

## Description

Title of the Invention: INSOLUBLE MINERAL FORTIFIED MILK BEVERAGE

### Technical Field

[0001] The present invention relates to a milk beverage, specifically a milk beverage which is fortified with an insoluble or slightly-soluble (hereinafter abbreviated as "insoluble") mineral and capable of prolonged storage. And the invention also relates to a method for producing the insoluble mineral fortified milk beverage.

More specifically, the invention relates to a insoluble mineral fortified milk beverage, such as a calcium, magnesium or iron fortified milk beverage, and what's more, that is capable of prolonged storage. The invention also relates to a method for producing the insoluble mineral fortified milk beverage, such as a calcium, magnesium or iron fortified milk beverage.

### Background Art

[0002] In addition to elements (such as carbon, hydrogen, nitrogen and oxygen) which are constituents of a general organic substance, minerals in dietetics refer to indispensable elements for every living body. Minerals are ranked with saccharides, lipids, proteins and vitamins, and counted among five main nutrients. To be concrete, in Japan at the least, the minerals in dietetics include 13 elements (namely zinc, potassium, calcium, chromium, selenium, iron, copper, sodium, magnesium, manganese, molybdenum, iodine and phosphorus) which are defined by the Ministry of Health, Labor and Welfare as the subjects of food-intake standards based on Health Promotion Act. Among those elements, supply of e.g. calcium, magnesium or iron in an insoluble state into a human body has been a matter of concern.

Calcium is not only essential to the growth of bone, but also it is a nutrient which plays important roles in keeping body fluids in alkaline conditions, promoting the coagulating action of the blood, dampening the excitation of nerves, and so on. However, calcium is one

of nutrients which the present-day dietary habits are likely to lack, and it is the present situation that even cow's milk and milk beverages, foods relatively rich in calcium, are fortified with calcium.

In addition, magnesium is an essential element to a living body in retention of the structure of ribosome, synthesis of proteins and other biological functions concerning energy metabolism, and the shortage of magnesium has been thought to be a cause of ischemic heart disease and so on.

Further, iron bears an important part in the biology of a living body. Hemoglobin present in red blood cells transports oxygen with the aid of iron ions. The coupling between hemoglobin and oxygen is weak, and the hemoglobin can easily release the oxygen upon arriving at oxygen-using tissue, such as muscle tissue.

In recent years, there has been a growth in the addition of the foregoing element as one of mineral elements to dietary supplements, beverages and the like.

[0003] To take calcium as an example of the mineral elements, mineral fortification for milk beverages based on milk has been mainly performed by addition of a water-soluble calcium salt, such as calcium lactate, or an insoluble calcium salt, such as calcium carbonate or synthetic calcium carbonate for food additive use.

However, the addition of a water-soluble calcium salt in a concentration of 0.02 wt% or higher on a calcium basis to a milk beverage causes a problem that, when heat sterilization treatment is given to the milk beverage, thermal coagulation and precipitation of proteins occur through the reaction between calcium ions and lactoproteins.

[0004] On the other hand, in the case of using calcium carbonate, one of insoluble calcium salts, as a food additive, there has been known a method of preparing calcium carbonate in a slurry state e.g. through the carbon dioxide gas process in which a water suspension of calcium hydroxide (lime milk) is generally made to react with carbon dioxide gas. And the calcium carbonate in a slurry state is dewatered, dried and then pulverized, thereby being

made available for use.

Additionally, though an insoluble calcium salt such as calcium carbonate may be incorporated into milk beverages at any time before or after heat sterilization because it doesn't cause aggregation through the reaction with proteins, such a salt inevitably has a drawback of forming precipitates or the like because of its insolubility.

Where magnesium is concerned, magnesium chloride is known as a food additive. Magnesium chloride is a main ingredient in "nigari", or a coagulant used in making tofu, and is a bitter-tasting ingredient as can be seen from the Japanese name thereof. Problems therefore arise in the case of using that magnesium salt as a nutrition-fortifying agent. Such a bitter taste appears strongly because the magnesium salt used is soluble in water, and the bitter-taste problem can be ameliorated by the use of an insoluble magnesium salt. The use of the insoluble salt, however, entails a drawback of forming precipitates or the like as in the case of calcium.

On the other hand, recent years have also seen a large number of women suffering the symptoms of anemia because of their iron shortage. This tendency is prominent especially among female students in senior high school and young women. With the invention of resolving the iron shortage, a great many iron-fortified products of cow's milk or the like have been launched, too. As to iron additives, water-soluble iron salts of organic acids, such as iron lactate, iron sodium citrate and ferrous gluconate, are available, but each has a strong iron taste, and therefore has a problem that, out of a mouthfeel concern, it cannot be used in so great quantity at a time. In the case of using a dispersion of water-insoluble or slightly-soluble iron salt such as ferric pyrophosphate, an iron-odor problem can be ameliorated, but such a dispersion has a high specific gravity of at least 2.75 and, when it is dispersed into soft drinks or the like, such an iron salt precipitates out of the drinks in a short time, and therefore has a problem with its suspension stability.

[0005] Use of a combination of crystalline cellulose and  $\kappa$ -carrageenan as a dispersant was

previously proposed (in JP-A-11-276132). It has been known that crystalline cellulose molecules are intertwined with each other in a liquid phase to form a reticular structure, and an insoluble calcium salt is trapped in the reticular structure. In addition, it has been thought that  $\kappa$ -carrageenan reacts with a milk component to form superfine, flowability-rich microgels and has a function of adsorbing calcium on the microgel surface and preventing the secondary aggregation of calcium particles, and therefore can achieve more excellent effect on the prevention of sedimentation in synergy with crystalline cellulose.

[0006] However, it has also been described in the foregoing proposal that the effect produced by the use of each one in isolation was insufficient as compared with the effect produced by the combined use of both, and even in the combined-use case, use of  $\kappa$ -carrageenan in too high a proportion, though produced the effect of preventing calcium sedimentation, caused a macroscopic gelling phenomenon in the liquid phase and rendered milk beverages unsuitable for drinking. In other words, in consideration of the prior art, some ingredient other than  $\kappa$ -carrageenan becomes indispensable to a dispersant in producing a milk beverage. Crystalline cellulose, even through incorporated as another dispersant into a milk beverage, must be difficult to mix with  $\kappa$ -carrageenan, and besides, it has a drawback of spoiling flavor of the milk beverage. In a case where a similar insoluble mineral, such as an insoluble magnesium or iron compound, is added, the same matters as mentioned above also arise, though the amounts causing precipitation are different in each salt.

Milk-based dairy foods give a natural and healthy image because of milk derivations, and their appealing power to consumers can be heightened by not using food's ingredients (food additives) spoiling their image, including e.g. crystalline cellulose. A further increase in the number of buyers can therefore be expected by offering insoluble mineral fortified milk beverages capable of prolonged storage with the aid of a minimum amount of additive.

Documents Concerning Related Art

Patent Document

[0007] Patent Document 1: JP-A-11-276132

## Summary of the Invention

### Problems that the Invention is to Solve

[0008] Problems the invention aims to solve are to provide an insoluble mineral fortified milk beverage which is capable of prolonged storage with the aid of a minimum amount of additive and to provide a method for producing the insoluble mineral fortified milk beverage.

More specifically, problems the invention aims to solve are to provide an insoluble mineral fortified milk beverage, such a calcium, magnesium or iron fortified milk beverage, which is capable of prolonged storage with the aid of a minimum amount of additive, and to provide a method for producing the insoluble mineral fortified milk beverage, such a calcium, magnesium or iron fortified milk beverage.

### Means for Solving the Problems

[0009] The present inventors have made intensive studies in order to solve the problems, and thereby have come to provide an insoluble mineral fortified milk beverage characterized in that the milk beverage contains a milk component, an insoluble mineral and a dispersant comprising  $\kappa$ -carrageenan and an amount of insoluble-mineral precipitate present in the milk beverage after storage for a period of 7 to 10 days is not greater than 240, with the amount of insoluble-mineral precipitate at the completion of the production being taken as 100 .

[0010] More specifically, we have made intensive studies in order to solve the problems, and thereby have come to provide a calcium fortified milk beverage characterized in that the milk beverage contains a milk component, an insoluble ingredient of calcium and a dispersant comprising  $\kappa$ -carrageenan and an amount of calcium precipitate present in the milk beverage after 10 days' storage is not greater than 120, with the amount of calcium precipitate at the completion of the production being taken as 100.

In addition, we have made intensive studies in order to solve the problems, and thereby have come to provide a magnesium fortified milk beverage characterized in that the

milk beverage contains a milk component, an insoluble ingredient of magnesium and a dispersant comprising  $\kappa$ -carrageenan and an amount of magnesium precipitate present in the milk beverage after 7 days' storage is not greater than 149, with the amount of magnesium precipitate at the completion of the production being taken as 100.

Further, we have made intensive studies in order to solve the problems, and thereby have come to provide an iron fortified milk beverage characterized in that the milk beverage contains a milk component, an insoluble ingredient of iron and a dispersant comprising  $\kappa$ -carrageenan and an amount of iron precipitate present in the milk beverage after 7 days' storage is not greater than 240, with the amount of iron precipitate at the completion of the production being taken as 100.

[0011] In other words, what is provided by the invention is an insoluble mineral fortified milk beverage characterized in that the milk beverage contains a milk component, an insoluble mineral and a dispersant comprising  $\kappa$ -carrageenan and, when the amount of calcium precipitate at the completion of the production is taken as 100, the amount of insoluble-mineral precipitate is not greater than 240 after storage for a period of 7 to 10 days. And it is particularly preferable in the invention that, in a case where the insoluble mineral is an insoluble ingredient of calcium, the amount of precipitate present in a calcium fortified milk beverage after 15 day's storage is not greater than 130, in a case where the insoluble mineral is an insoluble ingredient of magnesium, the amount of precipitate present in a magnesium fortified milk beverage after 15 days' storage is not greater than 205, and in a case where the insoluble mineral is an insoluble ingredient of iron, the amount of precipitate present in an iron fortified milk beverage after 15 days' storage is not greater than 400.

[0012] The term "an amount of insoluble mineral precipitate" as used herein refers to a value obtained directly by insoluble-mineral concentration measurement made on a lower layer (a lower part occupied 1/10 of the whole) of a milk beverage, such as milk, a milk beverage or a refreshing milk drink, according to ICP (Inductively Coupled Plasma) atomic

emission spectroscopy. The smaller the measurement value, the smaller the amount of insoluble mineral precipitate newly formed and the better the quality of the milk beverage.

[0013] Features of the invention can be seen from Examples (including Comparative Examples) described hereafter and Fig. 1 showing data obtained therein. Figure 1 is a distribution graph made by plotting the amount of calcium precipitate in a calcium fortified milk beverage, which is shown as a relative value, with the amount of precipitate just after production being taken as 100, versus the number of days lapsed under storage. From these data, a straight line given by the expression  $y=100+2x$  can be apparently drawn between data obtained in two of Examples and data obtained in one of Comparative Examples. More specifically, when the amount of calcium precipitate present in the milk beverage after 10 days' storage at 10°C is not greater than 120 and that after 15 days' storage at 10°C is not greater than 130, with the amount of calcium precipitate at the completion of the production being taken as 100, the calcium fortified milk beverage is regarded as having good quality. And with the amount of calcium precipitate at the completion of the production being taken as 100, the calcium fortified milk beverage is regarded as having better quality when the amount of calcium precipitate present therein after 10 days' storage at 10°C is not greater than 118 and that after 15 days' storage at 10°C is not greater than 127, it is regarded as having far better quality when the amount of calcium precipitate present therein after 10 days' storage at 10°C is not greater than 117 and that after 15 days' storage at 10°C is not greater than 126, and it is regarded as having further better quality when the amount of calcium precipitate present therein after 10 days' storage at 10°C is not greater than 116 and that after 15 days' storage at 10°C is not greater than 124.

[0014] The invention is an invention taking full advantage of a feature of  $\kappa$ -carrageenan without using any other food additives, and the feature thereof comes from such a  $\kappa$ -carrageenan's action that  $\kappa$ -carrageenan reacts with a milk component to form superfine, flowability-rich microgels and the microgels adsorb calcium on their surfaces, thereby

preventing secondary aggregation of calcium particles.

More specifically, in order to provide a calcium fortified milk beverage which a minimum amount of additive is incorporated into and thereby becomes capable of prolonged storage, the invention has figured out the most effective amount of  $\kappa$ -carrageenan to be incorporated by itself with respect to the amount of a calcium fortified milk beverage as a whole. For instance, it is preferable that, to the total amount of calcium fortified milk beverage, (a) a milk component in a proportion of 3 weight% or higher on a nonfat milk solids basis, (b) an insoluble ingredient of calcium in a proportion of 0.01 to 0.5 weight% on a calcium basis and (c) a dispersant comprising  $\kappa$ -carrageenan in a proportion of 0.005 to 0.02 weight% are compounded. In the thus compounded calcium fortified milk beverage, the amount of calcium precipitate in a lower layer after storage has been calculated as a relative value, with the calcium concentration in a lower layer (lower part occupied 1/10 of the whole) of the milk beverage just after production being taken as 100, and the amount of calcium precipitate has become 120 or smaller after 10 days' storage.

[0015] Another feature of the invention can be seen from Examples (including Comparative Examples) described hereafter and Fig. 2 showing data obtained therein. Figure 2 is a distribution graph made by plotting the amount of magnesium precipitate in a magnesium fortified milk beverage, which is shown as a relative value, with the amount of precipitate just after production being taken as 100, versus the number of days lapsed under storage. From these data, a straight line given by the expression  $y=100+7x$  can be apparently drawn between data obtained in one of Examples and data obtained in one of Comparative Examples. And with the amount of magnesium precipitate present at the completion of the production being taken as 100, the magnesium fortified milk beverage is regarded as having good quality when the amount of magnesium precipitate present after 7 days' storage at 10°C is not greater than 149 and that after 15 days' storage at 10°C is not greater than 205, it is regarded as having better quality when the amount of magnesium precipitate present after 7 days' storage at 10°C

is not greater than 142 and that after 15 days' storage at 10°C is not greater than 190, it is regarded as having far better quality when the amount of magnesium precipitate present after 7 days' storage at 10°C is not greater than 135 and that after 15 days' storage at 10°C is not greater than 175, and it is regarded as having further better quality when the amount of magnesium precipitate present after 7 days' storage at 10°C is not greater than 116 and that after 15 days' storage at 10°C is not greater than 124.

[0016] The invention is an invention taking full advantage of a feature of  $\kappa$ -carrageenan without using any other food additives, and a feature thereof comes from such a  $\kappa$ -carrageenan's action that  $\kappa$ -carrageenan reacts with a milk component to form superfine, flowability-rich microgels and the microgels adsorb magnesium on their surfaces, thereby preventing secondary aggregation of magnesium particles.

More specifically, in order to provide a magnesium fortified milk beverage which a minimum amount of additive is incorporated into and thereby becomes capable of prolonged storage, the invention has figured out the most effective amount of  $\kappa$ -carrageenan to be incorporated by itself with respect to the amount of a magnesium fortified milk beverage as a whole. For instance, it is preferable that, to the total amount of magnesium fortified milk beverage, (a) a milk component in a proportion of 3 weight% or higher on a nonfat milk solids basis, (b) an insoluble ingredient of magnesium in a proportion of 0.001 to 0.2 weight% on a magnesium basis and (c) a dispersant comprising  $\kappa$ -carrageenan in a proportion of 0.005 to 0.02 weight% are compounded. In the thus compounded magnesium fortified milk beverage, the amount of magnesium precipitate in a lower layer after storage has been calculated as a relative value, with the magnesium concentration in a lower layer (lower part occupied 1/10 of the whole) of the milk beverage just after production being taken as 100, and the amount of magnesium precipitate after 7 days' storage has become 149 or smaller.

[0017] Still another feature of the invention can be seen from Examples (including Comparative Examples) described hereafter and Fig. 3 showing data obtained therein.

Figure 3 is a distribution graph made by plotting the amount of iron precipitate in an iron fortified milk beverage, which is shown as a relative value, with the amount of precipitate just after production being taken as 100, versus the number of days lapsed under storage. From these data, a straight line given by the expression  $y=100+20x$  can be apparently drawn between data obtained in one of Examples and data obtained in one of Comparative Examples. More specifically, with the amount of iron precipitate present at the completion of the production being taken as 100, the iron fortified milk beverage is regarded as having good quality when the amount of iron precipitate present after 7 days' storage at 10°C is not greater than 240 and that after 15 days' storage at 10°C is not greater than 400, it is regarded as having better quality when the amount of iron precipitate present after 7 days' storage at 10°C is not greater than 226 and that after 15 days' storage at 10°C is not greater than 370, it is regarded as having far better quality when the amount of iron precipitate present after 7 days' storage at 10°C is not greater than 212 and that after 15 days' storage at 10°C is not greater than 340, and it is regarded as having further better quality when the amount of iron precipitate present after 7 days' storage at 10°C is not greater than 205 and that after 15 days' storage at 10°C is not greater than 325.

[0018] The invention is an invention taking full advantage of a feature of  $\kappa$ -carrageenan without using any other food additives, and a feature thereof comes from such a  $\kappa$ -carrageenan's action that  $\kappa$ -carrageenan reacts with a milk component to form superfine, flowability-rich microgels and the microgels adsorb iron on their surfaces, thereby preventing secondary aggregation of iron particles.

More specifically, in order to provide an iron fortified milk beverage which a minimum amount of additive is incorporated into and thereby becomes capable of prolonged storage, the invention has figured out the most effective amount of  $\kappa$ -carrageenan to be incorporated by itself with respect to the amount of an iron fortified milk beverage as a whole. For instance, it is preferable that, to the total amount of iron fortified milk beverage, (a) a milk

component in a proportion of 3 weight% or higher on a nonfat milk solids basis, (b) an insoluble ingredient of iron in a proportion of 0.0001 to 0.005 weight% on an iron basis and (c) a dispersant comprising  $\kappa$ -carrageenan in a proportion of 0.005 to 0.02 weight% are compounded. In the thus compounded iron fortified milk beverage, the amount of iron precipitate in a lower layer after storage has been calculated as a relative value, with the iron concentration in a lower layer (lower part occupied 1/10 of the whole) of the milk beverage just after production being taken as 100, and the amount of iron precipitate after 7 days' storage has become not greater than 240.

[0019] The invention also provides a method for producing a calcium fortified milk beverage, and the method is characterized by incorporating into a milk beverage (a) a milk component, (b) an insoluble ingredient of calcium and (c) a dispersant comprising  $\kappa$ -carrageenan in proportions of 3 weight% or higher on a nonfat milk solids basis, 0.01 to 0.5 weight% on a calcium basis and 0.005 to 0.02 weight%, respectively, to the total amount of milk beverage, and controlling the amount of calcium precipitate in the milk beverage after 10 days' storage, wherein a milk component, an insoluble ingredient of calcium and a dispersant comprising  $\kappa$ -carrageenan are incorporated, to 120 or smaller, with the amount of calcium precipitate at the completion of the production being taken as 100.

[0020] With the calcium fortified milk beverage obtained, the invention provides a method of producing the calcium fortified milk beverage by incorporating into a milk beverage (a) a milk component, (b) an insoluble ingredient of calcium and (c) a dispersant comprising  $\kappa$ -carrageenan in proportions of 3 weight% or higher on a nonfat milk solids basis, 0.01 to 0.5 weight% on a calcium basis and 0.005 to 0.02 weight%, respectively, to the total amount of milk beverage. To the present method of production, preparation methods general in this technical field can be applied except for the amounts of ingredients incorporated.

In the invention, a heat pasteurization process or a heat sterilization process may further be added to the method of production.

Likewise, the invention can also provide a method for producing a magnesium fortified milk beverage. And the method is characterized by incorporating into a milk beverage (a) a milk component, (b) an insoluble ingredient of magnesium and (c) a dispersant comprising  $\kappa$ -carrageenan in proportions of 3 weight% or higher on a nonfat milk solids basis, 0.001 to 0.2 weight% on a magnesium basis and 0.005 to 0.02 weight%, respectively, to the total amount of milk beverage, and besides, the method is characterized in that the amounts of magnesium precipitates in the milk beverage after 7 days' storage and 15 days' storage, wherein a milk component, an insoluble ingredient of magnesium and a dispersant comprising  $\kappa$ -carrageenan are incorporated, are controlled to 149 or smaller and 205 or smaller, respectively, with the amount of magnesium precipitate at the completion of the production being taken as 100.

[0021] With the magnesium fortified milk beverage obtained, the invention provides a method of producing the magnesium fortified milk beverage by incorporating into a milk beverage (a) a milk component, (b) an insoluble ingredient of magnesium and (c) a dispersant comprising  $\kappa$ -carrageenan in proportions of 3 weight% or higher on a nonfat milk solids basis, 0.001 to 0.2 weight% on a magnesium basis and 0.005 to 0.02 weight%, respectively, to the total amount of milk beverage. To the present method of production, preparation methods general in this technical field can be applied except for the amounts of ingredients incorporated.

In the invention, a heat pasteurization process or a heat sterilization process may further be added to the method of production.

[0022] As in the cases mentioned above, the invention can further provide a method for production of an iron fortified milk beverage. And the method is characterized by incorporating into a milk beverage (a) a milk component, (b) an insoluble ingredient of iron and (c) a dispersant comprising  $\kappa$ -carrageenan in proportions of 3 weight% or higher on a nonfat milk solids basis, 0.0001 to 0.005 weight% on an iron basis and 0.005 to 0.02 weight%,

respectively, to the total amount of milk beverage, and besides, the method is characterized in that the amounts of iron precipitates in the milk beverage after 7 days' storage and 15 days' storage, wherein a milk component, an insoluble ingredient of iron and a dispersant comprising  $\kappa$ -carrageenan are incorporated, are controlled to 240 or smaller and 400 or smaller, respectively, with the amount of iron precipitate at the completion of the production being taken as 100.

[0023] With the iron fortified milk beverage obtained, the invention provides a method of producing the iron fortified milk beverage by incorporating into a milk beverage (a) a milk component, (b) an insoluble ingredient of iron and (c) a dispersant comprising  $\kappa$ -carrageenan in proportions of 3 weight% or higher on a nonfat milk solids basis, 0.0001 to 0.005 weight% on an iron basis and 0.005 to 0.02 weight%, respectively, to the total amount of milk beverage. To the present method of production, preparation methods general in this technical field can be applied except for the amounts of ingredients incorporated.

In the invention, a heat pasteurization process or a heat sterilization process may further be added to the method of production.

### **Mode for Carrying Out the Invention**

[0024] The invention is illustrated below with the case of calcium taken as an example. In other cases, including the cases of magnesium and iron, the invention can be illustrated in common with the case of calcium.

[0025] The term "a milk component" used in the invention has no particular limitation so long as it originates in animal milk, vegetable milk, milk material derived from artificial milk and milk processed food. The term animal milk refers to mammal's milk, such as cow's milk, sheep's milk or water buffalo's milk, the term vegetable milk refers to milk derived from vegetable, such as bean milk or soybean milk, and the term artificial milk refers to milk prepared artificially by emulsifying oils and fats for cooking use and water with the aid of an emulsifier or the like. The term milk processed food is intended to include all the foods

produced by processing milk and, to take cow's milk as an example of the milk, they include raw milk, concentrated milk, skim milk, powdered skim milk, concentrated skim milk, whole milk powder, concentrated whole milk, condense milk, cream, butter, cheese and fermented milk.

[0026] The term "calcium fortified milk beverage" as used in the invention (hereafter referred simply to as "milk beverage") is intended to include e.g. calcium fortified cow's milk, processed milk, lactic acid bacteria beverages and milk component-containing coffee, tea, powdered green tea, cocoa and fruit juice beverages. The content of milk component in the milk beverage is, on a nonfat milk solids basis, preferably 3 weight% or higher, far preferably 4 weight% or higher, further preferably 6 weight% or higher, furthermore preferably 8 weight% or higher.

[0027] Calcium incorporated in the present milk beverage is calcium from an insoluble calcium salt. Besides using pulverized calcium carbonate, similar effects can also be achieved by using calcium formulations resistant to sticking of precipitates through the formation of slurry (chelation).

[0028] Examples of an insoluble calcium salt made into slurry which can be used in the invention include a calcium carbonate slurry and a calcium phosphate slurry, but not limited to these salts and any of insoluble calcium salts capable of being made into slurry may be used. The calcium carbonate to be made into slurry may be calcium carbonate of limestone origin, and the calcium phosphate to be made into slurry may be calcium phosphate of cow's milk origin or phosphorus ore origin.

The insoluble ingredient of calcium incorporated in the present milk beverage is an insoluble calcium salt, preferably an insoluble calcium salt made into slurry. The insoluble calcium salt has no particular restrictions as to its average grain size, but the average grain size thereof is preferably at most 100  $\mu\text{m}$ , far preferably at most 75  $\mu\text{m}$ , further preferably at most 50  $\mu\text{m}$ , furthermore preferably at most 25  $\mu\text{m}$ , particularly preferably at most 10  $\mu\text{m}$ ,

most preferably at most 1  $\mu\text{m}$ .

[0029] Such an insoluble ingredient of calcium as mentioned above is incorporated in a proportion of 0.01 to 0.5 weight%, preferably 0.01 to 0.4 weight%, on a calcium basis, to the total amount of milk beverage. It is undesirable that the concentration of an insoluble ingredient of calcium in a milk beverage is higher than 0.5 weight% on a calcium basis, because the milk beverage comes to form precipitates and have a gritty taste.

Such an insoluble ingredient of magnesium as mentioned above is incorporated in a proportion of 0.001 to 0.2 weight%, preferably 0.001 to 0.1 weight%, on a magnesium basis, to the total amount of milk beverage. It is undesirable that the concentration of an insoluble ingredient of magnesium in a milk beverage is higher than 0.2 weight% on a magnesium basis, because the milk beverage comes to form precipitates and have a gritty taste.

Such an insoluble ingredient of iron as mentioned above is incorporated in a proportion of 0.0001 to 0.005 weight%, preferably 0.0001 to 0.004 weight%, on an iron basis, to the total amount of milk beverage. It is undesirable that the concentration of an insoluble ingredient of iron in a milk beverage is higher than 0.005 weight% on an iron basis, because the milk beverage comes to form precipitates and have a gritty taste.

[0030] The amount of  $\kappa$ -carrageenan incorporated in a milk beverage is from 0.005 to 0.02 weight%, particularly preferably from 0.005 to 0.01 weight%, with respect to the total amount of milk beverage. With incorporation of  $\kappa$ -carrageenan alone in an amount in the foregoing range, the milk beverage can have the effect of becoming capable of prolonged storage by the use of the fewest possible additives. The  $\kappa$ -carrageenan has no particular restriction as to species of its origin. In the concrete, commercially available ones, such as Carrageenin CSK-1 (manufactured by San-Ei Gen F.F.I. Inc.) and SunColor V10 (manufactured by Taiyo Kagaku Co., Ltd.), can be used.

[0031] Because  $\kappa$ -carrageenan has a drawback that it resists being dispersed and dissolved in cold water, there is a necessity to prepare a dispersant by dispersing and dissolving

$\kappa$ -carrageenan in advance and then mix the dispersant with a milk beverage and other ingredients. Additionally, although into milk beverages were incorporated carrageenans other than  $\kappa$ -carrageenan or gummy substances in place of  $\kappa$ -carrageenan in amounts (from 0.005 to 0.02 weight%) equivalent to that of  $\kappa$ -carrageenan, the resulting milk beverages were unable to produce effects of the invention.

[0032] In the case of actually using the dispersant, it is appropriate that  $\kappa$ -carrageenan powder be dispersed in advance into e.g. hot water having a temperature of 30°C to 80°C and then put to use. Additionally, the milk beverage prepared by compounding the foregoing ingredients in specified proportions can be subjected to heat sterilization treatment. And it is instanced to carry out the heat sterilization treatment under the condition of continuing heating at 65°C for at least 30 minutes which is equivalent to the sterilizing condition for cow's milk, milk beverages and the like. More specifically, the sterilizing condition can be chosen appropriately from a low-temperature sterilization condition under which a heating temperature of 65°C is kept for at least 30 minutes, a high-temperature short-time sterilization condition under which a heating temperature of 85°C is kept for at least 15 seconds or a heating temperature of 130°C is kept for at least 2 seconds, or a UHT sterilization condition under which a temperature of 140°C is kept for at least 2 seconds.

[0033] Into the present calcium, magnesium or iron fortified milk beverage, usually-used auxiliary ingredients, such as a pH adjusting agent, an emulsifier, a stabilizer and a flavor, can be mixed as appropriate according to the type of beverage (coffee, tea or so on). The auxiliary ingredients in the present milk beverage have no particular limitations so long as the mixing of them into milk beverages is well-known in technological common sense at the time of application of the invention.

## **Examples**

[0034] The invention will now be illustrated in more detail by reference to examples given below. However, the invention should not be construed as being limited to these examples

in any way. An ingredient CSK-1 used in the examples signifies Carrageenin CSK-1, an example of  $\kappa$ -carrageenan. As to the average grain sizes of insoluble minerals, mention is made of measured values in measurements using a grain-size distribution analyzer (a laser diffraction type grain size distribution measuring apparatus SALD-2001 System (made by Shimadzu Corporation) ).

[0035] (Example 1)

A milk beverage base was prepared by mixing 15.0 weight% of raw milk, 9.1 weight% of powdered skim milk, 1.8 weight% of salt-free butter, 1.76 weight% of an insoluble calcium salt slurry (having a calcium content of 15 weight%), 0.01 weight% of CSK-1 and water as an ingredient in a proportion to make the total 100 weight%. The CSK-1 was dispersed and dissolved in advance into a portion of the water as an ingredient, and then admixed as a dispersant with the other ingredients. The composition of the thus prepared milk beverage base contained 2.2 weight% of milk fat, 9.8 weight% of nonfat milk solids and 0.38 weight% of calcium.

[0036] The milk beverage base was homogenized at 130°C for 2 seconds by means of a plate-type heat exchanging method, sterilized and then subjected to cooling treatment. After the cooling treatment, the milk beverage was charged into a 1L sterilized polycarbonate vessel, and stored at 10°C for 15 days at the maximum. After a period of storage, the supernatant constituting 90% of the milk beverage was removed by sucking out gently with a pipette so as not to involve a calcium precipitate having fallen on the bottom, and then calcium concentration measurements were made on the remainder constituting 10% of the milk beverage in accordance with ICP (Inductively Coupled Plasma) atomic emission spectroscopy. The calcium concentration thus determined was taken as the amount of precipitate. When the amount of precipitate just after the production (at the time of start of the storage) was taken as 100, the amount of precipitate after 5 days' storage was found to be 101, that after 10 days' storage was found to be 108 and that after 15 days' storage was found to be 118. The

change in the amount of precipitate has been shown using a mark “■” in Fig. 1.

[0037] (Example 2)

A milk beverage was prepared in the same manner as in Example 1, except that the amount of CSK-1 admixed was changed to 0.005 weight%. The composition of the thus prepared milk beverage contained 2.2 weight% of milk fat, 9.8 weight% of nonfat milk solids and 0.39 weight% of calcium. The milk beverage charged into the vessel was stored at 10°C for 15 days at the maximum, and amounts of precipitates formed under storage were measured. When the amount of precipitate just after the production (at the time of start of the storage) was taken as 100, the amount of precipitate after 4 days' storage was found to be 103, that after 10 days' storage was found to be 111 and that after 15 days' storage was found to be 114. The change in the amount of precipitate has been shown using a mark “▲” in Fig. 1.

### **Comparative Examples**

[0038] (Comparative Example 1)

A milk beverage was prepared in the same manner as in Example 1, except that CSK-1 was not admixed. The composition of the thus prepared milk beverage contained 2.2 weight% of milk fat, 9.8 weight% of nonfat milk solids and 0.39 weight% of calcium. The milk beverage charged into the vessel was stored at 10°C for 15 days at the maximum, and amounts of precipitates formed under storage were measured. When the amount of precipitate just after the production (at the time of start of the storage) was taken as 100, the amount of precipitate after 5 days' storage was found to be 113, that after 10 days' storage was found to be 125 and that after 15 days' storage was found to be 145. The change in the amount of precipitate has been shown using a mark “●” in Fig. 1.

[0039] (Comparative Example 2)

A milk beverage was prepared in the same manner as in Example 1, except that 0.01 % of  $\lambda$ -carrageenan was admixed in place of CSK-1, and charged into a sterilized glass

bottle. The composition of the thus prepared milk beverage contained 2.2 weight% of milk fat, 9.8 weight% of nonfat milk solids and 0.39 weight% of calcium. The glass bottle charged with the milk beverage was stored at 10°C for 14 days, and then the inside bottom part thereof was visually checked. In the visual check, an increase in the amount of precipitate was found as in the case of Comparative Example 1.

[0040] (Comparative Example 3)

A milk beverage was prepared in the same manner as in Example 1, except that 0.01 % of ι-carrageenan was admixed in place of CSK-1, and charged into a sterilized glass bottle. The composition of the thus prepared milk beverage contained 2.2 weight% of milk fat, 9.8 weight% of nonfat milk solids and 0.39 weight% of calcium. The glass bottle charged with the milk beverage was stored at 10°C for 14 days, and then the inside bottom part thereof was visually checked. In the visual check, an increase in the amount of precipitate was found as in the case of Comparative Example 1.

[0041] (Comparative Example 4)

A milk beverage was prepared in the same manner as in Example 1, except that 0.01 % of xanthan gum was admixed in place of CSK-1, and charged into a sterilized glass bottle. The composition of the thus prepared milk beverage contained 2.2 weight% of milk fat, 9.8 weight% of nonfat milk solids and 0.39 weight% of calcium. The glass bottle charged with the milk beverage was stored at 10°C for 14 days, and then the inside bottom part thereof was visually checked. In the visual check, an increase in the amount of precipitate was found as in the case of Comparative Example 1.

[0042] (Comparative Example 5)

A milk beverage was prepared in the same manner as in Example 1, except that 0.01 % of guar gum was admixed in place of CSK-1, and charged into a sterilized glass bottle. The composition of the thus prepared milk beverage contained 2.2 weight% of milk fat, 9.8 weight% of nonfat milk solids and 0.39 weight% of calcium. The glass bottle charged with

the milk beverage was stored at 10°C for 14 days, and then the inside bottom part thereof was visually checked. In the visual check, an increase in the amount of precipitate was found as in the case of Comparative Example 1.

[0043] (Comparative Example 6)

A milk beverage was prepared in the same manner as in Example 1, except that 0.01 % of Locust bean gum was admixed in place of CSK-1, and charged into a sterilized glass bottle. The composition of the thus prepared milk beverage contained 2.2 weight% of milk fat, 9.8 weight% of nonfat milk solids and 0.39 weight% of calcium. The glass bottle charged with the milk beverage was stored at 10°C for 14 days, and then the inside bottom part thereof was visually checked. In the visual check, an increase in the amount of precipitate was found as in the case of Comparative Example 1.

[0044] (Comparative Example 7)

A milk beverage was prepared in the same manner as in Example 1, except that 0.01 % of native gellan gum was admixed in place of CSK-1. The composition of the thus prepared milk beverage contained 2.2 weight% of milk fat, 9.8 weight% of nonfat milk solids and 0.39 weight% of calcium. By the storage of the charged milk beverage at 10°C for 14 days, the amount of precipitate increased as in the case of Comparative Example 1.

[0045] (Comparative Example 8)

A milk beverage was prepared in the same manner as in Example 1, except that 0.01 % of deacylation-type gellan gum was admixed in place of CSK-1. The composition of the thus prepared milk beverage contained 2.2 weight% of milk fat, 9.8 weight% of nonfat milk solids and 0.39 weight% of calcium. By the storage of the charged milk beverage at 10°C for 14 days, the amount of precipitate increased as in the case of Comparative Example 1.

[0046] (Example 3)

A milk beverage base was prepared by mixing 15.0 weight% of raw milk, 9.1

weight% of powdered skim milk, 1.8 weight% of salt-free butter, 0.084 weight% of magnesium oxide having an average grain size of 31  $\mu\text{m}$  (magnesium content: 60 weight%), 0.01 weight% of CSK-1 and water as an ingredient in a proportion to make the total 100 weight%. The CSK-1 was dispersed and dissolved in advance into a portion of the water as an ingredient, and then admixed as a dispersant with the other ingredients. The composition of the thus prepared milk beverage base contained 2.2 weight% of milk fat, 9.8 weight% of nonfat milk solids and 0.062 weight% of magnesium.

[0047] The milk beverage base was homogenized at 130°C for 2 seconds by means of a plate-type heat exchanging method, sterilized and then subjected to cooling treatment. After the cooling treatment, the milk beverage was charged into a 50 ml sterilized polypropylene vessel, and stored at 10°C for 15 days at the maximum. After a period of storage, the supernatant constituting 90% of the milk beverage was removed by sucking out gently with a pipette so as not to involve a magnesium precipitate having fallen on the bottom, and then magnesium concentration measurements were made on the remainder constituting 10% of the milk beverage in accordance with ICP (Inductively Coupled Plasma) atomic emission spectroscopy. The magnesium concentration thus determined was taken as the amount of precipitate. When the amount of precipitate just after the production (at the time of start of the storage) was taken as 100, the amount of precipitate after 7 days' storage was found to be 129 and that after 15 days' storage was found to be 139. The change in the amount of precipitate has been shown using a mark "◆" in Fig. 2.

[0048] (Comparative Example 9)

A milk beverage was prepared in the same manner as in Example 3, except that CSK-1 was not admixed. The composition of the thus prepared milk beverage contained 2.2 weight% of milk fat, 9.8 weight% of nonfat milk solids and 0.062 weight% of magnesium. The milk beverage charged into the vessel was stored at 10°C for 15 days at the maximum, and amounts of precipitates formed under storage were measured. When the amount of

precipitate just after the production (at the time of start of the storage) was taken as 100, the amount of precipitate after 7 days' storage was found to be 190 and that after 15 days' storage was found to be 214. The change in the amount of precipitate has been shown using a mark "■" in Fig. 2.

[0049] (Example 4)

A milk beverage base was prepared by mixing 15.0 weight% of raw milk, 9.1 weight% of powdered skim milk, 1.8 weight% of salt-free butter, 0.008 weight% of ferric pyrophosphate having an average grain size of 2  $\mu\text{m}$  (iron content: 24 weight%), 0.01 weight% of CSK-1 and water as an ingredient in a proportion to make the total 100 weight%. The CSK-1 was dispersed and dissolved in advance into a portion of the water as an ingredient, and then admixed as a dispersant with the other ingredients. The composition of the thus prepared milk beverage base contained 2.2 weight% of milk fat, 9.8 weight% of nonfat milk solids and 0.00192 weight% of iron.

[0050] The milk beverage base was homogenized at 130°C for 2 seconds by means of a plate-type heat exchanging method, sterilized and then subjected to cooling treatment. After the cooling treatment, the milk beverage was charged into a 50 ml sterilized polypropylene vessel, and stored at 10°C for 15 days at the maximum. After a period of storage, the supernatant constituting 90% of the milk beverage was removed by sucking out gently with a pipette so as not to involve an iron precipitate having fallen on the bottom, and then iron concentration measurements were made on the remainder constituting 10% of the milk beverage in accordance with ICP (Inductively Coupled Plasma) atomic emission spectroscopy. The iron concentration thus determined was taken as the amount of precipitate. When the amount of precipitate just after the production (at the time of start of the storage) was taken as 100, the amount of precipitate after 7 days' storage was found to be 195 and that after 15 days' storage was found to be 264. The change in the amount of precipitate has been shown using a mark "◆" in Fig. 3.

[0051] (Comparative Example 10)

A milk beverage was prepared in the same manner as in Example 4, except that CSK-1 was not admixed. The composition of the thus prepared milk beverage contained 2.2 weight% of milk fat, 9.8 weight% of nonfat milk solids and 0.00192 weight% of iron. The milk beverage charged into the vessel was stored at 10°C for 15 days at the maximum, and amounts of precipitates formed under storage were measured. When the amount of precipitate just after the production (at the time of start of the storage) was taken as 100, the amount of precipitate after 7 days' storage was found to be 1033 and that after 15 days' storage was found to be 1228. The change in the amount of precipitate has been shown using a mark "■" in Fig. 3.

[0052] (Example 5)

A milk beverage base was prepared by mixing 15.0 weight% of raw milk, 7.1 weight% of powdered skim milk, 2.9 weight% of salt-free butter, 0.173 weight% of calcium carbonate having an average grain size of 5  $\mu\text{m}$ , 0.015 weight% of CSK-1 and water as an ingredient in a proportion to make the total 100 weight%. The CSK-1 was dispersed and dissolved in advance into a portion of the water as an ingredient, and then admixed as a dispersant with the other ingredients. The composition of the thus prepared milk beverage base contained 3.0 weight% of milk fat, 8.1 weight% of nonfat milk solids and 0.18 weight% of calcium.

[0053] The milk beverage base was homogenized at 130°C for 2 seconds by means of a plate-type heat exchanging method, sterilized and then subjected to cooling treatment. After the cooling treatment, the milk beverage was charged into a 50 ml sterilized polypropylene vessel, and stored at 10°C for 7 days at the maximum. After a period of storage, the supernatant constituting 90% of the milk beverage was removed by sucking out gently with a pipette so as not to involve a calcium precipitate having fallen on the bottom, and then calcium concentration measurements were made on the remainder constituting 10% of the

milk beverage in accordance with ICP (Inductively Coupled Plasma) atomic emission spectroscopy. The calcium concentration thus determined was taken as the amount of precipitate. When the amount of precipitate just after the production (at the time of start of the storage) was taken as 100, the amount of precipitate after 7 days' storage was found to be 111.

[0054] (Comparative Example 11)

A milk beverage was prepared in the same manner as in Example 5, except that CSK-1 was not admixed. The composition of the thus prepared milk beverage contained 3.0 weight% of milk fat, 8.1 weight% of nonfat milk solids and 0.18 weight% of calcium. The milk beverage charged into the vessel was stored at 10°C for 15 days at the maximum, and amounts of precipitates formed under storage were measured. When the amount of precipitate just after the production (at the time of start of the storage) was taken as 100, the amount of precipitate after 7 days' storage was found to be 178.

### **Industrial Applicability**

[0055] According to the invention, there are provided insoluble mineral fortified milk beverages, notably milk beverages fortified by calcium, magnesium and iron, respectively, which cause neither protein precipitation by thermal coagulation nor precipitation of e.g. calcium by secondary aggregation during the production thereof, and besides, which can keep their own tastes for a long time because they have succeeded in controlling the amounts of mineral precipitates, such as calcium precipitate, to specific values or below even after a lapse of 7 days or from 10 to 15 days, and methods of producing such insoluble mineral fortified milk beverages.

### **Brief Description of the Drawings**

[0056] [Fig. 1] Graph showing distributions of amounts of calcium precipitates formed in milk beverages prepared in Examples 1 to 2 and Comparative Example 1, respectively, after storage for time periods up to 15 days.

[Fig. 2] Graph showing distributions of amounts of magnesium precipitates formed in milk beverages prepared in Example 3 and Comparative Example 9, respectively, after storage for time periods up to 15 days.

[Fig. 3] Graph showing distributions of amounts of iron precipitates formed in milk beverages prepared in Example 4 and Comparative Example 10, respectively, after storage for time periods up to 15 days.

## Claims

[Claim 1] An insoluble mineral fortified milk beverage, characterized in that the milk beverage contains a milk component in a proportion of 3weight% or higher on a nonfat milk solids basis, an insoluble mineral containing an insoluble ingredient of calcium or magnesium or iron and a dispersant comprising  $\kappa$ -carrageenan, and an amount of insoluble-mineral precipitate present in the milk beverage after storage for a period of 7 to 10 days is not greater than 240, with the amount of insoluble-mineral precipitate at the completion of the production being taken as 100,

wherein:

the insoluble ingredient of calcium is in a proportion of 0.01 to 0.5 weight% on a calcium basis;

the insoluble ingredient of magnesium is in a proportion of 0.001 to 0.2 weight% on a magnesium basis;

the insoluble ingredient of iron is in a proportion of 0.0001 to 0.005 weight% on an iron basis;

the proportion of  $\kappa$ -carrageenan is from 0.005 to 0.02 weight%; and

the values of the amount of insoluble-mineral precipitate being obtained directly by insoluble-mineral concentration made on a lower layer of the milk beverage according to Inductive Coupled Plasma atomic emission spectroscopy.

[Claim 2] A calcium fortified milk beverage, characterized in that the insoluble mineral in claim 1 is an insoluble ingredient of calcium and an amount of calcium precipitate present in the milk beverage after 10 days' storage is not greater than 120, with the amount of calcium precipitate at the completion of the production being taken as 100.

[Claim 3] A magnesium fortified milk beverage, characterized in that the insoluble material in claim 1 is an insoluble ingredient of magnesium and an amount of magnesium precipitate present in the milk beverage after 7 days' storage is not greater than 149, with the amount of magnesium precipitate at the completion of the production being taken as 100.

[Claim 4] An iron fortified milk beverage, characterized in that the insoluble mineral in claim 1 is an insoluble ingredient of iron and an amount of iron precipitate present in the milk beverage after 7 days' storage is not greater than 240, with the

amount of iron precipitate at the completion of the production being taken as 100.

[Claim 5] The calcium fortified milk beverage as described in claim 2, wherein an amount of calcium precipitate present in the milk beverage after 15 days' storage is not greater than 130, with the amount of calcium precipitate at the completion of the production being taken as 100.

[Claim 6] The magnesium fortified milk beverage as described in claim 3, wherein an amount of magnesium precipitate present in the milk beverage after 15 days' storage is not greater than 205, with the amount of magnesium precipitate at the completion of the production being taken as 100.

[Claim 7] The iron fortified milk beverage as described in claim 4, wherein an amount of iron precipitate present in the milk beverage after 15 days' storage is not greater than 400, with the amount of iron precipitate at the completion of the production being taken as 100.

[Claim 8] A method of producing the calcium fortified milk beverage as described in claim 2 and/or claim 5, characterized by incorporating into a milk beverage (a) a milk component, (b) an insoluble ingredient of calcium and (c) a dispersant comprising  $\kappa$ -carrageenan in proportions of 3 weight% or higher on a nonfat milk solids basis, 0.01 to 0.5 weight% on a calcium basis and 0.005 to 0.02 weight%, respectively, to the total amount of milk beverage.

[Claim 9] A method of producing the magnesium fortified milk beverage as described in claim 3 and/or claim 6, characterized by incorporating into a milk beverage (a) a milk component, (b) an insoluble ingredient of magnesium and (c) a dispersant comprising  $\kappa$ -carrageenan in proportions of 3 weight% or higher on a nonfat milk solids basis, 0.001 to 0.2 weight% on a magnesium basis and 0.005 to 0.02 weight%, respectively, to the total amount of milk beverage.

[Claim 10] A method of producing the iron fortified milk beverage as described in claim 4 and/or claim 7, characterized by incorporating into a milk beverage (a) a milk component, (b) an insoluble ingredient of iron and (c) a dispersant comprising  $\kappa$ -carrageenan in proportions of 3 weight% or higher on a nonfat milk solids basis, 0.0001 to 0.005 weight% on an iron basis and 0.005 to 0.02 weight%, respectively, to the total amount of milk beverage.

[Claim 11] The method of production as described in claim 8 to claim 10,

characterized by including a step of compounding a milk component, an insoluble ingredient of calcium, magnesium or iron and a dispersant comprising  $\kappa$ -carrageenan and a step of performing heat pasteurization treatment or heat sterilization treatment.

[Claim 12] The method of production as described in any one of claims 8 to 11, characterized in that the milk beverage is cow's milk, processed milk, a lactic acid bacteria beverage or a milk component-containing coffee, tea, powdered green tea, cocoa or fruit juice beverage.