

DESCRIPTION

SOLVENT-FREE FLAME-RESISTANT EPOXY PAINT COMPOSITION, THE TOXICITY OF THE SMOKE OF WHICH IS REDUCED IN THE EVENT OF AN OUTBREAK OF A FIRE

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Technical Field

The present invention relates to a binary liquid type foamable flame-resistant epoxy paint composition for use in oil or gas industrial facilities such as marine structures and plants, and more particularly, to a solvent-free flame-resistant epoxy paint composition having reduced gas toxicity during a fire by using, as the foaming agent of the primary composition, expandable graphite coated with a silane compound.

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Background Art

As for oil fires in marine structures, plants, etc., the fire temperature is drastically increased up to about 945°C within 5 min. Although curable epoxy-based flame-resistant paints are mainly employed in the fields where oil fires may occur, existing flame-resistant paints suffer from the emission of large amounts of noxious gases upon expansion of paint films.

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The epoxy-based flame-resistant paints are based on the following three US patents.

US Patent No. 4,529,467 describes a solvent-free flame-resistant epoxy paint wherein zinc (Zn) contributes to the formation of a small-celled structure in char upon expansion of the

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paint during a fire, thereby improving thermal insulation performance and adhesion to a substrate by virtue of such a structure. However, excessive use of zinc makes it impossible to expand the paint film, undesirably deteriorating thermal insulation performance.

US Patent No. 5,108,832 describes an epoxy-based flame-resistant paint having high flexibility from a synthesized epoxy resin having high flexibility. In this US patent, the epoxy resin was synthesized from an epoxy monomer having a chain structure, and the flame-resistant paint was prepared using the same, and thus flexibility was estimated by low-temperature cycle testing.

US Patent No. 6,096,812 describes a paint film having low density thanks to the use of hydrophobic fumed silica, thereby ensuring flame resistance while reducing the use of the paint.

All of these US patents disclose the foaming mechanism of the flame-resistant paint using boric acid and ammonium polyphosphate. Boric acid emits a gas in coincidence with a dehydration reaction at about 170°C, and such a gas allows the paint film to expand. However, such a foaming mechanism is problematic because noxious gases may be emitted upon foaming.

Meanwhile, Korean Patent Application Publication No. 2011-0051395 discloses a foamable flame-resistant paint having superior thermal insulation performance thanks to high expansion rate by heat, wherein the foamed flame-resistant paint layer (foaming layer) may be prevented from being separated by the wind pressure. This patent proposes a foamable flame-resistant paint technique wherein the paint includes an inorganic anti-scattering agent having a melting point higher or lower by at most 100°C than the expansion temperature of expandable graphite and further includes 1 ~ 20 wt% of a foaming agent. However, the above patent suffers

from the additional use of the foaming agent. Moreover, the paint film is not formed on a steel specimen and the back temperature of the circular paint film having a thickness of 10 mm and a diameter of 70 mm is measured using an IR laser thermometer, making it difficult to objectively verify the thermal insulation effects.

5 The common features of the patent techniques proposed to date are to additionally emit gases in coincidence with reaction of the inner materials of a paint film during a fire. While the gases are emitted, unreacted materials, decomposed materials or materials having low molecular weight are discharged together from the paint film, and thus the generated gases undesirably contain large amounts of noxious components. Accordingly, there are needs for novel
10 techniques able to reduce the emission of noxious gases upon expansion of flame-resistant paints during fires.

Disclosure

Technical Problem

15 Accordingly, the present invention has been made keeping in mind the above problems encountered in the related art, and the present invention is intended to provide a solvent-free flame-resistant epoxy paint composition, wherein accordion-like expansion of plate-shaped expandable graphite is newly proposed, thereby reducing emission of noxious gases during fires and ensuring superior flame resistance.

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Technical Solution

The present invention provides a solvent-free flame-resistant epoxy paint composition having reduced gas toxicity during a fire, suitable for use as a binary liquid type foamable flame-resistant epoxy paint composition including a primary composition and a hardener composition, comprising: a primary composition A comprising 5 ~ 70 wt% of an epoxy resin, 1 ~ 50 wt% of
5 a phosphorus-based flame retardant, 1 ~ 50 wt% of expandable graphite, 0.05 ~ 30 wt% of fibers, 0.01 ~ 10 wt% of a pigment and 1 ~ 20 wt% of an additive; and a hardener composition B comprising 10 ~ 80 wt% of an amine-based hardener, 1 ~ 40 wt% of a phosphorus-based flame retardant, 0.05 ~ 20 wt% of fibers, 1 ~ 40 wt% of a filler, 0.01 ~ 10 wt% of a pigment and 0.5 ~ 20 wt% of an additive, wherein the expandable graphite is expandable graphite coated with a
10 silane compound.

In the present invention, the mixing ratio of the primary composition A and the hardener composition B is preferably a weight ratio of 3.0:1 ~ 2.0:1.

In the present invention, the expandable graphite coated with the silane compound is preferably expandable graphite coated with a silane compound selected from the group
15 consisting of epoxysilane, aminosilane, phenyl-based silane and mixtures thereof, having a molecular weight of 100 ~ 400.

In the present invention, the expandable graphite coated with the silane compound is preferably expandable graphite coated with a silane compound in an amount of 0.1 ~ 30 wt% based on the total weight of the expandable graphite, and is more preferably expandable graphite
20 coated with a silane compound in an amount of 0.3 ~ 25 wt% based on the total weight of the expandable graphite.

In the present invention, the primary composition A preferably comprises 10 ~ 60 wt% of the epoxy resin selected from the group consisting of a bisphenol A epoxy resin, a phenol novolac epoxy resin and mixtures thereof, having a weight average molecular weight of 200 ~ 800; 5 ~ 40 wt% of the phosphorus-based flame retardant selected from the group consisting of triphenylphosphate, tris(2,3-dichloropropyl)phosphate, ammonium polyphosphate, phosphoric acid ester, tricresylphosphate, trichloroethylphosphate and mixtures thereof; 2 ~ 40 wt% of the expandable graphite coated with the silane compound; 0.1 ~ 20 wt% of the fibers having a length of 0.1 ~ 6.0 mm selected from the group consisting of mineral fibers, glass fibers, ceramic fibers, organic fibers and mixtures thereof; 0.02 ~ 8 wt% of the pigment; and 1 ~ 20 wt% of the additive selected from the group consisting of a thickener, a dispersant, an antifoaming agent, a plasticizer and mixtures thereof.

The hardener composition B preferably comprises 20 ~ 70 wt% of the amine-based hardener selected from the group consisting of diethylenetriamine, triethylenetetramine, tetraethylenepentamine, 3,3-aminobispropylamine, m-xylenediamine and mixtures thereof; 5 ~ 30 wt% of the phosphorus-based flame retardant selected from the group consisting of triphenylphosphate, tris(2,3-dichloropropyl)phosphate, ammonium polyphosphate, phosphoric acid ester, tricresylphosphate, trichloroethylphosphate and mixtures thereof; 0.1 ~ 15 wt% of the fibers having a length of 0.1 ~ 6.0 mm selected from the group consisting of mineral fibers, glass fibers, ceramic fibers, organic fibers and mixtures thereof; 2 ~ 30 wt% of the filler comprising a spherical filler selected from the group consisting of calcium carbonate, Wollastonite and mixtures thereof, having an average particle size of 0.1 ~ 20 μm , or a hollow filler selected from

the group consisting of alumina, glass, ceramic and mixtures thereof, having an average particle size of 0.1 ~ 2 μm ; 0.02 ~ 8 wt% of the pigment; and 0.5 ~ 20 wt% of the additive selected from the group consisting of a thickener, a dispersant, an antifoaming agent, a plasticizer and mixtures thereof.

- 5 In the paint composition according to the present invention, gas toxicity is measured to be 11 min or more by a gas toxicity testing method (KSF 2271).

Advantageous Effects

- According to the present invention, a solvent-free flame-resistant epoxy paint
10 composition having reduced gas toxicity during a fire includes, as a foaming agent, expandable graphite coated with a silane compound, and thus, during a fire, the expansion rate of a paint film can be controlled and the emission of noxious gases can be reduced, thereby lowering the risk of asphyxia during a fire. Also, because this composition is a solvent-free type having high durability, it is an eco-friendly paint that does not generate volatile organic compounds (VOCs).
15 Therefore, the composition according to the present invention can be effectively utilized as flame-resistant paints for oil- or gas-handling facilities such as marine structures or plants and also confined spaces such as tunnels, underground areas, etc.

Mode for Invention

- 20 The present invention addresses a solvent-free flame-resistant epoxy paint composition having reduced gas toxicity during a fire. This composition is a binary liquid type foamable

flame-resistant epoxy paint composition including a primary composition A and a hardener composition B, comprising a primary composition A comprising 5 ~ 70 wt% of an epoxy resin, 1 ~ 50 wt% of a phosphorus-based flame retardant, 1 ~ 50 wt% of expandable graphite, 0.05 ~ 30 wt% of fibers, 0.01 ~ 10 wt% of a pigment and 1 ~ 20 wt% of an additive; and a hardener
5 composition B comprising 10 ~ 80 wt% of an amine-based hardener, 1 ~ 40 wt% of a phosphorus-based flame retardant, 0.05 ~ 20 wt% of fibers, 1 ~ 40 wt% of a filler, 0.01 ~ 10 wt% of a pigment and 0.5 ~ 20 wt% of an additive, wherein the expandable graphite is expandable graphite coated with a silane compound.

Below is a detailed description of components of the composition according to the
10 present invention.

Primary composition A

1) Epoxy resin

According to the present invention, the epoxy resin exhibits durability on a dry paint film, and enables the paint film to become flexible when exposed to high temperature during a
15 fire, so that the paint film may expand. In the present invention, either or both of a bisphenol A epoxy resin based on a bisphenol A monomer and a phenol novolac epoxy resin based on phenol novolac may be used, with a weight average molecular weight of 200 ~ 800.

The amount of the epoxy resin is 5 ~ 70 wt%, and preferably 10 ~ 60 wt%, based on the total weight of the primary composition A. If the amount thereof is less than 5 wt%, adhesion of
20 the paint film may deteriorate due to the lack of the resin. In contrast, if the amount thereof is greater than 70 wt%, the viscosity of the paint may decrease and thus the paint may flow down

upon expansion of the paint film.

2) Phosphorus-based flame retardant

Useful in the present invention, the phosphorus-based flame retardant is a typical flame retardant for use in flame-resistant paints and preferably includes any material which is able to form a carbonaceous layer during a fire to increase thermal insulation performance. The flame retardant containing phosphorus may include phosphate, phosphite, phosphonate and phosphonium groups, and specific examples thereof preferably include triphenyl phosphate, tris(2,3-dichloropropyl)phosphate, ammonium polyphosphate, phosphoric acid ester, tricresylphosphate, trichloroethylphosphate, etc., which may be used alone or in mixtures of two or more.

The amount of the flame retardant is 1 ~ 50 wt%, and preferably 5 ~ 40 wt%, based on the total weight of the primary composition A. If the amount thereof is less than 1 wt%, the carbonaceous layer has poor strength and may thus be easily broken or the thermal insulation performance may decrease. In contrast, if the amount thereof is greater than 50 wt%, the carbonaceous layer becomes too hard, and may thus be easily broken and the thermal insulation performance cannot be exhibited.

3) Expandable graphite coated with silane compound

Expandable graphite has to be surface-treated with a silane compound so as to be efficiently wet into the paint composition. As the expandable graphite which was not surface-treated is poorly wet into the paint composition, durability may drastically decrease and mechanical properties may also deteriorate. To prepare expandable graphite coated with a silane

compound, expandable graphite is placed in a mixer such as a Henschel mixer or a container mixer, and then stirred while adding one or more of epoxysilane, aminosilane and phenyl-based silane, having a molecular weight of about 100 ~ 400. Thereby, the epoxy or amino component on the surface of the expandable graphite is crosslinked with the binder of the resin, thus
5 attaining superior wettability.

The silane compound is used in an amount of 0.1 ~ 30 wt%, and preferably 0.3 ~ 25 wt%, based on the total weight of the expandable graphite. If the amount thereof is less than 0.1 wt%, wettability may undesirably deteriorate due to the absence of surface coating effects. In contrast, if the amount thereof is greater than 30 wt%, the expandable graphite may not be
10 dispersed in the paint due to lowered free flowing properties, undesirably decreasing wettability.

The amount of the expandable graphite with the silane compound is 1 ~ 50 wt%, and preferably 2 ~ 40 wt%, based on the total weight of the primary composition A. If the amount thereof is less than 1 wt%, the proportion of the expandable graphite may excessively decrease, making it impossible to expand the paint, undesirably leading to decreased thermal insulation
15 performance. In contrast, if the amount thereof is greater than 50 wt%, the paint may excessively expand and thus the carbonaceous layer may crack and its strength may decrease, undesirably leading to decreased thermal insulation performance.

4) Fibers

Useful in the present invention, the fibers function to prevent the carbonaceous layer
20 from cracking and from being separated upon foaming. The fibers may include mineral, glass, ceramic, organic components, etc., and preferably have a length of 0.05 ~ 8.0 mm, and

preferably 0.1 ~ 6.0 mm. If the length of the fibers is less than 0.05 mm, cracking cannot be prevented due to the short fibers. In contrast, if the length thereof is greater than 8.0 mm, the tip of the application device may clog upon painting due to the long fibers.

The amount of the fibers is 0.05 ~ 30 wt%, and preferably 0.1 ~ 20 wt%, based on the total weight of the primary composition A. If the amount thereof is less than 0.05 wt%, the proportion of the fibers is low, making it impossible to exhibit an effect of preventing the cracking of the carbonaceous layer. In contrast, if the amount thereof is greater than 30 wt%, the paint may be less expanded due to the excess of the fibers, undesirably deteriorating thermal insulation performance.

10 5) Pigment

The pigment is typically added to impart a color to the paint, and a black or colored pigment is employed.

The amount of the pigment is 0.01 ~ 10 wt%, and preferably 0.02 ~ 8 wt%, based on the total weight of the primary composition A. If the amount thereof is less than 0.01 wt%, the color of the paint may become non-uniform due to lowered concealing performance. In contrast, if the amount thereof is greater than 10 wt%, flame resistance may deteriorate due to the excess of the pigment.

6) Additive

The additive comprising one or more of a thickener, a dispersant, an antifoaming agent, a plasticizer, etc. may be mixed at an appropriate ratio so as to manifest optimal paint and paint film performance. The additive is preferably used in an amount of 1 ~ 20 wt% based on the total

weight of the primary composition A. If the amount of the additive is less than 1 wt%, the paint may not be efficiently dispersed, and thus bubbles may be undesirably generated in the paint film. In contrast, if the amount thereof is greater than 20 wt%, adhesion performance of the paint film may decrease.

5 Hardener composition B

1) Amine-based hardener

Useful in the present invention, the hardener plays a role in curing the epoxy resin of the primary composition. To this end, an amine-based hardener such as amine, polyamide, amidoamine, etc., may be used, and specific examples thereof preferably include
10 diethylenetriamine, triethylenetetramine, tetraethylenepentamine, 3,3-aminobispropylamine, m-xylenediamine and mixtures thereof.

The amount of the amine-based hardener is 10 ~ 80 wt%, and preferably 20 ~ 70 wt%, based on the total weight of the hardener composition B. If the amount thereof is less than 10 wt%, adhesion of the paint film may decrease due to the lack of the hardener. In contrast, if the
15 amount thereof is greater than 80 wt%, paint film defects such as amine brushing, etc., may occur due to the excess of the hardener.

2) Phosphorus-based flame retardant

Useful in the present invention, the phosphorus-based flame retardant is a typical flame retardant for use in flame-resistant paints and preferably has a material that is able to form a
20 carbonaceous layer during a fire to thus increase thermal insulation performance. The phosphorus-based flame retardant may include phosphate, phosphite, phosphonate and

phosphonium groups, and specific examples thereof preferably include triphenyl phosphate, tris(2,3-dichloropropyl)phosphate, ammonium polyphosphate, phosphoric acid ester, tricresylphosphate, and trichloroethylphosphate, which may be used alone or in mixtures of two or more.

5 The amount of the phosphorus-based flame retardant is 1 ~ 40 wt%, and preferably 5 ~ 30 wt%, based on the total weight of the hardener composition B. If the amount thereof is less than 1 wt%, the carbonaceous layer may have poor strength and may thus be easily broken or the thermal insulation performance may decrease. In contrast, if the amount thereof is greater than 40 wt%, the carbonaceous layer may become too hard, and may thus be easily broken and
10 the thermal insulation performance cannot be exhibited.

3) Fibers

Useful in the present invention, the fibers function to prevent cracking of the carbonaceous layer and separation of the carbonaceous layer upon foaming. The fibers may include mineral, glass, ceramic, organic components, etc., and preferably have a length of 0.05 ~
15 6.0 mm, and preferably 0.1 ~ 5.0 mm. If the length of the fibers is less than 0.05 mm, cracking cannot be prevented due to the short fibers. In contrast, if the length thereof is greater than 6.0 mm, the tip of the application device may clog upon painting due to the long fibers.

The amount of the fibers is 0.05 ~ 20 wt%, and preferably 0.1 ~ 15 wt%, based on the total weight of the hardener composition B. If the amount thereof is less than 0.05 wt%, the
20 proportion of the fibers is low, making it impossible to show an effect of preventing the cracking of the carbonaceous layer. In contrast, if the amount thereof is greater than 20 wt%, the paint

may be less expanded due to the excess of the fibers, undesirably deteriorating thermal insulation performance.

4) Filler

Useful in the present invention, the filler is added to supplement flame resistance, and a
5 typical spherical filler and a hollow filler may be used alone or in combination. Such a typical spherical filler may include calcium carbonate, Wollastonite, etc., having an average particle size of about 0.1 ~ 20 μm , which may be used alone or in combination. The hollow filler may include one or more of alumina, glass, ceramic, etc., and the particle size thereof falls in the range of 0.1 ~ 2 μm .

10 The amount of the filler is 1 ~ 40 wt%, and preferably 2 ~ 30 wt%, based on the total weight of the hardener composition B. If the amount of the filler is less than 1 wt%, thermal insulation performance at high temperature may decrease. In contrast, if the amount thereof is greater than 40 wt%, the paint film may become hard, undesirably incurring cracking.

5) Pigment

15 The pigment is typically used to impart a color to the paint, and use is made of a white or colored pigment.

The amount of the pigment is 0.01 ~ 10 wt%, and preferably 0.02 ~ 8 wt%, based on the total weight of the hardener composition B. If the amount thereof is less than 0.01 wt%, the color of the paint may become non-uniform due to lowered concealing performance. In
20 contrast, if the amount thereof is greater than 10 wt%, flame resistance may deteriorate due to the excess of the pigment.

6) Additive

The additive comprising one or more of a thickener, a dispersant, an antifoaming agent, a plasticizer, etc. may be mixed at an appropriate ratio so as to exhibit optimal paint and paint film performance. The additive is preferably used in an amount of 0.5 ~ 20 wt% based on the total weight of the hardener composition B. If the amount of the additive is less than 0.5 wt%, the paint is not efficiently dispersed, undesirably generating bubbles in the paint film. In contrast, if the amount thereof is greater than 20 wt%, adhesion performance of the paint film may decrease.

Meanwhile, in order to form a paint film from the composition of the invention, the primary composition and the hardener composition are mixed at an appropriate ratio using a high-temperature unary or binary liquid type painting machine, or Hera. For example, the paint film may be formed using a high-temperature binary liquid type painting machine in such a manner that the primary composition and the hardener composition are mixed at an appropriate ratio by means of a static mixer and then sprayed. As such, the mixing ratio of the primary composition A and the hardener composition B according to the present invention is preferably 3.0:1 ~ 2.0:1.

When the painting process is performed once, the thickness of the paint film is preferably set to about 2 ~ 8 mm. If the thickness thereof is less than 2 mm, painting efficiency may remarkably decrease. In contrast, if the thickness thereof is greater than 8 mm, sagging may occur.

A better understanding of the present invention may be obtained through the following

examples which are set forth to illustrate, but are not to be construed to limit the present invention.

Preparative Example 1: Preparation of epoxy resin

Placed in a four-neck flask were 472 g of epichlorohydrin and 25 g of 2-methoxyethanol. The solution was maintained at a temperature of 55 ~ 60°C, and 177 g of a bisphenol A resin was slowly added for 3 hr with stirring. After completion of the addition, the resulting solution was allowed to stand for about 30 min, after which the temperature was lowered to 50 ~ 60°C and the pressure was reduced, followed by distilling epichlorine and water. During distillation for 4 hr, the temperature was gradually increased to about 120°C. As such, the distilled amount corresponded to about 300 g. The reaction compound remaining in the flask was cooled to 110°C, added with 240 g of water to remove NaCl and then stirred, resulting in two separate layers. The water layer was removed, and extraction with 360 g of water was performed once more. The compound remaining in the flask was heated to 140°C, so that compounds having low boiling points, which might be still left behind, were removed under low pressure for 30 min, thereby synthesizing 256 g of a liquid epoxy resin. The weight average molecular weight of the synthesized resin was 250 ~ 800.

Preparative Example 2: Preparation of expandable graphite coated with epoxysilane

In a mixer such as a Henschel mixer or a container mixer, 500 g of expandable graphite (EG58, available from ZJGHI) was placed, and 50 g of epoxysilane was slowly sprayed onto the expandable graphite using a spraying machine for 30 min with slow stirring. Additionally,

stirring for 1 hr was carried out, so that the expandable graphite was efficiently coated with epoxysilane, and then filtered with a 20 mesh filter and packaged.

Examples 1 and 2 and Comparative Examples 1 and 2: Preparation of flame-resistant paint composition

5 **(1) Primary composition A**

The primary composition of the flame-resistant paint composition was prepared using components in amounts shown in Table 1 below. To this end, a planetary mixer or a high-speed dissolver was used, and low-speed or high-speed stirring was conducted so as for efficient dispersion following addition of each of the components. Also, all of the added components
10 were dispersed by low-speed or high-speed stirring.

[Table 1]

	Material	Ex.1	Ex.2	C.Ex.1	C.Ex.2
Epoxy resin	Prep.Ex.1	35	41.4	35	41.4
	YDPN631 ¹⁾	9.4	0	9.4	0
Phosphorus-based flame retardant	AP422 ²⁾	24	26	24	26
	TCEP	1	1	1	1
Expandable graphite coated with silane compound	Prep.Ex.2	20	23	0	0
Expandable graphite	EG58 ³⁾	0	0	20	0
Foaming agent	Melamine ⁴⁾	0	0	0	21
Fibers	AS-70C ⁵⁾	5	3	5	5
Pigment	MA-100 ⁶⁾	0.1	0.1	0.1	0.1
Additive	BYK108 ⁷⁾	0.5	0.5	0.5	0.5

	DMP ⁸⁾	5	5	5	5
Total		100	100	100	100

(unit: g)

- 1) YDPN631: available from Kukdo Chemical
- 2) AP422: available from Clariant
- 3) EG58: available from ZJGHI
- 5 4) melamine: available from AMI
- 5) AS-70C: available from KCC Corp.
- 6) MA-100: available from Mitsubishi
- 7) BYK108: available from BYK Chemie
- 8) DMP: available from Lanxess

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(2) Hardener composition B

The hardener composition of the flame-resistant paint composition was prepared using components in amounts shown in Table 2 below. To this end, a planetary mixer or a high-speed dissolver was used, and low-speed or high-speed stirring was conducted so as for efficient dispersion following addition of each of the components. Also, all of the added components were dispersed by low-speed or high-speed stirring.

[Table 2]

	Material	Ex.1	Ex.2	C.Ex.1	C.Ex.2
Hardener	GA0432 ¹⁾	24.5	49.5	47.5	25.0

	R-9930 ²⁾	30	8	5	29.5
Phosphorus-based flame retardant	AP422 ³⁾	25	27	27	20
Fibers	AS-70C ⁴⁾	5	5	5	5
Filler	FAS-10 ⁵⁾	10	5	10	15
Pigment	CR-95 ⁶⁾	5	5	5	5
Additive	BYK-108 ⁷⁾	0.5	0.5	0.5	0.5
Total		100	100	100	100

(unit: g)

1) GA0432: available from Kukdo Chemical

2) R-9930: available from KCC Corp.

3) AP422: available from Clariant

5 4) AS-70C: available from KCC Corp.

5) FAS-10: available from ZJGHI

6) CR-95: available from Ishihara

7) BYK108: available from BYK Chemie

10 **Experimental Example: Measurement of properties after painting**

The primary composition and the hardener composition were added at a weight ratio of 2.4:1 to the container of a binary liquid type painting machine and then painted. Upon painting, the internal temperature of the container was controlled in the range of 50 ~ 70°C. For gas toxicity testing, a specimen having a size of 4 mm * 220 mm * 220 mm was used, and painting
15 was implemented so that the thickness of a paint film was 6 mm. Also, in flame resistance testing, heating was carried out according to a rapid heating fire temperature curve of ISO834, a

specimen having a size of 6 mm thickness * 320 mm * 500 mm was used, and painting was performed so that the thickness of a paint film was 10 mm. After painting, the paint film was dried and then underwent the following gas toxicity and flame resistance testing.

(1) Gas toxicity testing

5 Gas toxicity testing was performed according to KSF 2271. This was mainly carried out in such a manner that the specimen coated with the flame-resistant paint was heated and thus burned, and the generated smoke was collected and transferred into a room with mice, after which the average deed stopping time of mice was measured. The average deed stopping time of mice may increase in proportion to a reduction in gas toxicity. The gas toxicity results were
10 compared using the painted specimens. The test results are given in Table 3 below.

[Table 3]

	Ex.1	Ex.2	C.Ex.1	C.Ex.2
Average deed stopping time	12 min	11 min	8 min	7 min

As is apparent from the above test results, the average deed stopping time of the
15 comparative examples is 7 ~ 8 min, and the average deed stopping time of the examples is 11 ~ 12 min. Hence, the gas toxicity was reduced by 35% or more. Thereby, asphyxia due to noxious gases during fires may be lowered, ultimately attaining effects of reducing gas toxicity.

(2) Flame resistance testing

Flame resistance testing was performed using a rapid heating temperature curve

(ISO834) wherein an oil fire heating temperature was simulated, and the back temperature of the specimen was measured. This heating curve is characteristic in that the temperature is increased up to 945°C within 5 min, and is an international standard heating temperature graph for oil fire testing. The evaluation is as follows: when the back temperature of a specimen after testing does not exceed 140°C based on the average back temperature of a specimen at the start of testing, performance adequate for a flame-resistant structure may be regarded as ensured. The flame resistance results were compared using the painted specimens. The test results are given in Table 4 below.

10 [Table 4]

		Ex.1	Ex.2	C.Ex.1	C.Ex.2
Back Temperature (°C) of Specimen	0 min	25	25	25	25
	10 min	75	70	92	78
	20 min	97	97	102	106
	30 min	114	114	119	120
	40 min	129	128	152	147
	50 min	139	138	166	173
	60 min	150	148	185	195
Temperature difference, °C (60 min ~ 0 min)		125	123	160	175

As is apparent from the above test results, flame resistance of the examples satisfies the standard of IMO A754 because the temperature difference between the temperature after testing and the temperature at initial testing is less than 140°C. However, flame resistance of the

comparative examples does not satisfy the standard of IMO A754 because of the temperature difference of greater than 140°C between the temperature after testing and the temperature at initial testing. Therefore, the flame-resistant paints of the examples can satisfy the international standard of IMO A754 for flame-resistant paints for marine structures, etc. and can be confirmed
5 to have commercialization potential.

CLAIMS

1. A solvent-free flame-resistant epoxy paint composition having reduced gas toxicity during a fire, suitable for use as a binary liquid type foamable flame-resistant epoxy paint composition, comprising:

a primary composition A comprising 5 ~ 70 wt% of an epoxy resin, 1 ~ 50 wt% of a phosphorus-based flame retardant, 1 ~ 50 wt% of an expandable graphite, 0.05 ~ 30 wt% of fibers, 0.01 ~ 10 wt% of a pigment and 1 ~ 20 wt% of an additive; and

a hardener composition B comprising 10 ~ 80 wt% of an amine-based hardener, 1 ~ 40 wt% of a phosphorus-based flame retardant, 0.05 ~ 20 wt% of fibers, 1 ~ 40 wt% of a filler, 0.01 ~ 10 wt% of a pigment and 0.5 ~ 20 wt% of an additive,

wherein the expandable graphite is an expandable graphite coated with a silane compound.

2. The paint composition of claim 1, wherein a mixing ratio of the primary composition A and the hardener composition B is a weight ratio of 3.0:1 ~ 2.0:1.

3. The paint composition of claim 1, wherein the expandable graphite coated with the silane compound is an expandable graphite coated with a silane compound selected from the group consisting of epoxysilane, aminosilane, phenyl-based silane and mixtures thereof, having a molecular weight of 100 ~ 400.

4. The paint composition of claim 3, wherein the expandable graphite coated with the silane compound is an expandable graphite coated with a silane compound in an amount of 0.1 ~ 30 wt% based on a total weight of the expandable graphite.

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5. The paint composition of claim 4, wherein the expandable graphite coated with the silane compound is an expandable graphite coated with a silane compound in an amount of 0.3 ~ 25 wt% based on the total weight of the expandable graphite.

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6. The paint composition of claim 1, wherein the primary composition A comprises:

10 ~ 60 wt% of the epoxy resin selected from the group consisting of a bisphenol A epoxy resin, a phenol novolac epoxy resin and mixtures thereof, having a weight average molecular weight of 200 ~ 800;

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5 ~ 40 wt% of the phosphorus-based flame retardant selected from the group consisting of triphenylphosphate, tris(2,3-dichloropropyl)phosphate, ammonium polyphosphate, phosphoric acid ester, tricresylphosphate, trichloroethylphosphate and mixtures thereof;

2 ~ 40 wt% of the expandable graphite coated with the silane compound;

0.1 ~ 20 wt% of the fibers having a length of 0.1 ~ 6.0 mm selected from the group consisting of mineral fibers, glass fibers, ceramic fibers, organic fibers and mixtures thereof;

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0.02 ~ 8 wt% of the pigment; and

1 ~ 20 wt% of the additive selected from the group consisting of a thickener, a

dispersant, an antifoaming agent, a plasticizer and mixtures thereof.

7. The paint composition of claim 1, wherein the hardener composition B comprises:

20 ~ 70 wt% of the amine-based hardener selected from the group consisting of
5 diethylenetriamine, triethylenetetramine, tetraethylenepentamine, 3,3-aminobispropylamine, m-xylenediamine and mixtures thereof;

5 ~ 30 wt% of the phosphorus-based flame retardant selected from the group consisting of triphenylphosphate, tris(2,3-dichloropropyl)phosphate, ammonium polyphosphate, phosphoric acid ester, tricresylphosphate, trichloroethylphosphate and mixtures thereof;

10 0.1 ~ 15 wt% of the fibers having a length of 0.1 ~ 6.0 mm selected from the group consisting of mineral fibers, glass fibers, ceramic fibers, organic fibers and mixtures thereof;

2 ~ 30 wt% of the filler comprising a spherical filler selected from the group consisting of calcium carbonate, Wollastonite and mixtures thereof, having an average particle size of 0.1 ~ 20 μm , or a hollow filler selected from the group consisting of alumina, glass, ceramic and
15 mixtures thereof, having an average particle size of 0.1 ~ 2 μm ;

0.02 ~ 8 wt% of the pigment; and

0.5 ~ 20 wt% of the additive selected from the group consisting of a thickener, a dispersant, an antifoaming agent, a plasticizer and mixtures thereof.

20 8. The paint composition of claim 1, wherein gas toxicity is measured to be 11 min or more by a gas toxicity testing method (KSF 2271).