

[DESCRIPTION]

[TITLE OF INVENTION]

REFRIGERANT PACK

[Technical Field]

5 [0001]

The present invention relates to a refrigerant pack including a refrigerant composition in which a change in color during cooling can be easily observed.

Priority is claimed on Japanese Patent Application No. 2014-221679, filed October 30, 2014, the content of which is incorporated herein by reference.

10 [Background Art]

[0002]

Refrigerant packs are widely used for cooling various fresh items when they are stored or transported and are typically, used repeatedly. Such refrigerant packs have configurations that include a refrigerant composition having a cooling effect and the refrigerant composition is enclosed in a container having thermal conductivity.

As the refrigerant composition, a refrigerant composition containing a coloring agent so that the presence thereof is easily observed from the outside of the refrigerant pack is known. For example, a refrigerant pack in which a refrigerant composition colored with a dye is enclosed and the enclosed amount can be easily observed from the outside is disclosed (refer to Patent Document 1).

[0003]

However, the refrigerant pack described in Patent Document 1 has problems in that, even though the refrigerant composition contains a dye, it is difficult to observe a cooling state, for example, whether the refrigerant composition is frozen, and it is difficult to observe a cooling state or whether the refrigerant pack is sufficiently cooled to

a desired temperature to which cooling is possible.

[Citation List]

[Patent Literature]

[0004]

5 [Patent Document 1]

Japanese Unexamined Patent Application, First Publication No. 2006-97984

[Summary of Invention]

[Technical Problem]

[0005]

10 The present invention provides a refrigerant pack in which it is possible to easily observe whether the cooling state is in a desired state.

[Solution to Problem]

[0006]

The present invention provides a refrigerant pack including a refrigerant
15 composition that contains water, an inorganic salt, a thickener and a pH indicator. The thickener is a polysaccharide. In the refrigerant composition, pH(A) when all ingredients other than the inorganic salt and water are substituted with water is 7.0 or more and a relation of the following expression (I) is satisfied.

$$\text{pKa of pH indicator}-0.5 \leq \text{pH(A)} \leq \text{pKa of pH indicator}+3.5 \cdots (I)$$

20 [0007]

In the refrigerant pack of the present invention, a pH of the refrigerant composition may satisfy a relation of the following expression (II).

$$\text{pKa of pH indicator}-0.5 \leq \text{pH of refrigerant composition} \leq \text{pKa of pH indicator}+3.5 \cdots (II)$$

25 In the refrigerant pack of the present invention, in the refrigerant composition,

pH(B) when all ingredients other than the thickener and water are substituted with water may be 5.0 to 9.0.

In the refrigerant pack of the present invention, in the refrigerant composition, the amount of the inorganic salt may be 0.5 to 33 mass%, the amount of the thickener
5 may be 0.1 to 10 mass%, and the amount of the pH indicator may be 1 to 30 ppm.

[0008]

In the refrigerant pack of the present invention, the pH indicator has a pKa that may be 4.0 to 11.8.

In the refrigerant pack of the present invention, the inorganic salt may be one or
10 more types selected from the group including hydrochlorides, sulfates, nitrates, carbonates, hydrogen phosphates, bicarbonates, phosphates, alkali metal chlorides and alkaline earth metal chlorides.

In the refrigerant pack of the present invention, the thickener may be one or more types selected from the group including carboxyalkyl celluloses, guar gum,
15 hydroxyalkyl guar gums, pectin, xanthan gum, tamarind gum and carrageenan.

[Advantageous Effects of Invention]

[0009]

In the refrigerant pack of the present invention, it is possible to easily observe whether the cooling state is in a desired state.

20 [Description of Embodiments]

[0010]

Exemplary examples of a refrigerant pack of the present invention will be described below. However, the present invention is not limited to such examples. For example, additions, omissions, substitutions, and other modifications (for example,
25 amounts, numbers, positions, and sizes) can be made without departing from the spirit

and scope of the present invention.

[0011]

The refrigerant pack of the present invention is a refrigerant pack containing a refrigerant composition that includes water, an inorganic salt, a thickener and a pH indicator. The thickener is a polysaccharide thickener. The refrigerant composition has pH(A) that is 7.0 or more when all ingredients other than the inorganic salt and water are substituted with water and satisfy the relation of the following expression (I).

$$\text{pKa of pH indicator} - 0.5 \leq \text{pH(A)} \leq \text{pKa of pH indicator} + 3.5 \cdots (I)$$

[0012]

In the refrigerant pack, a color of the refrigerant composition influenced by color development of the pH indicator greatly differs before and after freezing. Therefore, it is possible to easily observe whether the cooling state is a desired state (a state in which an object can be sufficiently cooled). Therefore, the color of the refrigerant composition before and after freezing is not mainly influenced by colors of the ingredients themselves other than the pH indicator such as the inorganic salt and the thickener.

[0013]

pH(A) is a pH of a replacement composition when all ingredients other than the inorganic salt and water are substituted with water in the refrigerant composition and corresponds to a pH of inorganic salt-containing water (for example, an inorganic salt aqueous solution) that contains only the inorganic salt in the same amount (mass%) as the amount (mass%) in the refrigerant composition.

pH(A) is preferably a pH at a temperature at which the pH indicator is dissolved in the refrigerant composition, more preferably a pH when the inorganic salt-containing water has any temperature in the range of 23 to 27 °C, and most preferably a pH when

the inorganic salt-containing water has a temperature of 25 °C.

[0014]

pH(A) is 7.0 or more, preferably 7.05 or more, and more preferably 7.1 or more.

In addition, pH(A) is preferably 12.2 or less and more preferably 11.8 or less.

5 [0015]

In the refrigerant composition, a pH of a replacement composition when all ingredients other than the thickener and water are substituted with water is set as “pH(B).” In other words, pH(B) is a pH of thickener-containing water (for example, a thickener aqueous solution) that contains only the thickener in the same amount (mass%)
10 as the amount (mass%) in the refrigerant composition.

pH(B) is preferably a pH at a temperature at which the pH indicator is dissolved in the refrigerant composition, more preferably a pH when the thickener-containing water has any temperature in the range of 23 to 27 °C, and most preferably a pH when the thickener-containing water has a temperature of 25 °C.

15 [0016]

pH(B) is preferably 5.0 or more and more preferably 6.0 or more. In addition, pH(B) is still more preferably 9.0 or less and most preferably 8.2 or less.

[0017]

In the refrigerant composition, polysaccharides are used as the thickener, and an
20 inorganic salt that adjusts the acidity of the refrigerant composition, influences color development of the pH indicator and in which an aqueous solution thereof with a predetermined concentration has a pH in a specific range is used as the inorganic salt. Further, a pH indicator having a suitable color changing range is combined with the thickener and the inorganic salt. Therefore, a change in color depending on a change in
25 color development of the pH indicator or the presence or absence thereof significantly

increases.

The components will be described below.

[0018]

The inorganic salt (a salt of an inorganic compound) functions as one
5 component of the refrigerant. The freezing temperature of the refrigerant composition
is determined mainly according to the type and the amount thereof.

In addition, the inorganic salt does not correspond to the pH indicator and is a
component that may precipitate in a crystalline or non-crystalline (amorphous) form
when the refrigerant composition is frozen and may influence a change in color of the
10 refrigerant composition due to the precipitation. As described above, the color of the
refrigerant composition before and after freezing is mainly influenced by a color that
develops when color development of the pH indicator occurs, but the color of the
refrigerant composition after freezing (during freezing) is influenced somewhat by the
color (usually white) of a precipitated inorganic salt.

15 [0019]

The amount of the inorganic salt dissolved in the refrigerant composition before
freezing and preferably at 0 °C or more is preferably larger. Within the total amount of
the inorganic salt, the amount of a dissolved inorganic salt is preferably 90 mass% or
more, more preferably 95 mass% or more, and most preferably 98 mass% or more, and
20 may be 100 mass% (the total amount).

In addition, in the refrigerant composition after freezing, the amount of the
inorganic salt that precipitates is preferably 90 mass% or more, more preferably 95
mass% or more, and most preferably 98 mass% or more, and may be 100 mass% (the
total amount).

25 [0020]

The inorganic salt is not particularly limited as long as pH(A) satisfies the above condition.

As cationic metal ions of the inorganic salt, for example, alkali metal ions such as a lithium ion (Li^+), a sodium ion (Na^+), and a potassium ion (K^+); alkaline earth metal ions such as a magnesium ion (Mg^{2+}) and a calcium ion (Ca^{2+}); transition metal ions such as iron ions (Fe^{3+} and Fe^{2+}) and copper ions (Cu^{2+} and Cu^+); and metal ions in Group 12 or 13 such as a zinc ion (Zn^{2+}) and an aluminum ion (Al^{3+}) are exemplary examples.

As cationic non-metallic ions of the inorganic salt, for example, an ammonium ion (NH_4^+) is an exemplary example.

10 [0021]

As anions of the inorganic salt, for example, halogen ions such as a chloride ion (Cl^-), a bromide ion (Br^-), and an iodide ion (I^-); a sulfate ion (SO_4^{2-}); a nitrate ion (NO_3^-); a carbonate ion (CO_3^{2-}); a bicarbonate ion (HCO_3^-); a hydrogen sulfate ion (HSO_4^-); a phosphate ion (PO_4^{3-}); a hydrogen phosphate ion (HPO_4^{2-}); a dihydrogen phosphate ion (H_2PO_4^-); a sulfite ion (SO_3^{2-}); a thiosulfate ion ($\text{S}_2\text{O}_3^{2-}$); a chlorate ion (ClO_3^-); a perchlorate ion (ClO_4^-); and ions having a group in which a hydrogen ion (H^+) is removed from an acid group such as a carboxy group ($-\text{C}(=\text{O})-\text{OH}$) or a sulfo group ($-\text{S}(=\text{O})_2-\text{OH}$) are exemplary examples.

[0022]

20 The inorganic salt is not particularly limited. For example, alkali metal chlorides such as sodium chloride (NaCl) and potassium chloride (KCl); hydrochlorides such as ammonium chloride (NH_4Cl); sulfates such as sodium sulfate (Na_2SO_4), potassium sulfate (K_2SO_4), ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$), magnesium sulfate (MgSO_4), aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$), nickel sulfate (NiSO_4), aluminum potassium sulfate ($\text{AlK}(\text{SO}_4)_2$), and ammonium alum ($\text{Al}(\text{NH}_4)(\text{SO}_4)_2$); nitrates such as sodium nitrate

25

(NaNO_3), potassium nitrate (KNO_3), ammonium nitrate (NH_4NO_3), calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), and calcium nitrate ($\text{Ca}(\text{NO}_3)_2$); carbonates such as sodium carbonate (Na_2CO_3) and potassium carbonate (K_2CO_3); bicarbonates such as potassium bicarbonate (KHCO_3) and sodium bicarbonate (NaHCO_3); alkaline earth metal chlorides such as calcium chloride (CaCl_2) and magnesium chloride (MgCl_2); dihydrogen phosphates such as sodium dihydrogen phosphate (NaH_2PO_4), potassium dihydrogen phosphate (KH_2PO_4), and ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$); hydrogen phosphates such as disodium hydrogen phosphate (Na_2HPO_4), dipotassium hydrogen phosphate (K_2HPO_4), and diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$); phosphates such as trisodium phosphate (Na_3PO_4); sulfites such as sodium sulfite (Na_2SO_3); chlorates such as potassium chlorate (KClO_3); perchlorates such as sodium perchlorate (NaClO_4); thiosulfates such as sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$); alkali metal bromides such as potassium bromide (KBr) and sodium bromide (NaBr); alkali metal iodides such as potassium iodide (KI) and sodium iodide (NaI); and borates such as borax ($\text{Na}_2\text{B}_4\text{O}_7$) are exemplary examples.

[0023]

As the inorganic salt, one type may be used alone or two or more types may be used in combination.

[0024]

As the inorganic salt, one or more types selected from the group including hydrochlorides, sulfates, nitrates, carbonates, hydrogen phosphates, bicarbonates, phosphates, alkali metal chlorides, alkaline earth metal chlorides, sulfites, chlorates, perchlorates, thiosulfates, alkali metal bromides, and alkali metal iodides and borates are preferable.

Also, as the inorganic salt, one or more types selected from the group including

hydrochlorides, sulfates, nitrates, carbonates, hydrogen phosphates, bicarbonates, phosphates, alkali metal chlorides and alkaline earth metal chlorides are more preferable.

When such an inorganic salt is used, the refrigerant composition differs considerably in color before and after freezing and has more excellent handling
5 properties.

[0025]

In consideration of the greater variety of pH indicators that can be used in combination and greater difference in the color of the refrigerant composition before and after freezing, the inorganic salt is preferably a dihydrogen phosphate or hydrogen
10 phosphate and more preferably a dihydrogen phosphate.

[0026]

Among them, in consideration of greater difference in the color of the refrigerant composition before and after freezing, the inorganic salt is most preferably one or more types selected from the group including hydrogen phosphates, carbonates, sulfates and
15 alkali metal chlorides.

[0027]

The amount of the inorganic salt in the refrigerant composition is not particularly limited as long as pH(A) has a value in a predetermined range. The amount is preferably 0.5 to 33 mass%, more preferably 1 to 31 mass%, and may be, for example,
20 0.5 to 22 mass% or 1 to 19 mass%.

[0028]

The thickener is used to increase the viscosity of the refrigerant composition. The thickener is a component not corresponding to the pH indicator and is a polysaccharide in the present invention.

25 The thickener is generally a component that is prevented from precipitating

whether or not the refrigerant composition is frozen. Also, in this specification, when it is described that “the thickener does not precipitate when the refrigerant composition freezes,” this means that the thickener solidifies while dissolved in water when the refrigerant composition freezes, and it is assumed that a large amount of molecules of the thickener do not aggregate but solidify while surrounded by water molecules and the thickener is assumed not to be in a state in which a large amount of molecules of the thickener aggregate and solidify.

[0029]

In the refrigerant composition before freezing and after freezing, the amount of the thickener that precipitates is preferably smaller. Within the total amount of the thickener, the amount of a thickener that precipitates is preferably 10 mass% or less, more preferably 5 mass% or less, and most preferably 2 mass% or less, and may be 0 mass% (the thickener may not be precipitated at all).

[0030]

The thickener (polysaccharides) is not particularly limited. For example, carboxyalkyl celluloses such as carboxymethyl cellulose (CMC); guar gum; hydroxyalkyl guar gums such as hydroxypropyl guar gum; pectin; xanthan gum; tamarind gum; and carrageenan are exemplary examples.

[0031]

As the thickener, one type may be used alone or two or more types may be used in combination.

[0032]

The amount of the thickener in the refrigerant composition is not particularly limited as long as an effect of the present invention is not impaired. The amount is preferably 0.1 to 10 mass% and more preferably 0.3 to 4 mass%.

[0033]

The pH indicator (an acid base indicator) determines a color of the refrigerant composition by reflecting whether color development thereof occurs. When the refrigerant composition includes the pH indicator, the color differs before and after
5 freezing.

[0034]

The pH indicator may be a known indicator and is not particularly limited. For example, bromocresol purple, Alizarin Yellow R, phenol red, bromophenol blue, bromocresol green, bromothymol blue, methyl yellow, congo red, methyl orange, methyl
10 red, methyl purple, phenolphthalein, litmus, p-nitrophenol, chlorophenol red, neutral red, p-naphtholphthalein, cresol red, thymol blue, and thymolphthalein are exemplary examples.

[0035]

The pH indicator has a pKa (an acid dissociation constant) that is preferably 4.0
15 or more and more preferably 5.0 or more. In addition, the pH indicator has a pKa that is still more preferably 11.8 or less and most preferably 11.5 or less.

Note that, unless otherwise described, a pKa of the pH indicator in the present invention refers to a value when the solvent is water and the temperature is 25 °C.

[0036]

20 As the pH indicator, one type may be used alone or two or more types may be used in combination. In general, one type is preferably used alone.

[0037]

The amount of the pH indicator in the refrigerant composition is not particularly limited as long as the refrigerant composition has a desired change in color. The
25 amount is preferably 1 to 30 ppm and more preferably 5 to 20 ppm.

[0038]

The refrigerant composition satisfies the relation of the above expression (I). That is, the lower limit value of pH(A) is a value that is 0.5 smaller than the pKa of the pH indicator. The upper limit value of pH(A) is a value that is 3.5 greater than the pKa
5 of the pH indicator.

Also, the lower limit value of pH(A) is preferably a value that is 0.3 smaller than the pKa of the pH indicator and is more preferably a value that is 0.1 smaller than the pKa of the pH indicator. In addition, the upper limit value of pH(A) is preferably a value that is 3.3 greater than the pKa of the pH indicator and is more preferably a value
10 that is 3.0 greater than the pKa of the pH indicator. In such ranges, the refrigerant composition differs in color before and after freezing more considerably.

[0039]

In addition to water, the inorganic salt, the thickener and the pH indicator, the refrigerant composition may include other components that do not correspond to the
15 above components within a range in which an effect of the present invention is not impaired. As the other components, for example, a solvent other than water; various known additives such as a preservative; salts other than an inorganic salt (that is, an organic salt and a salt of an organic compound); and a thickener other than polysaccharides are exemplary examples.

20 [0040]

The solvent is preferably a solvent that can dissolve the inorganic salt, the thickener, and the pH indicator. As such a solvent, alcohol is an exemplary example.

As the solvent, one type may be used alone or two or more types may be used in combination.

25 [0041]

Water and the solvent function as one of components of the refrigerant. Along with the inorganic salt, mainly according to types and amounts thereof, a freezing temperature of the refrigerant composition is determined.

In the refrigerant composition, the ratio of the amount of the solvent with respect to the total amount of water and the solvent is preferably 10 mass% or less, more preferably 5 mass% or less, and most preferably 2 mass% or less, and may be 0 mass%.
[0042]

As the preservative, for example, a food preservative and an antioxidant are exemplary examples. Sodium pyrithione, paraben (paraoxybenzoic acid ester), protamine, an organic nitrogen sulfur-based compound and the like are exemplary examples.

The amount of the preservative in the refrigerant composition may be appropriately adjusted according to a type of the preservative.
[0043]

As the organic salt, for example, a salt of an organic acid and a salt of an organic base are exemplary examples.

As the salt of the organic acid, for example, salts obtained by reacting an acid group of an organic acid such as a carboxylic acid and a sulfonic acid with an inorganic base or an organic base are exemplary examples.

As the salt of the organic base, for example, salts obtained by reacting a group including a nitrogen atom of a nitrogen-containing organic compound such as primary amines, secondary amines, and tertiary amines with an inorganic acid or an organic acid are exemplary examples.

As the organic salt, one type may be used alone or two or more types may be used in combination.

[0044]

In the refrigerant composition, the ratio of the amount of the organic salt with respect to the total amount of the inorganic salt and the organic salt (the total amount of salts) is preferably 5 mass% or less, more preferably 3 mass% or less, and most
5 preferably 1 mass% or less, and may be 0 mass%.

[0045]

As a thickener other than the polysaccharides, for example, an acrylic polymer such as polyacrylic acid and sodium polyacrylate (polyacrylic acid and salts thereof in which one or more hydrogen atoms may be substituted with a group having an atom
10 other than a hydrogen atom, and a carboxyvinyl polymer); and alkylene glycols such as propylene glycol are exemplary examples.

As the thickener other than the polysaccharides, one type may be used alone or two or more types may be used in combination.

Note that, unless otherwise described in this specification, when the “thickener”
15 is simply described, it refers to a “polysaccharide thickener.”

[0046]

In the refrigerant composition, the ratio of the amount of the thickener other than the polysaccharides with respect to the total amount of the polysaccharide thickener and other thickeners (the total amount of thickeners) is preferably 10 mass% or less, more
20 preferably 5 mass% or less, and most preferably 2 mass% or less, and may be 0 mass%.

[0047]

In the refrigerant composition, with respect to the total amount of components (the inorganic salt, the polysaccharide thickener, the pH indicator, and components other than the solvent) other than water and the solvent, the ratio of the total amount of the
25 inorganic salt, the polysaccharide thickener and the pH indicator is preferably 90 mass%

or more and more preferably 95 mass% or more, and may be 100 mass%. When the ratio of the total amount is the lower limit value or more, the refrigerant composition differs in color before and after freezing more considerably.

[0048]

- 5 In consideration of the refrigerant composition that differs in color before and after freezing more considerably, when a pH before freezing (during non-freezing) is set as pH(C), pH(C) preferably satisfies a relation of the following expression (II).

$$\text{pKa of pH indicator} - 0.5 \leq \text{pH(C)} \leq \text{pKa of pH indicator} + 3.5 \dots (\text{II})$$

[0049]

- 10 pH(C) is a pH of the refrigerant composition before freezing (during non-freezing) and is preferably a pH at a temperature at which the pH indicator is dissolved in the refrigerant composition, more preferably a pH at which the refrigerant composition has any temperature in the range of 23 to 27 °C, and most preferably a pH when the refrigerant composition has a temperature of 25 °C.

- 15 [0050]

pH(C) is preferably 5.3 or more and more preferably 6.4 or more. In addition, pH(C) is still more preferably 12.0 or less and most preferably 11.5 or less.

[0051]

- In the refrigerant composition, as described above, the lower limit value of
20 pH(C) is preferably a value that is 0.5 smaller than the pKa of the pH indicator. The upper limit value of pH(C) is preferably a value that is 3.5 greater than the pKa of the pH indicator.

- Also, the lower limit value of pH(C) is more preferably a value that is 0.4 smaller than the pKa of the pH indicator and most preferably a value that is 0.3 smaller
25 than the pKa of the pH indicator. In addition, the upper limit value of pH(C) is

preferably a value that is 3.3 greater than the pKa of the pH indicator and more preferably a value that is 3.0 greater than the pKa of the pH indicator. In such ranges, the refrigerant composition differs in color before and after freezing more considerably.

[0052]

5 The refrigerant composition is obtained by blending water, the inorganic salt, the thickener, and the pH indicator, and the other components as necessary.

A method of blending the components is not particularly limited, and can be arbitrarily adjusted such that the components are uniformly dissolved or dispersed at a temperature higher than the freezing temperature of the refrigerant composition.

10 For example, when the components are blended, mixing may be performed while adding all of the components, mixing may be performed while adding some of the components sequentially, or mixing may be performed while all of the components sequentially.

The mixing method is not particularly limited and may be appropriately selected from known methods such as a method in which a stirring bar, a stirring blade or the like is rotated for mixing; a method in which a mixer, a three-roll mill, a kneader, a bead mill or the like is used for mixing; and a method in which ultrasonic waves are applied for mixing.

[0053]

20 The refrigerant pack of the present invention includes the refrigerant composition and is configured to store the refrigerant composition using, for example, a storing unit such as a container capable of enclosing a liquid product.

The material of the storing unit is not particularly limited as long as the material has transparency to an extent at which a change in color (discoloration) of the stored refrigerant composition can be observed. Preferable examples include synthetic resins

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of a polyolefin such as polyethylene and polypropylene; a polyamide; and a polyester is an exemplary example. Among them, a polyolefin is preferable because it has excellent low temperature brittleness resistance, water resistance and chemical resistance. High density polyethylene is more preferable because it is easily molded and has a high strength.

[0054]

Since the color of the refrigerant composition differs considerably before and after freezing, it can be easily observed whether it is frozen or not. Thus, a change in color of the refrigerant composition can be observed from the outside of the refrigerant pack. Accordingly, it is possible to easily observe whether the refrigerant pack is sufficiently cooled to a desired temperature.

In addition, even if cooling and heating are repeated, that is, freezing and thawing are repeated, since an effect of the refrigerant composition is not impaired, the refrigerant pack including the refrigerant composition is suitable for repeated use.

[Examples]

[0055]

The present invention will be described in further detail below with reference to specific examples. However, the present invention is not limited to the following examples. Note that, in the following, the unit “ppm” of the amount (the blending amount and the concentration) of the pH indicator is based on a mass ratio.

[0056]

Among raw materials used in examples and comparative examples, thickeners and pH indicators are as follows.

(Thickener)

·CMC (Sodium Carboxymethyl Cellulose): “Cellogen” commercially available from

DKS Co. Ltd.

·GG (guar gum): “GUARPAK PF-20” commercially available from Sansho Co., Ltd.

·CVP (carboxyvinyl polymer): “Aronvis AH-305X” commercially available from Toagosei Co., Ltd.

5 (pH indicator)

·BCP: Bromocresol purple (commercially available from Wako Pure Chemical Industries, Ltd.)

·AYR: Alizarine Yellow R (commercially available from Wako Pure Chemical Industries, Ltd.)

10 ·PR: Phenol red (commercially available from Wako Pure Chemical Industries, Ltd.)

·BPB: Bromophenol blue (commercially available from Wako Pure Chemical Industries, Ltd.)

·BCG: Bromocresol green (commercially available from Wako Pure Chemical Industries, Ltd.)

15 [0057]

[Example 1]

<Preparation of refrigerant composition and refrigerant pack>

At room temperature (20 to 25 °C), water (97 parts by mass), diammonium hydrogen phosphate (2 parts by mass), CMC (1 part by mass), and BCP were added and
 20 mixed to prepare a refrigerant composition. In this case, a blending amount of the BCP was adjusted so that an amount in the obtained refrigerant composition was 10 ppm. Ingredients other than water, the amounts (concentrations), pH(A), and pH(B) thereof and the like are shown in Table 1. Then, pH(C) of the obtained refrigerant composition before freezing was measured. The results are shown in Table 1. All of pH(A), pH(B),

and pH(C) were measured when measurement targets had a temperature of 25 °C.

Note that, in Table 1, the numerical value shown in the unit of “mass%” in the column of the inorganic salt indicates the amount of the inorganic salt in the refrigerant composition and a concentration of an inorganic salt aqueous solution when pH(A) was measured. Similarly, the numerical value described in the unit of “mass%” in the column of the thickener indicates the amount of the thickener in the refrigerant composition and a concentration of a thickener aqueous solution when pH(B) was measured. These are the same as in the following tables.

Next, the obtained refrigerant composition was enclosed in a container made of high density polyethylene to prepare a refrigerant pack.

[0058]

<Evaluation of refrigerant composition>

(Change in color)

The obtained refrigerant composition (the refrigerant pack) was cooled to -25 °C. A change in color of the refrigerant composition before and after freezing was visually evaluated according to the following criteria. The results are shown in Table 1.

Note that, in Table 1, the “change in color” described in the column of the evaluation results indicates a change in color of the refrigerant composition before and after freezing. For example, “blue purple→yellow” indicates that a color of the refrigerant composition is blue purple before freezing and yellow after freezing.

A: the difference in color before and after freezing is considerable and the cooling state can be very easily observed.

B: the difference in color before and after freezing is discriminable and the cooling state can be observed.

C: the difference in color before and after freezing is unclear and the cooling state is

difficult or not possible to observe

[0059]

<Preparation of refrigerant composition and refrigerant pack and evaluation of refrigerant composition>

5 [Examples 2 to 19 and Comparative Examples 1 to 13]

Refrigerant compositions and refrigerant packs were prepared in the same manner as in Example 1 except that ingredients and concentrations of refrigerant compositions were set as shown in Tables 1 to 5 and the refrigerant compositions were evaluated. The results are shown in Tables 1 to 5. For example, in Example 6, four
10 types including sodium chloride, potassium chloride, sodium sulfate and diammonium hydrogen phosphate were used in combination as inorganic salts. The amounts of the inorganic salts in the refrigerant compositions and concentrations of the inorganic salts in aqueous solutions when pH(A) was measured were as follows. The amount of sodium chloride was 10 mass%, the amount of potassium chloride was 5 mass%, the amount of
15 sodium sulfate was 2 mass%, and the amount of diammonium hydrogen phosphate was 0.1 mass%. Note that the mark “-” in the table indicates that a corresponding component was not blended in and corresponding pH(A) or pH(B) was accordingly not measured.

[0060]

[Table 1]

	Refrigerant composition			Thickener		pH indicator		pH(C)	Evaluation results
	Inorganic salt	pH(A)	Name (mass%)	Name (mass%)	pH(B)	Name	pKa		
Example 1	Diammonium hydrogen phosphate (2)	7.9	CMC (1)	7.9	7.9	BCP	6.3	7.8	A (blue purple→yellow)
Example 2	Diammonium hydrogen phosphate (10)	7.9	CMC (1)	7.9	7.9	BCP	6.3	7.8	A (blue purple→yellow)
Example 3	Disodium hydrogen phosphate (2)	9.1	CMC (1)	7.9	7.9	BCP	6.3	9.0	A (blue purple→yellow)
Example 4	Sodium carbonate (2)	11.5	CMC (1)	7.9	7.9	AYR	11.2	11.0	A (orange→yellow)
Example 5	Disodium hydrogen phosphate (2)	9.1	CMC (1)	7.9	7.9	PR	8.0	9.0	A (red purple→yellow)
Example 6	Sodium chloride (10) Potassium chloride (5) Sodium sulfate (2) Diammonium hydrogen phosphate (0.1)	7.1	CMC (1)	7.9	7.9	BCP	6.3	6.9	A (blue purple→yellow)
Example 7	Sodium chloride (10) Potassium chloride (5) Sodium sulfate (2) Diammonium hydrogen phosphate (0.2)	7.1	CMC (1)	7.9	7.9	BCP	6.3	6.9	A (blue purple→yellow)

[0061]

[Table 2]

	Refrigerant composition										Evaluation results
	Inorganic salt		pH(A)	Thickener		pH(B)	pH indicator		pH(C)		
	Name (mass%)			Name (mass%)			Name	pKa			
Example 8	Sodium chloride (10) Potassium chloride (5) Sodium sulfate (2) Diammonium hydrogen phosphate (0.3)		7.1	CMC (1)		7.9	BCP	6.3		6.9	A (blue purple→yellow)
Example 9	Sodium chloride (10) Potassium chloride (5) Sodium sulfate (2) Diammonium hydrogen phosphate (0.4)		7.1	CMC (1)		7.9	BCP	6.3		7.0	A (blue purple→yellow)
Example 10	Sodium chloride (10) Potassium chloride (5) Sodium sulfate (2) Diammonium hydrogen phosphate (0.5)		7.1	CMC (1)		7.9	BCP	6.3		7.0	A (blue purple→yellow)
Example 11	Sodium chloride (10) Potassium chloride (5) Sodium sulfate (2) Diammonium hydrogen phosphate (0.5)		7.1	GG (1)		6.3	BCP	6.3		7.3	A (blue purple→yellow)

[Table 3]

	Refrigerant composition					Thickener			pH indicator		pH(C)	Evaluation results
	Inorganic salt		pH(A)	Name (mass%)		pH(B)	Name	pKa				
	Name (mass%)			Name (mass%)								
Example 12	Sodium chloride (16) Potassium chloride (6) Sodium sulfate (3) Diammonium hydrogen		7.1	CMC (1)		7.9	BCP		6.3	6.9	A (blue purple→yellow)	

Example 13	phosphate (0.1) Sodium chloride (16) Potassium chloride (6) Sodium sulfate (3) Diammonium hydrogen phosphate (0.2)	7.1	CMC (1)	7.9	BCP	6.3	6.9	A (blue purple→yellow)
Example 14	Sodium chloride (16) Potassium chloride (6) Sodium sulfate (3) Diammonium hydrogen phosphate (0.3)	7.1	CMC (1)	7.9	BCP	6.3	6.9	A (blue purple→yellow)
Example 15	Sodium chloride (16) Potassium chloride (6) Sodium sulfate (3) Diammonium hydrogen phosphate (0.4)	7.1	CMC (1)	7.9	BCP	6.3	7.0	A (blue purple→yellow)

[0063]

[Table 4]

	Refrigerant composition						Evaluation results	
	Inorganic salt		Thickener		pH indicator			
	Name (mass%)	pH(A)	Name (mass%)	pH(B)	Name	pKa		
Example 16	Sodium chloride (16) Potassium chloride (6) Sodium sulfate (3) Diammonium hydrogen phosphate (0.5)	7.1	CMC (1)	7.9	BCP	6.3	7.0	A (blue purple→yellow)
Example 17	Sodium chloride (20) Potassium chloride (6) Sodium sulfate (3) Diammonium hydrogen phosphate (0.5)	7.1	CMC (1)	7.9	BCP	6.3	7.0	A (blue purple→yellow)
Example 18	Sodium chloride (16)	7.1	CMC	7.9	BCP	6.3	7.0	A

	Potassium chloride (10) Sodium sulfate (3) Diammonium hydrogen phosphate (0.5)	(1)					(blue purple→yellow)
Example 19	Sodium chloride (16) Potassium chloride (6) Sodium sulfate (3) Diammonium hydrogen phosphate (0.5)	GG (1)	7.1	6.3	BCP	6.3	7.3 A (blue purple→yellow)

[0064]

[Table 5]

	Refrigerant composition							Evaluation results	
	Inorganic salt		Thickener		pH indicator		pH(C)	Change in color (before freezing→after freezing)	
	Name (mass%)	pH(A)	Name (mass%)	pH(B)	Name	pKa			
Comparative Example 1	Trisodium phosphate (2)	12.2	CMC (1)	7.9	BCP	6.3	12.2	C (blue purple→blue purple)	
Comparative Example 2	Sodium carbonate (2)	11.5	CMC (1)	7.9	BCP	6.3	11.4	C (blue purple→blue purple)	
Comparative Example 3	Diammonium hydrogen phosphate (2)	7.9	CMC (1)	7.9	BPB	4.0	7.8	C (blue→blue)	
Comparative Example 4	Trisodium phosphate (2)	12.2	CMC (1)	7.9	PR	8.0	12.2	C (red purple→red purple)	
Comparative Example 5	Disodium hydrogen phosphate (2)	9.1	CMC (1)	7.9	AYR	11.2	9.0	C (yellow→yellow)	
Comparative Example 6	Sodium chloride (10) Potassium chloride (5) Sodium sulfate (2)	6.8	CMC (1)	7.9	BCP	6.3	6.8	C (blue purple→blue purple)	
Comparative Example 7	Sodium chloride (10)	6.5	GG (1)	6.3	BCG	4.9	7.1	C (blue→blue)	

Comparative Example 8	Sodium chloride (10)	6.5	CMC (1)	7.9	BCP	6.3	6.8	C (blue purple→blue purple)
Comparative Example 9	Trisodium phosphate (2)	12.2	-	-	BCP	6.3	12.2	C (blue purple→blue purple)
Comparative Example 10	Sodium carbonate (2)	11.5	-	-	BCP	6.3	11.5	C (blue purple→blue purple)
Comparative Example 11	Diammonium hydrogen phosphate (2)	7.9	-	-	BPB	4.0	7.9	C (blue→blue)
Comparative Example 12	Trisodium phosphate (2)	12.2	-	-	PR	8.0	12.2	C (red→red purple)
Comparative Example 13	-	-	CVP (1)	5.3	BCP	6.3	5.3	C (yellow→yellow)

[0065]

As can be clearly understood from the above results, in Examples 1 to 19, the thickeners used were polysaccharides. Regardless of the number of types of inorganic salt used, pH(A) was in a predetermined range, and the relation of Expression (I) was
5 satisfied. Accordingly, before and after freezing, a color of the refrigerant composition was clearly changed by reflecting a change in color development of the pH indicator, and the cooling state was easily observed. Also, the relation of Expression (II) was satisfied in all of Examples 1 to 19.

[0066]

10 On the other hand, in Comparative Examples 1 to 5, since the relation of Expression (I) was not satisfied, a change in color of the refrigerant composition before and after freezing was unclear, and the cooling state was difficult or not possible to observe. In addition, in Comparative Examples 6 to 8, since pH(A) was outside a predetermined range, a change in color of the refrigerant composition before and after
15 freezing was unclear and the cooling state was difficult or not possible to observe. In addition, in the refrigerant compositions in Comparative Examples 9 to 12, the thickeners in the refrigerant compositions of Comparative Examples 1 to 4 were entirely substituted with water (no thickener was used). Similarly to Comparative Examples 1 to 4, in Comparative Example 9 to 12, a change in color of the refrigerant composition before
20 and after freezing was unclear, and the cooling state was difficult or not possible to observe. In addition, in Comparative Example 13, a refrigerant composition in which no inorganic salt was used was used. However, similarly to the other comparative examples, a change in color of the refrigerant composition before and after freezing was unclear and the cooling state was difficult or not possible to observe.

25 [Industrial Applicability]

[0067]

The present invention can be used as a refrigerant pack for various fresh items.

[CLAIMS]

What is claimed is:

[Claim 1]

A refrigerant pack comprising a refrigerant composition that includes water, an
 5 inorganic salt, a thickener and a pH indicator,
 wherein the thickener is a polysaccharide,
 wherein, in the refrigerant composition, pH(A) when all ingredients other than
 the inorganic salt and water are substituted with water is 7.0 or more and a relation of the
 following expression (I) is satisfied,
 10 $\text{pKa of pH indicator} - 0.5 \leq \text{pH(A)} \leq \text{pKa of pH indicator} + 3.5 \dots (\text{I})$

[Claim 2]

The refrigerant pack according to claim 1,
 wherein the refrigerant composition has a pH that satisfies a relation of the
 following Expression (II),
 15 $\text{pKa of pH indicator} - 0.5 \leq \text{pH of refrigerant composition} \leq \text{pKa of pH}$
 $\text{indicator} + 3.5 \dots (\text{II})$

[Claim 3]

The refrigerant pack according to claim 1,
 wherein, in the refrigerant composition, pH(B) when all ingredients other than
 20 the thickener and water are substituted with water is 5.0 to 9.0.

[Claim 4]

The refrigerant pack according to claim 1,
 wherein, in the refrigerant composition, an amount of the inorganic salt is 0.5 to
 33 mass%, an amount of the thickener is 0.1 to 10 mass%, and an amount of the pH
 25 indicator is 1 to 30 ppm.

[Claim 5]

The refrigerant pack according to claim 1,
wherein the pH indicator has a pKa that is 4.0 to 11.8.

[Claim 6]

5 The refrigerant pack according to claim 1,
 wherein the inorganic salt is one or more types selected from the group
including hydrochlorides, sulfates, nitrates, carbonates, hydrogen phosphates,
bicarbonates, phosphates, alkali metal chlorides and alkaline earth metal chlorides.

[Claim 7]

10 The refrigerant pack according to claim 1,
 wherein the thickener is one or more types selected from the group including
carboxyalkyl celluloses, guar gum, hydroxyalkyl guar gums, pectin, xanthan gum,
tamarind gum and carrageenan.