

ISOTHIAZOLONE COMPOSITION AND METHOD FOR STABILIZING ISOTHIAZOLONE

BACKGROUND OF THE INVENTION

5 (a) Field of the Invention

The present invention relates to an isothiazolone composition and a method for stabilizing the same, and more specifically to an isothiazolone composition that does not comprise a divalent alkali earth metal salt such as magnesium chloride, which causes salt shock, and thus can be stably
10 used for a sterilizer in a dispersion or an emulsion such as paint acrylate or latex, etc., therefore effectively preventing the growth of microorganisms, and that has superior storage stability due to its low rate of precipitation formation.

(b) Description of the Related Art

15 Isothiazolone, which has extensive sterilizing activity for many harmful organisms originating from animals and plants such as bacteria, mold, algae, etc., is added to cosmetics, paints, etc. as an inhibitor for the growth of harmful microorganisms.

However, since isothiazolone is decomposed in a polar organic
20 solvent such as alcohol, or in water, its biological activity deteriorates with the passage of time. Therefore, many studies for increasing stability of isothiazolone in a polar organic solvent or water have been conducted.

In order to increase stability of isothiazolone in a polar organic

solvent or water, US Patent No. 3,870,785 has suggested a method of adding a metal nitrate salt, a nitrite salt, etc. to the composition as a stabilizer. And, US Patent No. 4,165,318 has suggested a method of adding formaldehyde or a formaldehyde-eluting material to an isothiazolone composition as a stabilizer. In addition, US Patent No. 4,824,957 has suggested a method of adding an organic hydroxylic solvent to an isothiazolone composition as a stabilizer.

However, for various reasons, it is preferable to reduce the amount of the stabilizer used for stabilizing a sterilizer comprising an isothiazolone compound.

For example, a dispersion or an emulsion such as paint acrylate or latex, etc., which requires prevention of change and decomposition by microorganisms, sensitively reacts with a salt, and particularly, it does not mix well with a sterilizer comprising salts of divalent ions which cause coagulation. Moreover, sterilization active ingredients may be incorporated into the coagulation, thus the sterilization active ingredient may be reduced or removed if a product to be stored is filtered.

At present, a metal nitrate salt, particularly magnesium chloride or magnesium nitrate, is added to a 3-isothiazolone composition as a stabilizer. A commonly used isothiazolone composition comprises 1 to 20 wt% of isothiazolone and 15 to 25 wt% of a nitrate salt.

In addition, isothiazolone compositions comprise divalent metal, particularly magnesium oxide, as a pH-neutralizing agent. However, an

isothiazolone composition comprising a substantial amount of a divalent metal salt such as magnesium oxide cannot be preferably used for a sterilizer because it has a problem due to "salt shock" of bivalent metal salts.

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SUMMARY OF THE INVENTION

The present invention relates to an isothiazolone composition and a method for stabilizing the same, and more specifically to an isothiazolone composition that does not comprise a divalent alkali earth metal salt such as magnesium chloride, which causes salt shock, and thus that can be
10 stably used for a sterilizer in a dispersion or an emulsion such as paint acrylate or latex, etc., therefore effectively preventing the growth of microorganisms, and that has superior storage stability due to its low rate of precipitation formation.

BRIEF DESCRIPTION OF THE DRAWINGS

15 Fig. 1 is a photograph showing salt shock results of isothiazolone compositions of Example 1, Comparative Example 1, and a Control according to Experiment 1.

Fig. 2 is a photograph showing salt shock results of 10-fold dilutions of the isothiazolone compositions of Example 1 and Comparative
20 Example 1 according to Experiment 1.

Fig. 3 is a photograph showing salt shock results of isothiazolone compositions of Example 1 and Comparative Example 1 according to Experiment 2 (paint acrylate emulsion).

Fig. 4 is a photograph showing the salt shock results of the isothiazolone compositions of Example 1 and Comparative Example 1 according to Experiment 3 (latex emulsion).

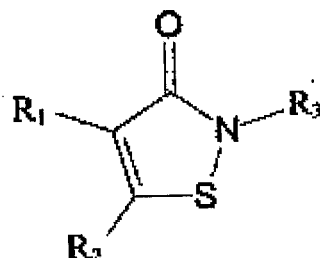
DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

5 The present invention is made to solve the above-mentioned problems, and it is an object of the present invention to provide an isothiazolone composition that does not comprise an alkali earth metal salt of a divalent metal such as magnesium chloride, which causes salt shock, and thus can be stably used for a microorganism inhibitor in a dispersion or
10 an emulsion such as paint acrylate or latex, etc., therefore effectively preventing the growth of harmful microorganisms, and that has superior storage stability because it comprises appropriate ratios of three kinds of stabilizers having synergy for increasing stability of an isothiazolone solution, and thus has a low rate of precipitation formation even at a much
15 lower concentration than those disclosed in the prior art.

It is another object of the present invention to provide a method for stabilizing isothiazolone.

In order to achieve these objects, the present invention provides an isothiazolone composition comprising (a) a 3-isothiazolone compound
20 represented by the following Chemical Formula 1; (b) an alkali metal nitrate salt; (c) an alkali metal chloride salt; and (d) a solvent:

[Chemical Formula 1]



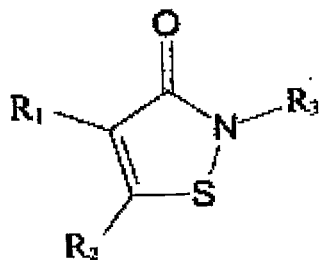
In the above Chemical Formula 1,

R_1 and R_2 are independently a hydrogen atom, a halogen atom, or
 5 a C_1 - C_4 alkyl group or aryl group; and,

R_3 is a hydrogen atom, a C_1 - C_{18} alkyl group, a C_2 - C_{18} alkenyl group,
 a C_2 - C_{18} alkynyl group, a C_3 - C_{12} cycloalkyl group having trigonal to
 octagonal rings, a C_{10} - C_{24} aralkyl group, or a C_{10} - C_{24} aryl group.

The present invention also provides a method for stabilizing
 10 isothiazolone comprising the step of adding (a) 0.1 to 20 wt% of a 3-
 isothiazolone compound represented by the above Chemical Formula 1;
 (b) 0.1 to 25 wt% of an alkali metal nitrate salt; and (c) 0.001 to 20 wt% of
 an alkali metal carbonate salt to (d) a solvent making up the balance to
 prepare a mixed solution:

15 [Chemical Formula 1]



In the above Chemical Formula 1,

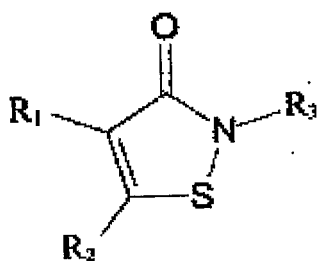
R_1 and R_2 are independently a hydrogen atom, a halogen atom, or a C_1 - C_4 alkyl group or aryl group; and,

R_3 is a hydrogen atom, a C_1 - C_{18} alkyl group, a C_2 - C_{18} alkenyl group, a C_2 - C_{18} alkynyl group, a C_3 - C_{12} cycloalkyl group having trigonal to octagonal rings, a C_{10} - C_{24} aralkyl group, or a C_{10} - C_{24} aryl group.

The present invention will now be explained in detail.

The present invention is characterized by comprising (a) a 3-isothiazolone compound represented by the following Chemical Formula 1;
 (b) an alkali metal nitrate salt; (c) an alkali metal chloride salt; and (d) a solvent as essential ingredients:

[Chemical Formula 1]



In the above Chemical Formula 1,

R_1 and R_2 are independently a hydrogen atom, a halogen atom, a C_1 - C_4 alkyl group or aryl group;

R_3 is a hydrogen atom, a C_1 - C_{18} alkyl group, a C_2 - C_{18} alkenyl group, a C_2 - C_{18} alkynyl group, a C_3 - C_{12} cycloalkyl group having trigonal to octagonal rings, a C_{10} - C_{24} aralkyl group, or C_{10} - C_{24} aryl group.

The (a) 3-isothiazolone compound, which has extensive sterilizing

activity for many harmful microorganisms originating from animals and plants such as bacteria, mold, algae, etc., is added to cosmetics, paints, etc. to be used for an inhibitor for growth of harmful microorganisms.

The (a) 3-isothiazolone compound of the above Chemical Formula 1 is preferably contained in an amount of 0.1 to 20 wt% in the isothiazolone composition of the present invention. If the content of the (a) 3-isothiazolone compound is less than 0.1 wt%, the resulting isothiazolone composition cannot be commercially used because of a low content of sterilizer. And, if the content exceeds 20 wt%, stability becomes
10 deteriorated.

As the (a) 3-isothiazolone compound, 5-chloro-2-methyl-4-isothiazolin-3-on, 2-methyl-4-isothiazolin-3-on, 4,5-dichloro-2-methyl-4-isothiazolin-3-on, 5-chloro-n-octyl-3-isothiazolone, 4,5-dichloro-2-n-octyl-3-isothiazolone, benzisothiazolone or a mixture thereof can be preferably
15 used.

In case the mixture of the (a) 3-isothiazolone compound of Chemical Formula 1 is used, the mixture of 5-chloro-2-methyl-4-isothiazolin-3-on and 2-methyl-4-isothiazolin-3-on is preferable, and the mixing ratio thereof is preferably 1 : 20 to 20 : 1.

20 In addition, the isothiazolone composition of the present invention comprises the (b) alkali metal nitrate salt as a stabilizer for preventing decomposition of isothiazolone.

In order to prevent formation of a precipitation of the isothiazolone

composition, a metal nitrate salt has been widely used, generally magnesium nitrate. However, if the content of the magnesium nitrate is less than 0.1 wt% of the isothiazolone composition, precipitation-preventing effects cannot be anticipated, and if it exceeds 25 wt%, solubility of magnesium nitrate decreases to cause precipitation of magnesium nitrate itself, and worse, divalent ion magnesium causes salt shock and thus aqueous polymer dispersion cannot be stabilized.

However, since the isothiazolone composition of the present invention comprises an alkali metal nitrate salt as a stabilizer, instead of an alkali earth metal salt of a divalent metal such as magnesium nitrate that has been predominantly used as a stabilizer in an isothiazolone composition of the prior art, salt shock is inhibited which makes the isothiazolone composition stable.

The content of the (b) alkali metal nitrate salt is preferably 0.1 to 25 wt% of the isothiazolone composition. If the content is less than 0.1 wt%, precipitation of isothiazolone cannot be effectively prevented, and if it exceeds 25 wt%, solubility decreases and product cost increases, making the composition uneconomical.

As the (b) alkali metal nitrate salt, lithium nitrate, sodium nitrate, potassium nitrate, or a mixture thereof can be preferably used, and sodium nitrate is most preferable.

In addition, the isothiazolone composition of the present invention comprises (c) an alkali metal chloride salt that is produced by the reaction

of an alkali metal introduced as a pH neutralizing agent with chloric acid.

Magnesium oxide, which has been widely used as a pH neutralizing agent of an isothiazolone composition, reacts in the composition to exist in the form of MgCl_2 (magnesium chloride). If the
5 content of the MgCl_2 exceeds 9 wt% of the composition, solubility of magnesium chloride decreases to cause precipitation of magnesium chloride itself, and more seriously, divalent metal magnesium causes salt shock and thus the aqueous polymer dispersion cannot be stabilized.

However, since the isothiazolone composition of the present
10 invention comprises an alkali metal carbonate salt as a pH- neutralizing agent, instead of magnesium oxide that has been predominantly used as a pH-neutralizing agent of an isothiazolone composition, salt shock is prevented.

The (c) alkali metal chloride salt is preferably contained in an
15 amount of 0.001 to 20 wt% of the isothiazolone composition, more preferably in an amount of 0.01 to 15 wt%, and most preferably 0.1 to 10 wt%. If the content is less than 0.001 wt%, the pH of the resulting isothiazolone composition cannot be controlled within a commercially acceptable range because the concentration of the alkali metal carbonate
20 salt introduced as a pH-neutralizing agent is too low, and if the content exceeds 20 wt%, stability of the composition decreases and product cost increases, thus making the composition uneconomical.

The (c) alkali metal chloride salt is preferably sodium chloride, or

potassium chloride with an alkali metal carbonate salt introduced thereto, or a mixture thereof. The alkali metal carbonate salt introduced as a pH-neutralizing agent is preferably sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, or a mixture thereof.

5 In addition, the isothiazolone composition comprises a (d) solvent. As the solvent, water, ethyleneglycol, propyleneglycol, dipropyleneglycol, polypropyleneglycol, diethyleneglycol, triethyleneglycol, 1,5-pentanediol, 2,4-pentanediol, benzyl alcohol or a mixture thereof can be preferably used.

 As another preferred embodiment of the present invention, the
10 isothiazolone composition of the present invention may further comprise (e) iodic acid, periodic acid, iodate, periodate or a mixture thereof; (f) a metal bromic acid; and (g) chlorite salt, alone or in combination of appropriate ratios, as a stabilizer for preventing the decomposition of isothiazolone. More preferably, a combination of the three kinds of precipitation-
15 preventing agents is added.

 In addition, during the storage of the isothiazolone composition, a small amount of precipitation, which is different from that of salt shock, forms due to the decomposition of by-products during the production process and compounds produced during storage. The precipitation is
20 commercially unfavorable because it damages the appearance of the product.

 However, the present invention can effectively inhibit the precipitation by introducing a small amount of a mixture of three kinds of

additives having superior effects for inhibiting formation of a precipitation to the isothiazolone composition. Specifically, the isothiazolone composition can be more effectively stabilized by using a mixture of compounds selected from a group consisting of (e) iodic acid, periodic acid, iodate salt, periodate salt, or a mixture thereof; (f) a metal bromic acid salt; and (g) chlorite salt, than by using the compound of (e), (f), and (g) alone.

The (e) iodic acid, periodic acid, iodate, periodate, or a mixture thereof is preferably contained in an amount of 0.0001 to 0.01 wt% of the isothiazolone composition, more preferably 0.001 to 0.005 wt%. If the content is less than 0.0001 wt%, precipitation of the isothiazolone compound cannot be effectively prevented, and if it exceeds 0.01 wt%, production cost increases, thus making the composition uneconomical.

The (e) iodic acid, periodic acid, iodate, periodate, or a mixture thereof is preferably selected from a group consisting of lithium iodate, sodium iodate, potassium iodate, ammonium iodate, lithium periodate, sodium periodate, potassium periodate, ammonium periodate, iodic acid, periodic acid dihydrate, or a mixture thereof, and more preferably iodic acid, periodic acid dihydrate, sodium iodic acid, potassium iodic acid or a mixture thereof.

The (f) metal bromic acid, the other precipitation-preventing agent, is preferably contained in an amount of 0.001 to 1.0 wt% of the isothiazolone composition, more preferably 0.01 to 0.2 wt%. If the content is less than 0.001 wt%, precipitation of isothiazolone cannot be effectively

prevented, and if it exceeds 1.0 wt%, production cost increases, thus making the composition uneconomical.

The (f) metal bromic acid salt is preferably selected from a group consisting of sodium bromate, potassium bromate and a mixture thereof.

5 In addition, the (g) chlorite salt, the other precipitation-preventing agent, is preferably contained in an amount of 0.001 to 10 wt%, more preferably 0.01 to 1.0 wt%, and most preferably 0.05 to 0.2 wt%. If the content is less than 0.001 wt%, precipitation of the isothiazolone cannot be effectively prevented, and if it exceeds 10 wt%, the production cost
10 increases, thus making the composition uneconomical.

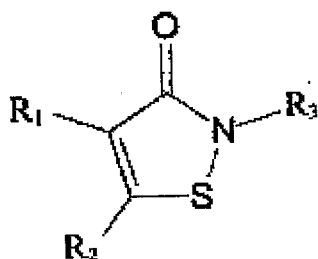
The (g) chlorite salt is preferably sodium chlorite, potassium chlorite or a mixture thereof.

The isothiazolone composition of the present invention preferably comprises (a) 0. to 20 wt% of a 3-isothiazolone compound; (b) 0.1 to 25
15 wt% of an alkali metal nitrate salt; (c) 0.001 to 20 wt% of an alkali metal chloride salt; and (d) a solvent making up the balance, and the three kinds of precipitation-preventing agents of (e), (f), and (g) alone or in combination. The three kinds of precipitation- preventing agents preferably comprise (e) 0.0001 to 0.01 wt% of iodic acid, periodic acid, iodate, periodate, or a
20 mixture thereof; (f) 0.01 to 1.0 wt% of a metal bromic acid salt; and (g) 0.001 to 10 wt% of chlorite salt.

The present invention also provides a method for stabilizing the isothiazolone composition comprising the step of (i) adding (a) 0.1 to 20

wt% of a 3-isothiazolone compound represented by the following Chemical Formula 1; (b) 0.1 to 25 wt% of an alkali metal nitrate salt; and (c) 0.001 to 20 wt% of an alkali metal carbonate salt to (d) a solvent making up the balance, to prepare a mixed solution of the isothiazolone composition:

5 [Chemical Formula 1]



In the above Chemical Formula 1,

R₁ and R₂ are independently a hydrogen atom, a halogen atom, or a C₁-C₄ alkyl group or aryl group; and,

10 R₃ is a hydrogen atom, a C₁-C₁₈ alkyl group, a C₂-C₁₈ alkenyl group, a C₂-C₁₈ alkynyl group, a C₃-C₁₂ cycloalkyl group having trigonal to octagonal rings, a C₁₀-C₂₄ aralkyl group, or a C₁₀-C₂₄ aryl group.

The (a) 3-isothiazolone compound is preferably selected from a group consisting of 5-chloro-2-methyl-4-isothiazolin-3-on, 2-methyl-4-
15 isothiazolin-3-on, 4,5-dichloro-2-methyl-4-isothiazolin-3-on, 5-chloro-2-n-octyl-3-isothiazolone, 4,5-dichloro-2-n-octyl-3-isothiazolone, benzisothiazolone, or a mixture thereof.

According to the method for stabilizing isothiazolone of the present invention, the (c) alkali metal carbonate salt is added as a pH-neutralizing
20 agent. The introduced alkali metal carbonate salt reacts with chloric acid

in the isothiazolone composition to exist in the form of an alkali metal chloride salt.

The (c) alkali metal carbonate is preferably introduced in an amount of 0.01 to 15 wt% of the isothiazolone composition, more preferably 0.1 to 10 wt%.

The (c) alkali metal carbonate is preferably sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate or a mixture thereof.

In addition, the (d) solvent is preferably selected from a group consisting of water, ethyleneglycol, propyleneglycol, dipropyleneglycol, polypropyleneglycol, diethyleneglycol, triethyleneglycol, 1,5-pentanediol, 2,4-pentanediol, benzyl alcohol or a mixture thereof.

As another preferred embodiment of the present invention, the method for stabilizing isothiazolone further adds a compound selected from a group consisting of (e) iodic acid, periodic acid, iodate, periodate or a mixture thereof; (f) a metal bromate; (g) chlorite salt, and a mixture thereof to the isothiazolone composition as a precipitation-preventing agent to further stabilize the isothiazolone composition. The mixture of two or more kinds of precipitation-preventing agents, which have different operation mechanisms, are preferably added in appropriate ratios.

The (e) iodic acid, periodic acid, iodate, periodate, or a mixture thereof is preferably added in an amount of 0.0001 to 0.01 wt% of the isothiazolone composition, more preferably 0.001 to 0.005 wt%. If the

content is less than 0.0001 wt%, precipitation of isothiazolone cannot be effectively prevented, and if it exceeds 0.01 wt%, the color changes with the passage of time, and production cost increases thus making the method uneconomical. The (e) iodic acid, periodic acid, iodate, periodate
5 or a mixture thereof is preferably selected from a group consisting of lithium iodate, sodium iodate, potassium iodate, ammonium iodate, lithium periodate, sodium periodate, potassium periodate, ammonium periodate, iodic acid, periodic acid dihydrate or a mixture thereof, and iodic acid, periodic acid dihydrate, sodium iodic acid, potassium iodic acid or a
10 mixture thereof are more preferable.

The (f) metal bromate is preferably added in an amount of 0.001 to 1.0 wt% of the isothiazolone composition, more preferably 0.001 to 0.2 wt%. If the content is less than 0.001 wt%, precipitation of isothiazolone cannot be effectively prevented, and if it exceeds 0.2 wt%, production cost
15 increases, thus making the method uneconomical. The (f) metal bromate is preferably selected from a group consisting of sodium bromate, potassium bromate and a mixture thereof.

The (g) chlorite salt is preferably added in an amount of 0.001 to 10 wt% of the isothiazolone composition, more preferably 0.01 to 1.0 wt%,
20 and most preferably 0.05 to 0.2 wt%. If the content is less than 0.001 wt%, precipitation of isothiazolone cannot be effectively prevented, and if it exceeds 10 wt%, production cost increases, thus making the method uneconomical. The (g) chlorite salt is preferably selected from sodium

chlorite, potassium chlorite and a mixture thereof.

As explained, the isothiazolone composition of the present invention can be stably used in a dispersion or emulsion such as paint acrylate or latex, etc. because it does not comprise a divalent metal alkali earth metal salt such as magnesium chloride, which causes salt shock, therefore
5 effectively inhibiting the growth of harmful microorganisms.

Accordingly, the isothiazolone composition of the present invention can be used for a microorganism inhibitor in microorganism habitats such as a cooling water tower, an air washer, a boiler, a mineral slurry, a
10 wastewater disposal plant, a decorative fountain, a reversed osmotic filtration system, an ultrafiltration system, ballast water, an evaporation condenser, a heat exchanger, and for pulp and paper processing oils, plastics, emulsions and dispersants, paint, latex, coating agents metal processing oils, etc., to effectively inhibit the growth of harmful
15 microorganisms such as bacteria, mold, algae, etc.

The present invention will be explained with reference to the following Examples and Comparative Examples. However, these are intended to only illustrate the present invention and the present invention is not limited to them.

20 Example

[Examples 1 to 13 and Comparative Example 1]

Concentrated 3-isothiazolone solutions were prepared with the compositions and contents given in the following Table 1. As the 3-

isothiazolone compound, a mixture of 5-chloro-2-methyl-4-isothiazolin-3-on (CMI) and 2-methyl-4-isothiazolin-3-on (MI) with the mixing ratio of approximately 3:1 was used.

As described in Table 1, the samples of Examples 1 to 13 and Comparative Example 1 were prepared by mixing the 3-isothiazolone compound, sodium nitrate, sodium carbonate, magnesium nitrate (Comparative Example), magnesium oxide (Comparative Example), and water and adding KIO_3 , NaBrO_3 , and NaClO_2 for preventing precipitation.

[Table 1] (wt%)

Sample	Isothiazolone compound	$\text{Mg}(\text{NO}_3)_2$	MgCl_2	NaNO_3	NaCl	KIO_3	NaBrO_3	NaClO_2
							3	2
Example 1	13.84	-	-	17.0	5.7	0.002		
Example 2	13.84	-	-	17.0	5.7	0.005		
Example 3	13.84	-	-	17.0	5.7	0.01		
Example 4	13.84	-	-	17.0	5.7		0.002	
Example 5	13.84	-	-	17.0	5.7		0.05	
Example 6	13.84	-	-	17.0	5.7		0.20	
Example 7	13.84	-	-	17.0	5.7			0.01
Example 8	13.84	-	-	17.0	5.7			0.1
Example 9	13.84	-	-	17.0	5.7			0.20
Example 10	13.84	-	-	17.0	5.7	0.005	0.05	

Example 11	13.84	-	-	17.0	5.7	0.005		0.1
Example 12	13.84	-	-	17.0	5.7		0.05	0.1
Example 13	13.84	-	-	17.0	5.7	0.005	0.05	0.1
Comparati ve Example 1	13.84	18.2	4.9	-	-	-	-	

In the above samples of Examples 1 to 13 and Comparative Example 1, the alkali metal carbonate (sodium chloride, potassium chloride) and magnesium chloride are those produced in the composition
5 by sodium carbonate, potassium carbonate, magnesium nitrate and magnesium oxide introduced for pH neutralization.

Specifically, the alkali metal carbonate (sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate) introduced as a pH-neutralizing agent exists in the form of an alkali metal
10 chloride salt (NaCl, KCl) in the composition of the present invention.

[Experiment 1]

Salt Shock Test

For samples prepared according to Examples 1 to 13 and Comparative Example 1, whether or not salt shock is caused was examined and the results are described in the following Table 2.

Generally, an isothiazolone composition causing salt shock
 5 comprises many magnesium ions as a stabilizer. It was confirmed whether or not samples prepared according to Examples 1 to 13 and Comparative Example 1 can be used as a sterilizer for a dispersion or emulsion such as paint acrylate or latex, etc. that sensitively reacts with divalent ions and coagulates, that is, whether or not they can stabilize a
 10 polymer aqueous dispersion.

For testing, 5 ml of a detecting agent was added to 10 ml of isothiazolone solutions to be tested by droplets. And, as a salt shock detecting agent, a 5% sodium methasilicate aqueous solution ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) was used.

15 [Table 2]

Sample	Formation of precipitation by salt shock
Example 1	No precipitation after 5 ml added
Example 2	No precipitation after 5 ml added
Example 3	No precipitation after 5 ml added
Example 4	No precipitation after 5 ml added
Example 5	No precipitation after 5 ml added
Example 6	No precipitation after 5 ml added
Example 7	No precipitation after 5 ml added

Example 8	No precipitation after 5 ml added
Example 9	No precipitation after 5 ml added
Example 10	No precipitation after 5 ml added
Example 11	No precipitation after 5 ml added
Example 12	No precipitation after 5 ml added
Example 13	No precipitation after 5 ml added
Comparative Example 1	Precipitation begins to form after 1 ml added

As can be seen from the Table 2, the salt shock composition forms precipitation, and the non salt shock types did not form precipitation.

When adding 5 ml of the detecting agent to 10 ml of the sample of Comparative Example 1, a white or gray precipitation formed. However,
5 adding a detecting agent to the sample of Example 1 did not cause formation of a precipitation.

Accordingly, it can be identified that the sample of Comparative Example 1 is of a salt shock type, and that of Example 1 is of a non salt shock type.

10 In the above Experiment 1, a salt free isothiazolone solution stabilized by a glycol solvent was used as a control.

Fig. 1 is a photo showing the salt shock results of isothiazolone composition samples of Example 1, Comparative Example 1, and a control, in Experiment 1.

15 In addition, Fig. 2 is a photo showing the salt shock results of 10-fold dilutions of isothiazolone composition samples of Example 1, and

Comparative Example 1 in Experiment 1.

As shown in Fig. 1, the sample of Comparative Example 1 formed a white or gray precipitation, and that of Example 1 did not form a precipitation. And, as shown in Fig. 2, the experiment with the 10-fold dilutions of samples of Example 1 and Comparative Example 1 showed the same results.

Accordingly, it was confirmed that the isothiazolone composition that does not comprise an alkali earth metal salt of a divalent metal such as magnesium chloride, that is, an isothiazolone composition stabilized by an alkali metal nitrate salt, can stabilize a polymer aqueous dispersion of a high concentration.

[Experiment 2]

Salt shock generation test in paint acrylate emulsion

Whether or not the samples of Examples 1 to 13 and Comparative Example 1 caused salt shock was examined by the same method as the Experiment 1, except that, in order for practical confirmation, after adding the samples of Examples 1 to 13 and Comparative Example 1 to a paint acrylate emulsion in a ratio of 5 ml : 10 ml, whether or not coagulation (precipitation) occurred as a result of salt shock was examined and the results are described in the following Table 3.

[Table 3]

Sample	Formation of coagulation (precipitation) by salt shock
Example 1	No coagulation (precipitation) after 5 ml added
Example 2	No coagulation (precipitation) after 5 ml added
Example 3	No coagulation (precipitation) after 5 ml added
Example 4	No coagulation (precipitation) after 5 ml added
Example 5	No coagulation (precipitation) after 5 ml added
Example 6	No coagulation (precipitation) after 5 ml added
Example 7	No coagulation (precipitation) after 5 ml added
Example 8	No coagulation (precipitation) after 5 ml added
Example 9	No coagulation (precipitation) after 5 ml added
Example 10	No coagulation (precipitation) after 5 ml added
Example 11	No coagulation (precipitation) after 5 ml added
Example 12	No coagulation (precipitation) after 5 ml added
Example 13	No coagulation (precipitation) after 5 ml added
Comparative Example 1	Coagulation (precipitation) begins to form after 1 ml added

As can be seen from the Table 3, the salt shock type composition coagulated (precipitation), but the non salt shock type compositions did not coagulate (precipitation).

The sample of Comparative Example 1 coagulated (precipitation) by salt shock when introduced in a polymer aqueous dispersion paint acrylate

emulsion.

Accordingly, it can be confirmed that the sample of Comparative Example 1 is of a salt shock type, and those of Examples 1 to 13 are of non salt shock types.

5 Fig. 3 is a photo showing the salt shock results of isothiazolone composition samples of Example 1 and Comparative Example 1.

As shown in Fig. 3, the paint acrylate emulsion into which the isothiazolone composition of Comparative Example 1 was introduced was seriously coagulated, and the paint acrylate emulsion into which the
10 isothiazolone composition of Example 1 was introduced maintained a solution state without coagulation.

Accordingly, it can be identified that an isothiazolone composition that does not comprise an alkali earth metal salt of a divalent metal such as magnesium chloride, that is, an isothiazolone composition stabilized by an
15 alkali metal nitrate salt can stabilize a polymer aqueous dispersion of a high concentration, and thus it can be used for a process such as let down during preparation of paint, to which the existing commercial products cannot be applied.

[Experiment 3]

20 Salt shock test in latex emulsion

Whether or not the samples of Examples 1 to 13 and Comparative Example 1 caused salt shock was examined by the same method in Experiment 1, except that, for practical confirmation, after adding the

samples of Examples 1 to 13 and Comparative Example 1 to a latex emulsion in a ratio of 5 ml : 10 ml, whether or not coagulation (precipitation) by salt shock occurred was examined and the results are presented in the following Table 4.

5 [Table 4]

Sample	Formation of coagulation (precipitation) by salt shock
Example 1	No coagulation (precipitation) after 5 ml added
Example 2	No coagulation (precipitation) after 5 ml added
Example 3	No coagulation (precipitation) after 5 ml added
Example 4	No coagulation (precipitation) after 5 ml added
Example 5	No coagulation (precipitation) after 5 ml added
Example 6	No coagulation (precipitation) after 5 ml added
Example 7	No coagulation (precipitation) after 5 ml added
Example 8	No coagulation (precipitation) after 5 ml added
Example 9	No coagulation (precipitation) after 5 ml added
Example 10	No coagulation (precipitation) after 5 ml added
Example 11	No coagulation (precipitation) after 5 ml added
Example 12	No coagulation (precipitation) after 5 ml added
Example 13	No coagulation (precipitation) after 5 ml added
Comparative Example 1	Coagulation (precipitation) begins to form after 1 ml added

As can be seen from the Table 4, the salt shock type composition formed coagulation (precipitation), but the non salt shock type compositions did not form coagulation (no precipitation).

The sample of Comparative Example 1 formed coagulation
5 (precipitation) by salt shock, when introduced in a polymer aqueous dispersion of latex emulsion. However, those of Examples 1 to 13 did not form coagulation (no precipitation).

Accordingly, it can be identified that the sample of Comparative Example 1 is of a salt shock type, but those of Examples 1 to 13 are of non
10 salt shock types.

Fig. 4 is a photo showing the salt shock results of isothiazolone composition samples of Example 1 and Comparative Example 1 in Experiment 3.

As shown in Fig. 4, the latex emulsion into which the isothiazolone
15 composition of Comparative Example 1 was introduced was seriously coagulated, and the latex emulsion into which the sample of Example 1 was introduced maintained a solution state without coagulation.

[Experiment 4]

Precipitation Formation Test

20 For the samples prepared according to Examples 1 to 13 and Comparative Example 1, a storage stability test was conducted and the results are described in the following Table 5.

In order to confirm storage stability, the isothiazolone compositions

(samples of Examples 1 to 13 and Comparative Example 1) were kept in an oven at 65 °C for 28 days, and the concentrations of main ingredients (MIT, CMIT) remaining in the compositions were analyzed using HPLC. The results are described in the following Table 5.

5 [Table 5]

Sample	Days of storage	Changes in contents of valid ingredients at 65°C				
		MIT	CMIT	Total (CMI+MI)	Ratio (CMI/MI)	%
Example 1	Initial stage	3.43	10.41	13.84	3.04	100
	28th days	3.12	7.87	10.99	2.52	83.0
Example 2	Initial stage	3.43	10.41	13.84	3.04	100
	28 th days	3.15	8.11	11.26	2.57	84.7
Example 3	Initial stage	3.43	10.41	13.84	3.04	100
	28 th days	3.11	8.20	11.31	2.64	86.8
Example 4	Initial stage	3.43	10.41	13.84	3.04	100
	28 th days	3.09	7.63	10.72	2.47	81.3
Example 5	Initial stage	3.43	10.41	13.84	3.04	100
	28 th days	3.17	8.31	11.48	2.62	86.3
Example 6	Initial stage	3.43	10.41	13.84	3.04	100
	28 th days	3.15	8.11	11.34	2.62	85.6
Example 7	Initial stage	3.43	10.41	13.84	3.04	100
	28th days	3.10	7.70	10.80	2.48	81.8
Example 8	Initial stage	3.43	10.41	13.84	3.04	100

	28 th days	3.10	7.72	10.82	2.49	82
Example 9	Initial stage	3.43	10.41	13.84	3.04	100
	28 th days	3.11	7.78	10.90	2.50	82.4
Example 10	Initial stage	3.43	10.41	13.84	3.04	100
	28 th days	3.32	10.07	13.39	3.03	100
Example 11	Initial stage	3.43	10.41	13.84	3.04	100
	28 th days	3.34	10.15	13.49	3.04	100
Example 12	Initial stage	3.43	10.41	13.84	3.04	100
	28 th days	3.03	9.22	12.25	3.04	100
Example 13	Initial stage	3.43	10.41	13.84	3.04	100
	28 th days	3.28	9.93	13.21	3.03	100
Comparative	Initial stage	3.46	10.44	13.90	3.01	100
Example 1	28 th days	3.10	7.30	10.39	2.36	78

As can be seen from the Table 5, the sample of Comparative Example 1 showed a large change in concentration of main ingredients after being stored at 65°C for 28 days, thus the ratio of CMI/MI decreased and precipitate formed. Since, of the two main ingredients of the isothiazolone solution, i.e. CMIT and MIT, the stability of CMIT is lower than that of MIT, the result that the initial ratio of 3:1 decreased means that CMI precipitated by the amount of decrease.

Meanwhile, the samples of Examples 1 to 13, which were prepared by adding KIO₃, NaBrO₃, and NaClO₂ as stabilizers, showed minor

changes in concentrations of main ingredients after being stored for 28 days, and particularly when the mixture of KIO_3 , NaBrO_3 and NaClO_2 of appropriate ratios were added, there was little change of concentrations of main ingredients, and the ratio of CMI/MI was large, hence a stabilized
5 isothiazolone composition in which precipitation does not occur could be obtained.

Accordingly, from the above experiment, it can be confirmed that a more stabilized 3-isothiazolone composition can be obtained by introducing a small amount of iodate, metal bromate, and chlorite in combination of
10 appropriate ratios, compared to when using each of the compounds alone.

The isothiazolone composition of the present invention can be stably used as a sterilizer in a dispersion or emulsion such as paint acrylate or latex, etc. because it does not include an alkali earth metal salt of a divalent metal such as magnesium chloride, which causes salt shock, and
15 thus it can effectively inhibit growth of harmful microorganisms, and it has superior storage stability due to its low precipitation forming rate.

WHAT IS CLAIMED IS:

1. An isothiazolone composition comprising:

(a) a 3-isothiazolone compound represented by the following

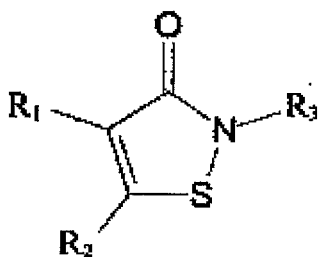
5 Chemical Formula 1;

(b) an alkali metal nitrate;

(c) an alkali metal chloride; and

(d) a solvent:

[Chemical Formula 1]



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wherein,

R₁ and R₂ are independently a hydrogen atom, a halogen atom, or a C₁-C₄ alkyl group or aryl group;

R₃ is a hydrogen atom, a C₁-C₁₈ alkyl group, a C₂-C₁₈ alkenyl group,
 15 a C₂-C₁₈ alkynyl group, a C₃-C₁₂ cycloalkyl group having trigonal to octagonal rings, a C₁₀-C₂₄ aralkyl group, or a C₁-C₂₄ aryl group.

2. The isothiazolone composition according to Claim 1, wherein the (a) 3-isothiazolone compound represented by the Chemical Formula 1 is selected from the group consisting of 5-chloro-2-methyl-4-isothiazolin-3-on,
 20 2-methyl-4-isothiazolin-3-on, 4,5-dichloro-2-methyl-4-isothiazolin-3-on, 5-

chloro-2-n-octyl-3-isothiazolone, 4,5-dichloro-2-n-octyl-3-isothiazolone and benzisothiazolone.

3. The isothiazolone composition according to Claim 1, wherein the (b) alkali metal nitrate is selected from the group consisting of lithium nitrate,
5 sodium nitrate and potassium nitrate.

4. The isothiazolone composition according to Claim 1, wherein the (c) alkali metal chloride is selected from a group consisting of sodium chloride and potassium chloride.

5. The isothiazolone composition according to Claim 1, wherein the (d)
10 solvent is selected from a group consisting of water, ethylene glycol, propyleneglycol, dipropyleneglycol, polypropyleneglycol, diethyleneglycol, triethyleneglycol, 1,5-pentanediol, 2,4-pentanediol and benzyl alcohol.

6. The isothiazolone composition according to Claim 1, which comprises:

- (a) 0.1 to 20 wt% of the 3-isothiazolone compound;
- 15 (b) 0.1 to 25 wt% of the alkali metal nitrate;
- (c) 0.001 to 20 wt% of the alkali metal chloride; and
- (d) the solvent making up the balance.

7. The isothiazolone composition according to Claim 6, wherein the (c) alkali metal chloride is contained in an amount of 0.1 to 15 wt%, based on
20 the weight of the isothiazolone composition.

8. The isothiazolone composition according to Claim 6, wherein the (c) alkali metal chloride is contained in an amount of 0.1 to 10 wt%, based on the weight of the isothiazolone composition.

9. The isothiazolone composition according to Claim 1, which further comprises a precipitation-preventing agent selected from a group consisting of (e) iodic acid, periodic acid, iodate, periodate or a mixture thereof; (f) metal bromate; and (g) chlorite.
- 5 10. The isothiazolone composition according to Claim 9, wherein the (e) iodic acid, periodic acid, iodate, periodate, or a mixture thereof is contained in an amount of 0.0001 to 0.01 wt%, based on the weight of the isothiazolone composition.
- 10 11. The isothiazolone composition according to Claim 9, wherein the (e) iodic acid, periodic acid, iodate, periodate or a mixture thereof is contained in an amount of 0.001 to 0.005 wt%, based on the weight of the isothiazolone composition.
- 15 12. The isothiazolone composition according to Claim 9, wherein the (f) metal bromate is contained in an amount of 0.001 to 1.0 wt%, based on the weight of the isothiazolone composition.
13. The isothiazolone composition according to Claim 9, wherein the (f) metal bromate is contained in an amount of 0.001 to 0.2 wt%, based on the weight of the isothiazolone composition.
- 20 14. The isothiazolone composition according to Claim 9, wherein the (g) chlorite is contained in an amount of 0.001 to 10 wt%, based on the weight of the isothiazolone composition.
15. The isothiazolone composition according to Claim 9, wherein the (g) chlorite is contained in an amount of 0.01 to 1 wt%, based on the weight of

the isothiazolone composition.

16. The isothiazolone composition according to Claim 9, wherein the (g) chlorite is contained in an amount of 0.05 to 0.2 wt%, based on the weight of the isothiazolone composition.

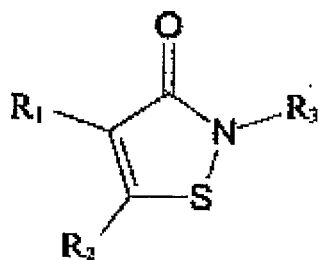
5 17. The isothiazolone composition according to Claim 9, wherein the (e) iodic acid, periodic acid, iodate, periodate or a mixture thereof is selected from a group consisting of lithium iodate, sodium iodate, potassium iodate, ammonium iodate, lithium periodate, sodium periodate, potassium periodate, ammonium periodate, iodic acid, periodic acid dihydrate and a
10 mixture thereof.

18. The isothiazolone composition according to Claim 9, wherein the (f) metal bromate is sodium bromate or potassium bromate.

19. The isothiazolone composition according to Claim 9, wherein the (g) chlorite is sodium chlorite or potassium chlorite.

15 20. A method for stabilizing isothiazolone comprising the step of adding (a) 0.1 to 20 wt% of a 3-isothiazolone compound represented by the following Chemical Formula 1; (b) 0.1 to 25 wt% of an alkali metal nitrate ; and (c) 0.001 to 20 wt% of an alkali metal carbonate, to (d) a solvent making up the balance, to prepare a mixed solution:

[Chemical Formula 1]



wherein,

R_1 and R_2 are independently a hydrogen atom, a halogen atom, or
 5 a C_1 - C_4 alkyl group or aryl group;

R_3 is a hydrogen atom, a C_1 - C_{18} alkyl group, a C_2 - C_{18} alkenyl group,
 a C_2 - C_{18} alkynyl group, a C_3 - C_{12} cycloalkyl group having trigonal to
 octatonal rings, a C_{10} - C_{24} aralkyl group, or a C_{10} - C_{24} aryl group.

21. The method for stabilizing isothiazolone according to Claim 20, wherein
 10 the (a) 3-isothiazolone compound of the Chemical Formula 1 is selected
 from a group consisting of 5-chloro-2-methyl-4-isothiazolin-3-on, 2-methyl-
 4-isothiazolin-3-on, 4,5-dichloro-2-methyl-4-isothiazolin-3-on, 5-chloro-2-n-
 octyl-3-isothiazolone, 4,5-dichloro-2-n-octyl-3-isothiazolone and
 benzisothiazolone.

15 22. The method for stabilizing isothiazolone according to Claim 20, wherein
 the (b) alkali metal nitrate is selected from a group consisting of lithium
 nitrate, sodium nitrate and potassium nitrate.

23. The method for stabilizing isothiazolone according to Claim 20, wherein
 the (c) alkali metal carbonate is selected from a group consisting of
 20 sodium carbonate, potassium carbonate, sodium bicarbonate and

potassium bicarbonate.

24. The method for stabilizing isothiazolone according to Claim 20, wherein the (d) solvent is selected from a group consisting of water, ethyleneglycol, propyleneglycol, dipropyleneglycol, polypropyleneglycol, diethyleneglycol, triethyleneglycol, 1,5-pentanediol, 2,4-pentanediol and benzyl alcohol.

25. The method for stabilizing isothiazolone according to Claim 20, wherein the (c) alkali metal carbonate is contained in an amount of 0.01 to 15 wt%, based on the weight of the isothiazolone composition.

26. The method for stabilizing isothiazolone according to Claim 20, wherein the (c) alkali metal carbonate is contained in an amount of 0.1 to 10 wt%, based on the weight of the isothiazolone composition.

27. The method for stabilizing isothiazolone according to Claim 20, which further comprises the step of adding a precipitation-preventing agent selected from a group consisting of (e) iodic acid, periodic acid, iodate, periodate and a mixture thereof; (f) metal bromate; and (g) chlorite, to the mixed solution.

28. The method for stabilizing isothiazolone according to Claim 27, wherein the (e) iodic acid, periodic acid, iodate, periodate or a mixture thereof is contained in an amount of 0.0001 to 0.01 wt% , based on the weight of the isothiazolone composition.

29. The method for stabilizing isothiazolone according to Claim 27, wherein the (e) iodic acid, periodic acid, iodate, periodate, or a mixture thereof is contained in an amount of 0.001 to 0.005 wt% , based on the weight of the

isothiazolone composition.

30. The method for stabilizing isothiazolone according to Claim 27, wherein the (f) metal bromate is contained in an amount of 0.001 to 1.0 wt%, based on the weight of the isothiazolone composition.

5 31. The method for stabilizing isothiazolone according to Claim 27, wherein the (f) metal bromate is contained in an amount of 0.001 to 0.2 wt%, based on the weight of the isothiazolone composition.

32. The method for stabilizing isothiazolone according to Claim 27, wherein the (g) chlorite is contained in an amount of 0.001 to 10 wt%, based on the
10 weight of the isothiazolone composition.

33. The method for stabilizing isothiazolone according to Claim 27, wherein the (g) chlorite is contained in an amount of 0.01 to 1 wt%, based on the weight of the isothiazolone composition.

34. The method for stabilizing isothiazolone according to Claim 27, wherein
15 the (g) chlorite is contained in an amount of 0.05 to 0.2 wt%, based on the weight of the isothiazolone composition.

35. The method for stabilizing isothiazolone according to Claim 27, wherein the (e) iodic acid, periodic acid, iodate, periodate or a mixture thereof is selected from a group consisting of lithium iodate, sodium iodate,
20 potassium iodate, ammonium iodate, lithium periodate, sodium periodate, potassium periodate, ammonium periodate, iodic acid, periodic acid dihydrate or a mixture thereof.

36. The method for stabilizing isothiazolone according to Claim 27, wherein

the (f) metal bromate is sodium bromate or potassium bromate.

37. The method for stabilizing isothiazolone according to Claim 27, wherein the (g) chlorite is sodium chlorite or potassium chlorite.

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