed) (height: 25 mm, inner diameter of bottom surface: 16 mm, hole diameter: 2 mm). An example of a bubble generation mechanism having another shape was one
15 having a rectangular solid shape (height: 25 mm, longitudinal: 10 mm, lateral: 10 mm), in which two holes were provided at an angle of 180° (namely, such holes being respectively located on planes facing each other). An example of the case of no bubble generation mechanism was one where two holes having
20 the same diameter were disposed on a boundary plane between the middle tank section and the lower tank section.

(2) Eddy-current generation mechanism

25 The eddy-current generation mechanism for use in the fine bubble generation apparatus of the present invention was subjected to comparison of the generation state of bubbles, with the change of a larger-diameter outer pipe (skirt section) in two pipes (inner diameter of outer pipe: 17 mm, length of outer pipe: 75 mm, inner diameter of inner pipe: 15 mm, length of inner pipe: 75 mm, spiral pitch: 15 mm, groove width of spiral
30 section: 10 mm, length of spiral section: 55 mm). Specifically, one where a skirt section was disposed with being shifted upward by 5 mm from the lowest end of the middle tank section was used as one including a general skirt section, and one without any skirt section and one where the length of the skirt
35 section was decreased by half were used as examples of other modes.

(3) Procedure

Water was introduced into the fine bubble generation apparatus according to the present invention at an output of 8.9 L/min by use of a pump (manufactured by ASANO MFG. Co., Ltd.), and fine bubbles were generated in a water tank in which 10 L of water (tap water, room temperature) was placed. The generation was stopped after 1 minute from the start of operation of the apparatus, and the generation state of bubbles was examined. The generation state of fine bubbles was visually observed.

(4) Results

The results of generation of bubbles are summarized in Table 4 below.

[0102]

15 [Table 4]

Table 4

Number	Generation mechanism	Skirt section	Generation state of bubbles
6-1	Cone	General (5 mm from lower end)	Fine bubbles favorably generated.
6-2	No	General (5 mm from lower end)	Not generated.
6-3	Rectangular solid	General (5 mm from lower end)	Fine bubbles generated, but not completely clouded.
6-4	Cone	No	Millibubbles generated.
6-5	Cone	Half	Millibubbles (mostly) and microbubbles generated.

[0103]

Example 6-1 corresponded to one where a conical generation mechanism was used and the skirt section (outer pipe) was disposed with being shifted upward by 5 mm from the lower end of the second tank section. The apparatus according to the present Example was used to perform the test, and thus water in the water tank was completely clouded and fine bubbles were favorably generated.

[0104]

Example 6-2 corresponded to one where the generation mechanism was removed and the skirt section was disposed as in Example 6-1. The apparatus according to the present Example was used to perform the test, and thus bubbles were not generated. It was found from favorable generation of fine bubbles in Example 6-1 that the generation mechanism having a conical shape was placed to result in generation of fine bubbles even in a condition of no generation of fine bubbles by no generation mechanism having a conical shape. Accordingly, it is considered that the bubble generation mechanism plays a role in generation of fine bubbles at a low pressure of water and in a small amount of water.

[0105]

Example 6-3 corresponded to one where the shape of the generation mechanism had a rectangular solid shape and the skirt section was disposed as in Example 6-1. The apparatus according to the present Example was used to perform the test, and thus generation of fine bubbles was observed, but the concentration was low and water in the water tank was not completely clouded. Accordingly, the shape of the bubble generation mechanism is considered to be more preferably a cone than a rectangular solid.

[0106]

Example 6-4 corresponded to one where a conical generation mechanism was used as in Example 6-1 and the skirt section was removed. The apparatus according to the present Example was used to perform the test, and thus not fine

bubbles, but large-size millibubbles were generated. The length of the skirt section in Example 6-5 was decreased by half that in Example 6-1, and thus bubbles generated were mostly millibubbles, and only small amounts of microbubbles were generated. It is considered from the results that the skirt section exhibits a strong ascending force for inhibition of formation of fine bubbles and large-size bubbles mass is prevented from flowing in the eddy-current generation mechanism and the bubble generation mechanism having a conical shape.

[0107]

Example 7: Effect of bubble generation mechanism having conical shape on pressure in generation limit

In order to examine the effect of the generation mechanism in the fine bubble generation apparatus of the present invention on the limit pressure in generation of bubbles, the generation state of fine bubbles was compared by the change in the amount of water to be introduced into the apparatus between one where the generation mechanism having a conical shape was removed and one where the generation mechanism having a conical shape was provided as usual. The test conditions other than the presence of a conical shape and the amount of water to be introduced were the same as those in Example 6-1 of Example 6. The results are described in Table 5 below.

[0108]

[Table 5]

Table 5

Number	Conical shape	Pressure of inlet of apparatus	Amount of water	Generation state of bubbles
7-1	Yes	0.1 MPa	3.12 L/min	Fine bubbles generated.
7-2	Yes	0.04 MPa	2.04 L/min	Fine bubbles generated in small amount. (generation limit)
7-3	No	0.1 MPa	7.02 L/min	Not generated.

[0109]

Use of the generation mechanism having a conical shape allowed fine bubbles to be generated at a lower pressure of water and in a smaller amount of water than no use of the generation mechanism having a conical shape. Accordingly, the generation mechanism having a conical shape according to the present invention can be used to provide no need for sending of water by a large pump to a large apparatus at a high pressure as in a conventional mechanism, and thus enables generation of fine bubbles by a small apparatus using a small pump.

[0110]

The bubble generation apparatus according to the present invention can be used to thereby generate fine bubbles in a sufficient concentration at a lower pressure of inlet of the apparatus, of 0.1 MPa, than that of a conventional apparatus. Fine bubbles can be generated in a sufficient concentration for use in a desired application at a lower pressure than that of a conventional case, and thus there is no need for use of a high-pressure and large-size pump and there can be provided a fine bubble generation apparatus excellent in terms of installation space and cost.

[0111]

The output of a pump was increased to thereby allow for generation of fine bubbles at an output of 9.2 L/min (pressure of inlet of apparatus 0.16 MPa), at an output of 16 L/min (pressure of inlet of apparatus 0.2 MPa) and at an output of 22 L/min (pressure of inlet of apparatus 0.25 MPa). The output was increased using a larger pump, to 68 L/min, to thereby increase the pressure of inlet of the apparatus to 1 MPa, but the concentration of fine bubbles generated was the same as that in the case where the output was 22 L/min by use of the pump in the present embodiment. Accordingly, the fine bubble generation apparatus according to the present invention can generate fine bubbles at a level comparable to a conventional large apparatus even without use of any large pump.

[0112]

Example 8 Effects of position and number of holes in conical shape on bubble generation

The effects of the position of each hole and the number of holes in the bubble generation mechanism in the present invention on generation state of bubbles were examined. The position of each hole and the number of holes are defined by parameters a to f as illustrated in FIG. 7. Herein, parameter a represents the distance from the bottom section of the cone to the lower end of each hole in the axial direction, parameter b represents the distance from the top of the cone to the upper end of each hole in the axial direction, parameter c represents the number of holes, parameter d represents the inner diameter of each hole, parameter e represents the inner diameter of the bottom section of the cone, parameter f represents the length of the cone section in the axial direction, and parameter g represents the angle of disposing of each hole. The test conditions other than the position of each hole and the number of holes were the same as those in Example 1. The results are described in Table 6 below.

[0113]
[Table 6]

Table 6

No.	Shape	a (mm)	b (mm)	c (holes)	d (mm)	e (mm)	f (mm)	g (°)	Generation state
8-1	Truncated cone	15	10	2	2	12	25	180	Most favorably generated
8-2	Cone	20	5	2	2	12	25	180	Generated
8-3	Cone	7	18	2	2	12	25	180	Slightly generated
8-4	Cone	15	10	1	4	12	25	-	Slightly generated, but insufficiently generated
8-5	Cone	15	10	4	1	12	25	90	Generated
8-6	Cone	15	10	2	2	12	25	90	Generated, but slightly generated lightly
8-7	Cone	15	10	2	2	12	25	45	Generated, but slightly generated lightly

[0114]

From the results, the number of holes provided in a cone is desirably two or more. In the case where two or more holes are disposed, the holes can be disposed at an angle of 45° to 180°. In particular, in the case where two holes are disposed, the holes are most preferably disposed at an angle of 180°. A preferable size of each hole is needed to be appropriately adjusted depending on the amount of water to be set, although being 1 to 4 mm in terms of the inner diameter in the present Examples. A too large number of holes decreases generation of bubbles, and the number of holes is preferably six or less.

[0115]

The amount of water output from the pump was increased to 22 L/min in the same conditions as in the present Example 8-1, and thus sufficient generation of fine bubbles could be observed in an inner diameter of each hole of up to 8 mm. In the case where the inner diameter of each hole was increased to 10 mm, generation of fine bubbles could be observed, although the concentration was low. Accordingly, in the case of use in the apparatus according to the present invention, the inner diameter of each hole provided in the conical section of the bubble generation mechanism preferably falls within the range from 1 to 10 mm.

[0116]

25 Example 9: Fine bubble generation test using improved mode

Fine bubbles were generated using the fine bubble generation apparatus illustrated in FIG. 4, and the particle size was measured.

(1) Measurement conditions of particle size

30 Measurement instrument

Microtrack Series (microtrac version 10.5.3-225R)

Optical bench: MT3000II

Volume of water tank: 4 L

[0117]

35 (2) Measurement method of particle size

Fine bubbles were generated in tap water and in water to

which 0.01% of casein sodium was added. The particle size of each of the samples was measured in the above measurement conditions after operation of the apparatus for 5 minutes and after 5 minutes from the stop of the operation.

5 [0118]

(3) Results of particle size measurement

Table 7 below describes the measurement values of the mode particle sizes, the average particle sizes and the 50% cumulative particle sizes, of fine bubbles generated by adding casein sodium among the additives in the present invention and of fine bubbles generated in tap water with no addition of any additive, after 5 minutes from the start of operation of the fine bubble generation apparatus and after 5 minutes from the stop of the operation of the apparatus.

15 [0119]

[Table 7]

Table 7: Comparison in particle size between addition of casein sodium and no addition thereof

Sample name	Mode particle size (µm)	Average particle size (µm)	50% cumulative particle size (µm)
Solution in tap water immediately after operation with fine bubbles for 5 minutes	37	72	59.77
Solution in tap water left for 5 minutes after generation of fine bubbles	37	70.38	54.96
Solution with 0.01% casein sodium added, immediately after operation for 5 minutes	31.11	62.75	49.85
Solution with 0.01% casein sodium added, left for 5 minutes after operation	44	91.4	79.13

[0120]

It was thus confirmed that fine bubbles were generated using the fine bubble generation apparatus of the present invention, illustrated in FIG. 4.

5 [0121]

Example 10: Ultrafine bubble generation test

The generation state of ultrafine bubbles along with generation of fine bubbles in the case of use of the fine bubble generation apparatus illustrated in FIG. 4 was confirmed.

10 (1) Measurement conditions of particle size distribution
Measurement instrument

Microtrack Series (microtrac version 10.5.3-225R)

Optical bench: UPA-UZ

Volume of water tank: 4 L

15 [0122]

(2) Measurement method of particle size distribution

Bubbles were generated in tap water (room temperature) by operating the apparatus illustrated in FIG. 4. The particle size distribution (number distribution) in the measurement
20 range from 0.800 nm to 6,540 nm, of the sample, was measured in the above measurement conditions after operation of the apparatus for 5 minutes and after 5 minutes from the stop of the operation thereof.

[0123]

25 (3) Measurement results of particle size distribution

Table 8 below describes the measurement values of the mode particle sizes, the average particle sizes and the 50% cumulative particle sizes after operation of the bubble generation apparatus in tap water for 5 minutes and after 5
30 minutes from the stop of the operation thereof.

[0124]

[Table 8]

Table 8			
Sample name	Mode particle size (nm)	Average particle size (nm)	50% cumulative particle size (nm)
Solution in tap water immediately after operation with fine bubbles for 5 minutes	121.5	115.3	111.4
Solution in tap water, left for 5 minutes after generation of fine bubbles	72.3	86.7	75.2

[0125]

It could be confirmed from the above results that ultrafine bubbles of 1 μm (= 1000 nm) or less were generated. It could also be confirmed that a decrease in the particle size over time, as a characteristic behavior of ultrafine bubbles, was observed. Generation of ultrafine bubbles usually requires a larger and more expensive apparatus than generation of fine bubbles, and it can be thus said that the apparatus according to the present invention is very excellent in terms of having a very small and simple structure.

[0126]

Industrial Applicability

The aqueous composition for fine bubble production and the washing method with fine bubbles, and the fine bubble generation apparatus and the method for producing fine bubbles by use of the apparatus, according to the present invention, are useful in, for example, washing of cloths, and bathing in a medical facility.

Reference Signs List

[0127]

10 washing object, 11 fouling, 12 water tank, 13 fine bubbles, 14 fine bubbles aggregated, 15 ascending force, 20, 30 fine bubble generation apparatus, 21 gas-liquid inflow pipe, 22 bubble generation mechanism, 23a, 40 lower tank section, 23b upper tank section, 24 eddy-current generation mechanism, 25 gas-liquid mixed phase generation mechanism, 26, 39 discharge pipe, 27a upper surface, 27b bottom surface, 28, 29, 32a, 36a, 38a, 51 through-hole, 31 large-size-bubble separation mechanism, 31a cylindrical mechanism, 32 first partition section, 33 middle tank section, 34 skirt section, 35 eddy-current generation mechanism, 36 bubble generation mechanism, 37 gas-liquid inflow pipe, 38 bubble shredding mechanism, 50 wall

CLAIMS

1. Use of an aqueous composition comprising:
 - one or more components selected from the group consisting of an alkali metal salt of casein, polyoxyethylene dodecyl ether, soybean lecithin, sodium 1-octanesulfonate, saponin and trimethyl stearyl ammonium chloride; and
 - water,for the production of fine bubbles in a fine bubble generation apparatus comprising a fine bubble generation mechanism wherein the fine bubble generation mechanism generates a fine bubble-containing fluid from a mixed fluid of a liquid and air;
 - the fine bubble generation apparatus comprising:
 - the fine bubble generation mechanism that generates a fine bubble-containing fluid from a mixed fluid of a liquid and air;
 - a gas-liquid inflow pipe that allows for introduction of the mixed fluid;
 - a cylindrical gas-liquid mixed phase generation mechanism where the gas-liquid inflow pipe is provided at the center of a cylinder;
 - an eddy-current generation mechanism which is provided so as to divide the interior of the gas-liquid mixed phase generation mechanism into two sections, which comprises an upper surface having 2 to 4 holes and a lower surface having 2 to 4 holes disposed with being shifted from the holes of the upper surface, and in which the holes of the upper surface and the holes of the lower surface are pierced so as to correspond to each other; and
 - a discharge pipe provided on a side surface of the gas-liquid mixed phase generation mechanism,
 - wherein said fine bubble generation mechanism comprises a wall that partitions the mixed fluid to be introduced and the fine bubble-containing fluid to be discharged,
 - the wall has a cone shape opened at a bottom,
 - a through-hole for introduction of the mixed fluid into the interior of the wall is formed on at least a part of a side surface of a shape partitioned by the wall, and
 - the mixed fluid is introduced through the through-hole into the interior of the wall and discharged as the fine bubble-containing fluid

from the opening,

the bubble generation mechanism is provided on an end of the gas-liquid inflow pipe, through which the mixed fluid is discharged, and

the gas-liquid inflow pipe is centrally pierced from an upper surface of the cylinder, and an end thereof, through which the mixed fluid is discharged, is placed with a gap from a bottom section of the main body of the cylinder, and

the fine bubbles have a diameter of 100 μm or less.

2. The use according to claim 1, wherein the alkali metal salt of casein is casein sodium.

3. The use according to claim 2, wherein the concentration of casein sodium is equal to or more than 0.004 % by mass and the fine bubble generation apparatus comprises two bubble generation mechanism having a conical shape.

4. A washing method comprising:

(1) a step of generating fine bubbles by use of a fine bubble generation apparatus as defined in claim 1 and an aqueous composition for fine bubble production as defined in claim 1;

(2) a step of allowing fine bubbles generated in step (1) to penetrate into fouling of a washing object;

(3) a step of allowing fine bubbles penetrating into the fouling in step (2) to be aggregated; and

(4) a step of allowing fine bubbles aggregated in step (3) to ascend, thereby peeling the fouling from the washing object,

wherein the fine bubbles have a diameter of 100 μm or less.

5. The washing method according to claim 4, wherein the aqueous composition contains 0.01 % by mass of casein sodium, and the fine bubble generated in the step (1) has a 50% cumulative particle size of 10 μm to 65 μm after 5 minutes from the start of the operation of the bubble generation apparatus.

6. The washing method according to claim 4, wherein the aqueous composition contains 0.01 % by mass of polyoxyethylene dodecyl ether or 0.01 % by mass of trimethyl stearyl ammonium, and the fine bubble generated in the step (1) has a 50% cumulative particle size of 0.5 μm to 65 μm after 5 minutes from the start of the operation of the bubble generation apparatus.

7. The washing method according to claim 5 or 6, wherein the fine bubble aggregated in the step (3) has a 50% cumulative particle size of 40 μm to 90 μm after 5 minutes from the stop of the operation of the bubble generation apparatus.

COMPOSITION FOR FINE BUBBLE PRODUCTION, AND GENERATION APPARATUS

ABSTRACT

5

The present invention relates to an aqueous composition for production of fine bubbles having desired properties, and a fine bubble generation apparatus. More specifically, the present invention relates to an aqueous composition for production of fine bubbles having properties suitable for use in washing, and a fine bubble generation apparatus which does not need any facilities such as a large pump and which is small in size and low in cost. Furthermore, the present invention also relates to a washing method with fine bubbles produced by use of the aqueous composition and/or the fine bubble generation apparatus.

10

15

(Fig. 4)