

TITLE

NON-TAR TYPE EPOXY RESIN PAINT COMPOSITIONS, PAINTING
METHODS OF OUTSIDE SHELLS OF SHIPS' HULLS AND PAINTED
SHIPS' HULLS ✓

FIELD OF THE INVENTION

The present invention relates to non-tar type epoxy resin paint compositions, heavy-duty coating films formed from the compositions, painting methods of outside shells of ships' hulls and painted ships' hulls. More particularly, the invention relates to non-tar type epoxy resin paint compositions which exhibit excellent performance as heavy-duty coating compositions employable for all of the parts of ships such as outside shells of ships' hulls, exposed decks, super structures, holds and ballast tanks, and which are capable of forming films having excellent adhesive strength to films of organotin-free hydrolyzable antifouling paints or other various top coats provided thereon. The invention also relates to heavy-duty coating films formed from the paint compositions. The invention further relates to painting methods of outside shells of ships' hulls, by the use of which films of excellent anticorrosive properties, weathering resistance and antifouling properties can be formed with few kinds of paints to thereby accomplish shortening of the painting time and reduction of the costs for paint storage, and which are advantageous in the hygienic qualities for painting workers and the

environmental protection. The invention furthermore relates to ships' hulls painted by these methods.

BACKGROUND OF THE INVENTION

For various parts of ships' hulls such as outside shells of ships' hulls, exposed decks, super structures, holds and ballast tanks, different heavy-duty coating compositions have been hitherto used.

Of these ship parts, the outside shells of ships' hulls can be roughly divided into three regions of a bottom that is always immersed in water (including freshwater and seawater), a topside that is not immersed in water and a boot topping that is located between the bottom and the topside and repeatedly subjected to immersion in water and exposure to the atmosphere. In the painting of the outside shells of ships' hulls, the paint for the topside is desired to have weathering resistance because this region is exposed to intensive sunlight and rough seas, the paint for the bottom is desired to have antifouling properties because this region is always submerged, and the paint for the boot topping is desired to have weathering resistance, water resistance and occasionally antifouling properties because this region suffers rough seas and is repeatedly subjected to immersion in water and exposure to dry air.

In order to coat the regions with paints satisfying the above requirements, therefore, plural kinds of primers for exclusive use are currently prepared in consideration

of adhesive strength or the like, and thereby adhesive strength and anticorrosive properties are ensured.

The bottom and occasionally the boot topping have been hitherto coated with tar-type epoxy resin heavy-duty coating compositions having excellent anticorrosive properties in a large thickness, but the paints of this type have a problem in carcinogenesis of tar or a problem in that rusting after painting, burned defects caused by heat of welding or cutting and condition of the paint film can be hardly judged by visual observation because the tar is black.

Further, the paints containing tar have another problem in that the tar component bleeds out into a top coat film provided on the paint film to cause bad appearance of the ships' hulls or to exert evil influences on various functions such as antifouling properties and weathering resistance.

As the primers for the topside and occasionally the boot topping of the outside shell, non-tar type primers are generally used to avoid the above-mentioned tar bleeding. Accordingly, in the use of the tar type epoxy heavy-duty coating compositions having excellent anticorrosive properties as primers for the bottom or primers for the bottom and the boot topping, much care must be taken. For example, the tar type and the non-tar type primers should be painted by protecting the boundaries of these primers (i.e., protecting the non-paint region by means of attachment of a sheet or a tape). The overlapping portion

(portion wherein different paints overlap to each other) should be treated with care in the painting process. In addition, when a different paint is used, the painting machine needs to be sufficiently washed, and this results in complicated process and waste of thinners.

In the conventional painting method, further, when the surface of a film of the tar type epoxy heavy-duty coating composition is coated with an organotin-free hydrolyzable antifouling paint, it is necessary to previously apply a vinyl type or tar vinyl type binder coat to the tar type epoxy heavy-duty coating film and then apply the organotin-free hydrolyzable antifouling paint to the binder coat, because the adhesive strength between the films is low. If a top coat is applied to the tar type epoxy heavy-duty coating film, application of the top coat is carried out at an interval of a given period of time. In case of the tar type epoxy heavy-duty coating compositions, the interval is relatively short, and this results in complicated process and complicated execution control.

In the conventional painting method, heavy-duty coating compositions for regions other than the submerged region in the outside shell and for the exposed deck are different from each other as described above, and for each region, an exclusive top coat and an exclusive binder coat are used. Further, with various needs of the customers, an extremely large number of paints must be prepared, and complicated execution control is necessary. Hence, the costs for paint storage and for transportation of paints

become high. Moreover, because of complicated painting process, a long period of time is required for painting, and the process control becomes complicated.

Accordingly, now desired is development of a heavy-duty coating composition which can form a uniform primer film on all of the parts of a ship's hull, such as an outside shell (including a bottom, boot topping and topside), an exposed deck, a super structure, a hold and a ballast tank, to impart anticorrosive properties to those parts, which can form a top coat film of excellent adhesive strength and antifouling properties when the primer film is optionally overcoated with an organotin-free hydrolyzable antifouling paint or the like, and which can shorten the painting time.

Also desired is development of a painting method of an outside shell of a ship's hull, which is capable of forming excellent antifouling films by coating the outside shell of a ship's hull with few kinds of paints in a specific order, which is capable of shortening the painting time and reducing the costs for paint storage, and which is advantageous in the hygienic qualities for painting workers and the environmental protection.

OBJECT OF THE INVENTION

The present invention is intended to solve such problems associated with the prior art as described above, and it is an object of the invention to provide a non-tar type epoxy resin paint composition which is useful as a

heavy-duty coating composition employable as a primer capable of being applied to all of ship parts such as an outside shell of a ship's hull and an exposed deck, by which application of a binder coat is omissible when an organotin-free hydrolyzable antifouling paint is further provided, which can give the outside shell or other ship parts various properties such as anticorrosive properties, weathering resistance, water resistance and antifouling properties equal to or higher than those of the conventional tar type epoxy heavy-duty coating compositions, which can accomplish rationalization of the painting process and reduction of the costs for paint storage, and which is advantageous in the hygienic qualities for painting workers and the environmental protection.

It is another object of the invention to provide a heavy-duty coating film formed from the paint composition.

It is a further object of the invention to provide a painting method of an outside shell of a ship's hull, which can impart desired properties such as anticorrosive properties, weathering resistance, water resistance and antifouling properties to the outside shell by using only one kind of a specific outside shell paint as a primer and by applying few kinds of paints without using any binder coat, which can accomplish rationalization of the painting process and reduction of the costs for paint storage, and which is advantageous in the hygienic qualities for painting workers and the environmental protection.

It is a still further object of the invention to provide a ship's hull painted by the method.

SUMMARY OF THE INVENTION

The non-tar type epoxy resin paint composition according to the present invention comprises:

- (a) a bisphenol epoxy resin (preferably a bisphenol epoxy resin having an epoxy equivalent of 100 to 500),
- (b) a vinyl chloride copolymer, and
- (c) a hardener comprising a polyamide or its modified product.

The paint composition of the invention preferably further contains (d) an aluminum powder in addition to the components (a), (b) and (c). In the paint composition of the invention, tricresyl phosphate is preferably contained. In this invention, the vinyl chloride copolymer is preferably a vinyl chloride/alkyl vinyl ether copolymer.

The non-tar type epoxy resin paint composition is useful as a heavy-duty coating composition.

The heavy-duty coating film according to the present invention is formed from the non-tar type epoxy resin paint composition.

According to the non-tar type epoxy resin paint composition of the invention, heavy-duty coating compositions for various ship parts such as an outside shell and an exposed deck can be unified to one kind of a heavy-duty coating composition, and use of a binder coat is omissible when an organotin-free hydrolyzable antifouling

paint is further provided. Moreover, the outside shell and other parts of a ship's hull can be imparted with various functions, e.g., anticorrosive properties, weathering resistance, water resistance and antifouling properties, which are equal to or higher than those of the conventional tar type epoxy heavy-duty coating compositions.

Further, even if a top coat such an organotin-free hydrolyzable antifouling paint is applied to the film of the non-tar type epoxy resin paint composition at an interval of a long period of time without using a binder coat, excellent adhesive strength between layers can be obtained. That is, the paint composition of the invention can contribute rationalization of the painting process, rationalization of the ship-building process and reduction of the costs for paint storage. Furthermore, the non-tar type epoxy resin paint composition is advantageous in the hygienic qualities for painting workers and the environmental protection.

The painting method of the outside shell of a ship's hull according to the present invention comprises the steps of:

coating (i) a bottom of a ship's hull or (ii) a bottom and a boot topping of a ship's hull with a non-tar type epoxy resin heavy-duty coating composition as a primer to form a primer film; and

then further coating the surface of the primer film with an organotin-free hydrolyzable antifouling paint.

In this invention, it is possible that:

the whole outside shell of a ship's hull including a bottom, a boot topping and a topside is coated with a non-tar type epoxy resin heavy-duty coating composition as a primer to form a primer film; and

then the surface of the primer film provided on (i) the bottom or (ii) the bottom and the boot topping out of the thus primer-treated outside shell is further coated with an organotin-free hydrolyzable antifouling paint.

In this invention, it is also possible that:

the whole outside shell of a ship's hull including a bottom, a boot topping and a topside is coated with a non-tar type epoxy resin heavy-duty coating composition as a primer to form a primer film;

then the surface of the primer film provided on (i) the bottom or (ii) the bottom and the boot topping out of the thus primer-treated outside shell is further coated with an organotin-free hydrolyzable antifouling paint, and the surface of the primer film provided on the topside is coated with a topside top coat;

and if necessary,

the boot topping is furthermore coated with a boot topping top coat.

The painted ship's hull according to the present invention has:

a non-tar type epoxy resin heavy-duty coating primer film applied on (i) a bottom of the ship's hull or (ii) a bottom and a boot topping of the ship's hull, and

an organotin-free hydrolyzable antifouling film applied on the primer film.

The painted ship's hull of the invention may have:

a non-tar type epoxy resin heavy-duty coating primer film applied on the whole outside shell of the ship's hull including a bottom, a boot topping and a topside, and

an organotin-free hydrolyzable antifouling film applied on the primer film provided on (i) the bottom or (ii) the bottom and the boot topping out of the whole primer film.

The painted ship's hull of the invention may have:

a non-tar type epoxy resin heavy-duty coating primer film applied on the whole outside shell of the ship's hull including a bottom, a boot topping and a topside,

an organotin-free hydrolyzable antifouling film applied on the primer film provided on (i) the bottom or (ii) the bottom and the boot topping out of the whole primer film,

a topside top coat film applied on the primer film provided on the topside,

and if necessary

a boot topping top coat film applied on the boot topping.

In any of the above-mentioned painting methods and painted ships' hulls of the invention, the non-tar type epoxy resin heavy-duty coating composition (primer) or the primer film obtained by applying and hardening said

composition preferably further contains a thermoplastic resin.

The thermoplastic resin is preferably at least one resin selected from a chlorinated polyolefin, an acrylic resin, a vinyl acetate resin, a styrene resin and a vinyl chloride resin. The vinyl chloride resin is preferably a vinyl chloride/vinyl alkyl ether copolymer, more preferably a vinyl chloride/vinyl isobutyl ether copolymer.

In the present invention, the non-tar type epoxy resin heavy-duty coating composition or the film obtained by applying and hardening said paint preferably contains an aluminum powder.

In the present invention, the topside top coat or the film obtained by applying and hardening said top coat preferably comprises an urethane paint, an epoxy paint, an acrylic paint or a chlorinated polyolefin paint (chlorinated rubber paint); and the boot topping top coat or the film obtained by applying and hardening said top coat preferably comprises an urethane paint, an epoxy paint, an acrylic paint, a chlorinated polyolefin paint (chlorinated rubber paint), an organotin-free antifouling paint or a mixture of these paints.

In the present invention, the organotin-free hydrolyzable antifouling paint or the film obtained by applying and hardening said paint preferably contains a trialkylsilyl ester copolymer containing 20 to 65 % by weight of constituent units derived from a trialkylsilyl ester of a polymerizable unsaturated carboxylic acid and

having a number-average molecular weight (M_n) of 1,000 to 50,000.

In the present invention, the organotin-free hydrolyzable antifouling paint or the film obtained by applying and hardening said paint preferably contains a vinyl resin in which an organic acid is linked to at least one side chain terminal through a metallic ester linkage.

According to the painting method of the outside shell of a ship's hull of the invention, films having excellent anticorrosive properties, weathering resistance and antifouling properties can be formed with few kinds of paints. Therefore, the method can accomplish shortening of the painting time and reduction of the costs for paint storage, and is advantageous in the hygienic qualities for painting workers and the environmental protection.

The painted ship's hull according to the present invention can be obtained by conducting hygienic painting work for a short period of time using few kinds of paints, and has excellent anticorrosive properties, weathering resistance and antifouling properties.

DETAILED DESCRIPTION OF THE INVENTION

The non-tar type epoxy resin paint composition, the film formed from the composition, the painting method of the outside shell of ship's hull and the painted ship's hull according to the invention are described in detail hereinafter.

Non-tar type epoxy resin paint composition

The non-tar type epoxy resin paint composition of the invention comprises:

- (a) a bisphenol epoxy resin,
- (b) a vinyl chloride copolymer, and
- (c) a hardener comprising a polyamide or its modified product.

(a) Bisphenol epoxy resin

The epoxy resin for use in the invention is a bisphenol epoxy resin having an epoxy equivalent of preferably 160 to 500, more preferably 160 to 300. The epoxy resin is ordinarily liquid to solid. The epoxy equivalent of the bisphenol epoxy resin for use in the paint composition of the invention is preferably within the above range from the viewpoints of adhesive strength of the paint composition and workability in the painting process.

The paint composition of the invention contains a bisphenol epoxy resin from among various epoxy resins, so that the film formed from the composition has toughness and flexibility and thereby shows excellent adhesive strength.

Examples of the bisphenol epoxy resins include epoxy resins of bisphenol A type, epoxy resins of bisphenol F type, dimer acid-modified epoxy resins, polysulfide-modified epoxy resins and hydrogenated products of these bisphenol epoxy resins.

Particular examples of the epoxy resins of bisphenol A type include diglycidyl ethers of bisphenol A type, such as a bisphenol A diglycidyl ether, a bisphenol A polypropylene oxide diglycidyl ether, a bisphenol A ethylene oxide

diglycidyl ether, a hydrogenated bisphenol A diglycidyl ether and a hydrogenated bisphenol A propylene oxide diglycidyl ether. Particular examples of the epoxy resins of bisphenol F type include diglycidyl ethers of bisphenol F type, such as a bisphenol F diglycidyl ether.

Of these, the epoxy resins of bisphenol A type are preferable.

Examples of the epoxy resins which are liquid at ordinary temperature include those under the trade names of Epikote 828 (available from Shell Co., epoxy equivalent: 180 - 190, viscosity: 12,000 - 15,000 cPs/25°C), Epotohto YDF-170 (available from Tohto Kasei Co., Ltd., epoxy equivalent: 160 - 180, viscosity: 2,000 - 5,000 cPs/25°C) and Frep 60 (available from Toray Thiokol K.K., epoxy equivalent: about 280, viscosity: about 17,000 cPs/25°C).

Examples of the epoxy resins which are semi-solid at ordinary temperature include those under the trade names of Epikote 834 (available from Shell Co., epoxy equivalent: 230 - 270) and Epotohto YD134 (available from Tohto Kasei Co., Ltd., epoxy equivalent: 230 - 270). Examples of the epoxy resins which are solid at ordinary temperature include an epoxy resin under the trade name of Epikote 1001 (available from Shell Co., epoxy equivalent: 450 - 500).

Together with the bisphenol epoxy resin (a) having an epoxy equivalent of 160 to 500, other epoxy resins can be used in the present invention. For example, epoxy resins having an epoxy equivalent of more than 500 and epoxy resins other than the bisphenol epoxy resins can be used in

such small amounts as not prejudicial to the objects of the invention, e.g., in an amount of not more than 60 parts by weight based on 100 parts by weight of the bisphenol epoxy resin (a).

The epoxy resin not having an epoxy equivalent of 160 to 500 is, for example, an epoxy resin under the trade name of Epotohto YD-172 (available from Tohto Kasei Co., Ltd., epoxy equivalent: 600 - 700). Examples of the epoxy resins of non-bisphenol type include those of cyclic aliphatic type, non-cyclic aliphatic type and epoxidized oil type.

(b) Vinyl chloride copolymer

Examples of the vinyl chloride copolymer (b) include a vinyl chloride/vinyl acetate copolymer, a vinyl chloride/vinyl propionate copolymer, a vinyl chloride/alkyl vinyl ether copolymer, a vinyl chloride/acrylonitrile copolymer, a vinyl chloride/diethyl maleate copolymer, a vinyl chloride/ethylene copolymer, a vinyl chloride/maleic anhydride copolymer, a vinyl chloride/alkyl (meth)acrylate copolymer (number of carbon atoms of alkyl group: about 1 to 5), a vinyl chloride/styrene copolymer, a vinyl chloride/vinylidene chloride copolymer, a vinyl chloride/vinyl stearate copolymer, a vinyl chloride/maleic acid (or maleic acid ester) copolymer and a vinyl chloride/aliphatic vinyl copolymer.

Also available are graft modified products of polyvinyl chloride obtained by graft modifying polyvinyl chloride with "other monomers" than vinyl chloride and

copolymers obtained by graft modifying "other polymers" than the polyvinyl chloride with a polyvinyl chloride monomer.

Examples of the other monomers include (meth)acrylic acid alkyl esters (number of carbon atoms of alkyl group: about 1 to 5), styrene, acrylonitrile, diethyl maleate, olefins (e.g., ethylene, propylene), maleic anhydride, vinylidene chloride, stearic acid, maleic acid, maleic acid esters and aliphatic vinyl, which are monomers for forming the vinyl chloride copolymer.

Of the above vinyl chloride copolymers (b), the vinyl chloride/alkyl vinyl ether copolymer is preferable because it shows good affinity for the bisphenol epoxy resin (a) and has excellent overcoatability and anticorrosive properties.

Examples of the vinyl chloride/alkyl vinyl ether copolymers preferably used in the invention include copolymers of vinyl chloride and alkyl vinyl ethers having alkyl groups of 1 to 10 carbon atoms, preferably 2 to 5 carbon atoms, such as a vinyl chloride/isobutyl vinyl ether copolymer, a vinyl chloride/isopropyl vinyl ether copolymer and a vinyl chloride/ethyl vinyl ether copolymer.

The vinyl chloride copolymer (b) is desired to have a weight-average molecular weight (M_w) of usually 10,000 to 100,000, preferably 20,000 to 50,000, particularly preferably 22,000 to 40,000. When the weight-average molecular weight is within this range, the affinity of the copolymer for the epoxy resin tends to be improved.

As the vinyl chloride/isobutyl vinyl ether copolymer from among the vinyl chloride/alkyl vinyl ether copolymers, there can be mentioned, for example, Laroflex LR8829, Laroflex MP25, Laroflex MP35 and Laroflex MP45 (all being trade names, available from BASF Co.)

These vinyl chloride copolymers can be used singly or in combination of two or more kinds.

The vinyl chloride copolymer (b) is used in an amount of usually 5 to 90 parts by weight, preferably 10 to 30 parts by weight, based on 100 parts by weight of the bisphenol epoxy resin (a) which is one component of the non-tar epoxy resin paint composition. When the vinyl chloride copolymer (b) is contained in this amount in the paint composition, the copolymer shows good affinity for the bisphenol epoxy resin (a) and the composition tends to have good anticorrosive properties and overcoatability. The compounding proportion of the vinyl chloride copolymer (b) is desirably in the above range from the viewpoints of both of anticorrosive properties of the resulting film and overcoatability with the top coat.

Together with the vinyl chloride copolymer (b) that is a thermoplastic resin, other thermoplastic resins than the vinyl chloride copolymer can be contained in the paint composition of the invention within limits not prejudicial to the objects of the invention. In the non-tar type epoxy resin paint composition, the thermoplastic resin other than the vinyl chloride copolymer (b) may be contained in such an amount that the total amount of the thermoplastic resin

components including the vinyl chloride copolymer (b) becomes usually 5 to 90 parts by weight, preferably 7 to 50 parts by weight, particularly preferably 10 to 30 parts by weight, based on 100 parts by weight of the bisphenol epoxy resin (a).

The thermoplastic resins (rubbers) including the vinyl chloride copolymer (b) act as relaxation agents of internal stress when the non-tar type epoxy resin paint composition (epoxy paint, epoxy heavy-duty coating composition) is hardened, and thereby adhesive strength between a substrate or an undercoating film and an epoxy film formed from the epoxy paint can be improved. The thermoplastic resins (rubbers) are solvent-soluble and are dissolved in a solvent contained in the top coat, so that they can improve adhesive strength of the epoxy film to the top coat or can ease restrictions on the painting interval of the epoxy paint (i.e., can extend the painting interval), and they contribute increase in the kinds of top coats capable of being applied onto the epoxy film.

Examples of the thermoplastic resins (rubbers) other than the vinyl chloride copolymer (b) include chlorinated polyolefins, such as chlorinated rubber, chlorinated polyethylene and chlorinated polypropylene; acrylic resins, such as methyl (meth)acrylate copolymers, propyl (meth)acrylate copolymers, butyl (meth)acrylate copolymers and cyclohexyl (meth)acrylate copolymers; styrene resins; aromatic petroleum resins; aliphatic petroleum resins;

urea-aldehyde condensation resins; ketone resins; coumarone-indene resin; and pentadiene polymers.

These thermoplastic resins (rubbers) can be used singly or in combination of two or more kinds.

(c) Hardener comprising polyamide or
modified product thereof

As the hardener (c) for the bisphenol epoxy resin (a), a polyamide or its modified product is employed. The non-tar type epoxy resin paint composition containing the hardener (c) can be hardened at ordinary temperature, and therefore the composition is favorably used for painting work generally performed at ordinary temperature, e.g., painting of outside shells of ships' hulls.

The polyamide and its modified product are desired to have an amine value of usually 50 to 1,000, preferably 80 to 500. When the amine value of the hardener is in this range, the balance between drying characteristics and adhesive strength tends to be improved. The hardener is ordinarily liquid to solid.

Examples of the polyamides include those under the trade names of Luckamide N-153 (available from Dainippon Ink & Chemicals Inc., amine value: 80 - 120), Luckamide TD-966 (available from Dainippon Ink & Chemicals Inc., amine value: 150 - 190) and Sunmide 315 (available from Sanwa Kagaku Kogyo K.K., amine value: 280 - 340).

Examples of the modified products of polyamides include epoxy adducts obtained by the addition of epoxy compounds to polyamides, such as PA-23 (trade name,

available from Otake Kagaku K.K., amine value: 80 - 150), and Mannich modified products of modified polyamides, such as Adeca Hardener EH-350 (trade name, available from Asahi Denka Kogyo K.K., amine value: 320 - 380).

Of the polyamides and their modified products, the adducts of epoxy compounds are preferably employed.

The polyamides and their modified products can be used singly or in combination of two or more kinds.

In the present invention, the polyamide or its modified product is desirably used in such an amount that the equivalent ratio between the epoxy of the bisphenol epoxy resin (a) and the amine of the hardener in the non-tar type epoxy resin paint composition becomes usually 1 : 0.35 (epoxy component : amine component) to 1 : 0.9, preferably 1 : 0.4 to 1 : 0.8. When the polyamide or its modified product is used in this amount, a paint film formed from the composition tends to have excellent drying characteristics, anticorrosive properties and overcoatability. In other words, the polyamide or its modified product is used in an amount of usually 10 to 80 parts by weight, preferably 20 to 70 parts by weight, based on 100 parts by weight of the bisphenol epoxy resin (a) in the non-tar type epoxy resin paint composition.

In the present invention, hardeners for the epoxy resin other than the polyamide and its modified product may be contained within limits not prejudicial to the objects of the invention.

There is no specific limitation on the other hardeners, as far as they react with the epoxy resin to harden it. For example, amine type hardeners other than the polyamides and their modified products, carboxylic acid type hardeners, acid anhydride type hardeners and silanol type hardeners are employable. The amine type hardeners are preferably those of liquid to solid having an amine value of 50 to 1,000, preferably 80 to 500.

Examples of the amine type hardeners for the epoxy resin include aliphatic amines such as polyalkylenepolyamine, aromatic amines and alicyclic amines. Also employable are epoxy adducts obtained by the addition of epoxy compounds to these amines, Mannich modified products and carboxylic acid modified products.

Hardeners of ketimine type obtained by modifying these amine compounds with ketones are also employable.

Examples of the amine compounds optionally used in the invention include modified alicyclic polyamine of ketimine type, such as Anchamine MCA (trade name, available from Anchor Chemical, Ltd., amine value: 250 - 350); modified phenol amine, such as Cardlite 541LV (trade name, available from Cardlite Corporation, amine value: 260 - 350); and modified aromatic polyamine, such as Adeca Hardener EH101 (trade name, available from Asahi Denka Kogyo K.K., amine value: 400 - 500).

These amine compounds can be used singly or in combination of two or more kinds.

The amine compound is used in such an amount that the total amount of the polyamide or its modified product (c) and the amine compound becomes usually 10 to 80 parts by weight, preferably 20 to 70 parts by weight, based on 100 parts by weight of the bisphenol epoxy resin (a) in the non-tar type epoxy resin paint composition. In other words, the amine compound is used in such an amount that the equivalent ratio between the epoxy of the resin (a) and the amine of the hardener becomes usually 1 : 0.35 (epoxy equivalent : amine equivalent) to 1 : 0.9, preferably 1 : 0.4 to 1 : 0.8.

Other additives

In the non-tar type epoxy resin paint composition (heavy-duty coating composition) of the invention, various additives, such as plasticizer, extender pigment, color pigment, rust proof pigment, solvent, hardening accelerator, anti-sagging agent and anti-settling agent, may be contained in addition to the above components.

The non-tar type epoxy resin paint composition of the invention preferably contains an aluminum powder as the pigment component. Examples of the aluminum powders include those of leafing type and non-leafing type having a mean particle diameter of 1 to 100 μm .

When the aluminum powder is added to the paint composition in an amount of 3 to 30 % by weight, preferably 4 to 10 % by weight, the anticorrosive properties are greatly improved, and the water resistance in the submergence environment becomes good. If the amount of the

aluminum powder exceeds the upper limit of the above range, the viscosity of the paint composition increases with improvement of the anticorrosive properties, and consequently kneading properties in the preparation of paint and handling properties in the painting process tend to lower.

The non-tar type epoxy resin paint composition (non-tar type epoxy resin paint) is used as (1) a two-pack (two-part) type consisting of (I) a composition comprising the epoxy resin component (a) and the vinyl chloride copolymer (b) and (II) a composition comprising the hardener component (c), or used as (2) a two-pack (two-part) type consisting of (I-a) a composition comprising the epoxy resin component (a) and (II-a) a composition comprising the vinyl chloride copolymer (b) and the hardener component (c). Of these, preferable is the two-pack type (1).

These parts are stored in separate containers, and in the use thereof, they are mixed immediately before the primer coating process or they are mixed by means of a mixing spray such as a twin spray gun in the coating process.

The non-tar type epoxy resin paint composition of the invention has excellent adhesive strength to various top coats. As the top coat for ship parts, the later-described organotin-free hydrolyzable antifouling paint is particularly preferably used.

That is, it is preferable that (i) a bottom of a ship's hull or (ii) a bottom and a boot topping of a ship's

hull, which are brought into contact with seawater, preferably the whole outside shell of a ship's hull including the bottom, the boot topping and the topside, are coated with the non-tar type epoxy resin heavy-duty coating composition as a primer to form a primer film, and then the surface of the primer film is further coated with an organotin-free hydrolyzable antifouling paint to form an antifouling paint film, whereby excellent adhesive strength between the primer film and the antifouling paint film can be obtained.

Painting methods of outside shells of ships' hulls

In the painting method of an outside shell of a ship's hull according to the invention, (i) a bottom of a ship's hull or (ii) a bottom and a boot topping of a ship's hull are coated with the later-described non-tar type epoxy resin heavy-duty coating composition as a primer to form a primer film, preferably followed by drying the primer film. Then, the thus treated primer film are further coated with the later-described organotin-free hydrolyzable antifouling paint.

In the present invention, it is also possible that the whole outside shell of a ship's hull including a bottom, a boot topping and a topside are coated with the non-tar type epoxy resin heavy-duty coating composition as a primer, preferably followed by drying the resultant primer film. Then, the surface of the primer film provided on (i) the bottom or (ii) the bottom and the boot topping out of the

thus primer-treated outside shell is coated with the organotin-free hydrolyzable antifouling paint.

The flat bottom portion of the ship bottom is located at the most deeply submerged place of the ship's hull, and sunlight hardly reaches the place. Therefore, this portion is unsuitable for growth of algae and is less fouled with organisms than other portions, that is, the flat bottom portion is under relatively mild environmental conditions.

Accordingly, the flat bottom portion can be coated with, not the organotin-free hydrolyzable antifouling paint of excellent antifouling properties, but the conventional antifouling paints which are inexpensive and economically advantageous (e.g., antifouling paints of chlorinated rubber type, vinyl type and acrylic type) or hydration-decomposable antifouling paints. According to the ship running environment, the flat bottom portion does not need to be coated with an antifouling paint.

In the present invention, the topside (outside shell above the boot topping) having been subjected to the primer treatment is coated with a topside top coat, because this region is exposed to intensive sunlight or rough seas and is desired to have weathering resistance.

The topside top coat is preferably an urethane paint, an epoxy paint, an acrylic paint or a chlorinated polyolefin paint (chlorinated rubber paint), particularly an urethane paint.

The boot topping having been subjected to the primer treatment undergoes dry-wet alternate attacks of immersion

in seawater and exposure to the atmosphere and is under severe environmental conditions, so that this region is desired to have weathering resistance, water resistance, and occasionally, antifouling properties. For this reason, the boot topping is coated with the below-described organotin-free hydrolyzable antifouling paint or boot topping top coat.

The boot topping top coat is preferably an urethane paint, an epoxy paint, an acrylic paint, a chlorinated polyolefin paint (chlorinated rubber paint) or an organotin-free antifouling paint, particularly preferably an epoxy paint or an organotin-free hydrolyzable antifouling paint.

In the painting of the outside shell of a ship's hull, the following methods are available.

(1) The whole outside shell composed of a bottom, a boot topping and a topside is subjected to primer coating at a time, preferably followed by drying the resultant primer film. Then, the bottom (i) or the bottom and boot topping (ii) are coated with an organotin-free hydrolyzable antifouling paint.

(2) For each region of the outside shell, i.e., a bottom, a boot topping or a topside, or for each portion of each region, coating with the primer and overcoating with the organotin-free hydrolyzable antifouling paint ((i) bottom, or (ii) bottom and boot topping) are carried out, or coating with the primer and coating of the topside with the topside top coat or coating of the boot topping with

the boot topping top coat are carried out. After the primer coating of the outside shell, the individual regions may be subjected to the prescribed overcoating one after another as soon as being dried.

Next, the non-tar type epoxy resin paint, the organotin-free hydrolyzable antifouling paint, the topside top coat and the boot topping top coat for use in the above-mentioned painting method are described.

Non-tar type epoxy resin heavy-duty coating composition

In the non-tar type epoxy resin heavy-duty coating composition used for the painting method of the outside shell of a ship's hull according to the invention, a pigment component and a thermoplastic resin may be optionally contained in addition to the bisphenol epoxy resin and the hardener for the epoxy resin. Further, various additives which are added to the conventional paint compositions, such as a plasticizer, extender pigment, color pigment, rust proof pigment, solvent, hardening accelerator, anti-sagging agent and anti-settling agent, may be contained.

In the preferred embodiment of the invention, a non-tar type epoxy resin heavy-duty coating composition using a bisphenol epoxy resin of liquid to solid having an epoxy equivalent of 160 to 500 is preferably employed.

The bisphenol epoxy resin is preferably an aromatic epoxy resin of bisphenol A type or bisphenol F type. Details of the bisphenol epoxy resin are as described hereinbefore.

There is no specific limitation on the hardener, as far as it reacts with the epoxy resin to harden the resin, and various hardeners, such as those of amine type, carboxylic acid type, acid anhydride type and silanol type, can be arbitrarily employed. The painting of the outside shell of a ship's hull is often conducted at ordinary temperature. Therefore, preferably used are hardeners capable of being hardened at ordinary temperature, and particularly preferably used are hardeners of amine type. Details of the amine type hardeners are as described hereinbefore.

Of the amine type hardeners, particularly preferable are polyamides, epoxy adducts of polyamide amines and modified phenol amines.

The non-tar type epoxy resin heavy-duty coating composition preferably contains an aluminum powder as the pigment component. Details of the aluminum powder are as described hereinbefore.

The non-tar type epoxy resin heavy-duty coating composition preferably further contains a thermoplastic resin. The amount of the thermoplastic resin contained in the composition is preferably in the range of 5 to 90 parts by weight based on 100 parts by weight of the total amount of the epoxy resin and the hardener.

The thermoplastic resin acts as a relaxation agent of internal stress when the non-tar type epoxy resin heavy-duty coating composition (epoxy paint) is hardened, and thereby adhesive strength between a substrate or an

undercoating film and an epoxy film formed from the epoxy paint can be improved.

The thermoplastic resin is solvent-soluble and is dissolved in a solvent contained in the top coat, so that the resin can improve adhesive strength of the epoxy film to the top coat film or can ease restrictions on the painting interval of the epoxy paint (i.e., can extend the painting interval), and the resin contributes increase in the kinds of top coats capable of being applied onto the epoxy film.

Details of the thermoplastic resin are as described above with respect to the vinyl chloride copolymer (b). Of various thermoplastic resins, a vinyl chloride/alkyl vinyl ether copolymer such as a vinyl chloride/isobutyl vinyl ether copolymer is most preferable.

In the non-tar type epoxy resin heavy-duty coating composition, various additives which are generally used for the conventional paints, such as a plasticizer, extender pigment, color pigment, rust proof pigment, solvent, hardening accelerator, anti-sagging agent and anti-settling agent, may be contained in addition to the above components.

The non-tar epoxy resin heavy-duty coating composition is generally used as a two-pack (two-part) type consisting of (I) a composition comprising the epoxy resin component and (II) a composition comprising the hardener component. These parts are stored in separate containers, and in the use thereof, they are mixed immediately before the primer

coating process or they are mixed by means of a mixing spray such as a twin spray gun in the coating process.

When a hardener having been modified so as not to react with the epoxy component during the storage (e.g., amine block hardener of ketimine type) is used, the non-tar type epoxy resin heavy-duty coating composition may be a one-pack type paint.

For preparing the non-tar type epoxy resin heavy-duty coating composition, the epoxy resin component and the hardener component are preferably mixed (compounded) in an equivalent ratio of 1 : 0.4 to 1 : 0.8.

Differently from the tar type epoxy resin paints, the non-tar type epoxy resin heavy-duty coating composition does almost not cause skin eruption or irritation of workers in the painting process.

Organotin-free hydrolyzable antifouling paint

The organotin-free hydrolyzable antifouling paint is, for example, an antifouling paint containing (i) a trialkylsilyl ester copolymer, or an antifouling paint containing (ii) a vinyl resin in which an organic acid is linked to at least one side chain terminal through a metallic ester linkage.

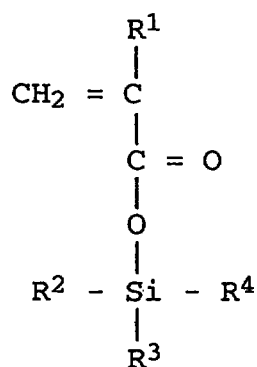
The trialkylsilyl ester copolymer (i) and the vinyl resin (ii) preferably used in the invention are described below in detail.

(i) Trialkylsilyl ester copolymer

The trialkylsilyl ester copolymer contains constituent units derived from a trialkylsilyl ester of a polymerizable

unsaturated carboxylic acid in amounts of 20 to 65 % by weight and has a number-average molecular weight (Mn) of 1,000 to 50,000.

The trialkylsilyl ester is represented by, for example, the following formula (I).



(I)

In the formula (I), R¹ is a hydrogen atom or an alkyl group such as methyl; R², R³ and R⁴ are each an alkyl group of about 1 to 18 carbon atoms, such as methyl, ethyl, propyl or butyl; and R², R³ and R⁴ may be the same as or different from each other.

Examples of the trialkylsilyl esters include;

trialkylsilyl esters of the above formula wherein R², R³ and R⁴ are the same as each other, such as trimethylsilyl (meth)acrylate, triethylsilyl (meth)acrylate, triisopropylsilyl (meth)acrylate and tributylsilyl (meth)acrylate; and

trialkylsilyl esters of the above formula wherein a part of or all of R², R³ and R⁴ are different from each other, such as dimethylpropylsilyl (meth)acrylate,

amount of usually not less than 30 % by weight, preferably not less than 50 % by weight.

In the copolymer, the constituent units derived from the polymerizable unsaturated compound such as an (meth)acrylic acid alkyl ester and the constituent units derived from the trialkylsilyl ester are bonded usually at random by means of cleavage of ethylene bond of each monomer used as the starting material.

In this film-forming copolymer, the constituent units (trialkylsilyl ester constituent units) derived from one or more of the trialkylsilyl esters of polymerizable unsaturated carboxylic acids may be contained as described above, and the trialkylsilyl ester constituent units are desirably contained in the total amounts of 20 to 65 % by weight, preferably 30 to 55 % by weight. When the constituent units are contained in the above amounts, an antifouling film having excellent long-term antifouling properties can be formed from the antifouling paint composition containing this copolymer.

The copolymer desirably has a number-average molecular weight (M_n), as measured by GPC, of 1,000 to 50,000, preferably 2,000 to 20,000, more preferably 2,500 to 15,000, particularly preferably 3,000 to 12,000, and has a weight-average molecular weight (M_w) of usually 1,000 to 150,000, preferably 2,000 to 60,000, more preferably 3,000 to 30,000. The copolymer desirably has a molecular weight distribution (M_w/M_n) of usually 1.0 to 4.0, preferably 1.0 to 3.0, particularly preferably 1.0 to 2.5. Further, the

Examples of the vinyl resin (ii) include vinyl resins described in Japanese Patent Laid-Open Publication No. 73536/1996 and Japanese Patent Publication No. 108927/1995.

As described in Japanese Patent Laid-Open Publication No. 73536/1996, the vinyl resin (ii) can be prepared by copolymerizing a (meth)acrylic acid ester wherein the alcohol residue of its ester is a branched alkyl group of 4 or more carbon atoms having at least one side chain on the second to the fourth carbon atom from the main chain terminal or a cycloalkyl group of 6 or more carbon atoms with a polymerizable unsaturated organic acid monomer and a neutral polymerizable unsaturated monomer to synthesize a base resin; and then causing the acid group (e.g., $-\text{COOH}$, $-\text{SO}_3\text{H}$) of the base resin to react with a metallic compound (e.g., metallic oxide, metallic hydroxide, metallic chloride, metallic sulfide) and a monobasic organic acid (e.g., acetic acid, naphthenic acid) at the same time, or causing the base resin to react with a metallic salt of the monobasic organic acid.

Examples of the (meth)acrylic acid esters include *t*-butyl (meth)acrylate and cyclohexyl (meth)acrylate. Examples of the polymerizable organic acid monomers include (meth)acrylic acid, maleic acid and *p*-styrenesulfonic acid. Examples of the neutral polymerizable unsaturated monomers include ethylene, methyl (meth)acrylate and ethyl (meth)acrylate. Examples of metals for forming the metallic compounds include di- or higher-valent metals such as Cu, Zn, Mn, Ca, Fe, Al, Te and Ba.

Topside top coat

Examples of the topside top coats include oil (alkyd) paint, phthalic acid resin paint, chlorinated polyolefin paint (chlorinated rubber paint), vinyl paint, acrylic paint, epoxy paint, urethane paint, silicone alkyd paint, acrylic silicone paint and fluorine resin paint.

Of these, the urethane paint, epoxy paint, acrylic paint or the chlorinated polyolefin paint (chlorinated rubber paint) is preferably used as the topside top coat, in consideration of weathering resistance, adhesive strength and economical advantage.

Particular examples of the topside top coats include those available from Chugoku Marine Paints Ltd. under the trade names of Uny Marine (isocyanate crosslinked two-pack type urethane resin top coat), Epicon Marine Top Coat and Epicon Marine HB (modified polyamide crosslinked two-pack type epoxy resin top coat), Ravax Top Coat (chlorinated polyolefin top coat), and Acri 700 Top Coat (acrylic resin top coat).

Boot topping top coat

As the boot topping top coat, organotin-free antifouling paints as well as the above-mentioned various topside top coats are employable.

Under such severe environmental conditions that dry-wet alternate attacks of immersion in seawater and exposure to the atmosphere are repeated by ups and downs of a ship as in the outside shell of a ship's hull, water resistance, weathering resistance, anticorrosive properties and

occasionally antifouling properties are desired.

Therefore, of the above paints, the urethane paint, epoxy paint, acrylic paint, chlorinated polyolefin paint (chlorinated rubber paint) or the organotin-free antifouling paint is preferably used as the boot topping top coat.

Particular examples of the boot topping top coats include those available from Chugoku Marine Paints Ltd. under the trade names of Uny Marine (isocyanate crosslinked two-pack type urethane resin top coat), Epicon Marine Top Coat and Epicon Marine HB (modified polyamide crosslinked two-pack type epoxy resin top coat), Ravax Top Coat (chlorinated polyolefin top coat), and Acri 700 Top Coat (acrylic resin top coat).

The top coats for use in the invention may contain various components which are added to conventional outside shell paints, such as an antifouling agent, plasticizer, hydrolysis adjusting agent, pigment, solvent, viscosity modifier and other additives.

In the present invention, the non-tar type epoxy resin paint composition (heavy-duty coating composition) or the top coats are applied to the surface of the outside shell of ship's hull by the conventional coating methods using, for example, airless spray, air spray, brush or roller, and hardened to form paint films (hardened film). Prior to the primer treatment, substances attached to the outside shell surface, such as a rust, fat, oil, water, dust, slime and salt, may be removed to clean the surface. The paints may

be diluted with thinners or the like to obtain proper concentrations.

The coating weight (amount) of the paints varies according to the type of the ship to be coated, the type of the overcoating paint, the combination of paints, etc., and cannot be discriminatingly determined. However, the non-tar type epoxy resin heavy-duty coating composition (primer) is applied, for example, in an amount of 100 to 500 g/m² and in a coating thickness of about 50 to 500 μ m to give a dry film thickness of about 30 to 300 μ m.

The organotin-free hydrolyzable antifouling paint is applied to the primer film on the bottom and boot topping of the ship outside shell, for example, in an amount of 200 to 800 g/m² and in a coating thickness of about 50 to 500 μ m to give a dry film thickness of about 30 to 300 μ m.

The urethane paint is applied to the primer film on the topside of the ship outside shell, for example, in an amount of 50 to 300 g/m² and in a coating thickness of about 40 to 300 μ m to give a dry film thickness of about 30 to 150 μ m.

In the air spray coating, coating conditions of a primary (air) pressure of about 4 to 8 kgf/cm², a secondary (paint) pressure of about 100 to 180 kgf/cm² and a gun moving rate of about 50 to 120 cm/sec are adopted.

The number of painting times of each paint is not specifically limited and can be optionally determined according to the concentration of the paint, the desired

film thickness, etc. Each paint can be applied once or plural times.

The ships' hulls having films of the above thicknesses formed by applying the above paints and hardening them are, for example, metal ships' hulls such as tankers, cargo boats, passenger boats, fishing boats, lighters and floating docks.

If the non-tar type epoxy resin heavy-duty coating composition having excellent overcoatability is used as a primer for not only the outside shell but also other parts, such as an exposed deck, a super structure (housing), a hold and a ballast tank, the number of kinds of paints used for the whole ship's hull can be remarkably decreased.

If not only the outside shell but also the exposed deck, super structure (housing), hold and ballast tank are coated with the same undercoating primer and then coated with the same overcoating primer, effects of the present invention can be further expected.

EFFECT OF THE INVENTION

By the non-tar type epoxy resin paint composition according to the invention, an outside shell or other parts of a ship's hull can be imparted with various functions, e.g., anticorrosive properties, weathering resistance, water resistance and antifouling properties, which are equal to or higher than those of the conventional tar type epoxy resin heavy-duty coating compositions. Differently from the tar type epoxy resin heavy-duty coating

compositions, the paint composition of the invention does not cause bad appearance or lowering of antifouling properties of the top coat film because of no bleeding. Therefore, protection of boundaries between the different paint regions is unnecessary.

Further, the film (heavy-duty coating film) formed by applying the non-tar type epoxy resin paint composition (heavy-duty coating composition) has excellent adhesive strength to paint films of various top coats (e.g., organotin-free hydrolyzable antifouling paints, top coats of chlorinated rubber type, urethane type and epoxy type), and is free from deterioration of appearance and lowering of the antifouling properties because of no bleeding, unlike the tar type paints. Therefore, the heavy-duty coating composition can be used for both the submerged region and the exposed region of the outside shell of a ship's hull, that is, conventional primers for various ship parts such as an outside shell and exposed deck can be replaced with one kind of this heavy-duty coating composition to thereby accomplish rationalization and conservation of labor in the painting process.

If top coats such as organotin-free hydrolyzable antifouling paints are further applied to a film of the non-tar type epoxy resin paint composition, various top coats are employable at intervals of long periods of time. Moreover, the film of the paint composition of the invention has excellent adhesive strength to the films of various top coats. Therefore, application of a binder coat

(intermediate coat) before application of a top coat is omissible, whereby rationalization of the ship-painting or the ship-building process and reduction of the costs for paint storage can be accomplished.

Differently from the conventional tar type epoxy resin paints, the non-tar type epoxy resin paint composition scarcely causes skin eruption or irritation of workers in the painting process and is advantageous in the hygienic qualities for the painting workers and the environmental protection.

In the painting method of the outside shell of a ship's hull according to the invention, paint films of excellent antifouling properties can be formed using few kinds of paints including a non-tar type epoxy resin heavy-duty coating composition and an organotin-free hydrolyzable antifouling paint. Therefore, the method can accomplish shortening of the painting time and reduction of the costs for paint storage and is advantageous in the hygienic qualities for painting workers and the environmental protection. The ship's hull painted by the method, particularly the outside shell of a ship's hull, has excellent antifouling properties.

EXAMPLE

The present invention is further described with reference to the following examples, but it should be construed that the invention is in no way limited to those examples.

In the following examples, the film thickness (μm) means a dry film thickness unless it is departed from the spirit of the invention. The term "part(s)" means "part(s) by weight".

In the following tables, the amount of each component is expressed by "part(s) by weight" unless otherwise noted.
Preparation of non-tar type epoxy resin heavy-duty coating composition

A main agent (composition containing an epoxy resin) and a hardener (composition containing a hardener component) of each non-tar type epoxy resin heavy-duty coating composition having the compounding ratio shown in Table 1 were prepared.

In the preparation of each non-tar type epoxy resin heavy-duty coating composition having the compounding ratio shown in Table 1, the main agent was prepared by sufficiently dispersing the components with a paint shaker using glass beads, and the hardener was prepared by uniformly mixing the components with a high-speed disperser.

Painting of the non-tar type epoxy resin heavy-duty coating composition is carried out immediately after the main agent and the hardener were mixed in the mixing ratio (by weight) shown in Table 1.

Table 1

Heavy-duty coating composition	Examples							
	OT-1	OT-2 (A)	OT-2 (B)	OT-3	OT-4	OT-5	OT-6	OT-7
Main agent								
Epikote 828		15	15					
Epikote 834-85x	20			20	23.5	23.5	29	29
Epikote 1001-70		8	8					
Laroflex MP-25	3	3	3	5	6	3	6	6
TCP	3	3	3	3	3	3	3	3
Talc NKK	30	27	27	25	30	30	20	20
Tar solution								
Red iron oxide	2	2	2	2	5	5	5	5
Alpaste 1900xs	7	7	7	10	7	7	10	10
Disparon 6600	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Xylene	14.5	14.5	14.5	14.5	9.5	12.5	11	11
MIBK	2	2	2	2	2	2	2	2
Methoxypropanol	2	2	2	2	2	2	2	2
1-butanol					2	2	2	2
Hardener								
Luckamide TD966	15	15	15	15	12	20	25	-
TAP	0.3	0.3	0.3	0.3	0.3	0.6	0.6	0.2
Adeca Hardener EH350								8
Mixing ratio in coating process	85:	85:	73:	85:	91.5:	91.5:	91.5:	91.5:
Main agent: hardener (by weight)	15.3	15.3	8.3	15.3	12.3	20.6	25.6	8.2

Table 1 (Continued)

Heavy-duty coating composition	Comparative example		Reference example
	H-1	H-2	E-2
Main agent			
Epikote 828		23.5	5
Epikote 834-85x	19		17
Epikote 1001-70			
Laroflex MP-25		3	
TCP			
Talc NKK	28	35	35
Tar solution	22		
Red iron oxide	5	5	7
Alpaste 1900xs		7	
Disparon 6600	1.5	1.5	1.5
Xylene	13.5	14	17
MIBK	4	2	8
Methoxypropanol		2	
1-butanol		2	
Hardener			
Luckamide TD966	7	12	10
TAP	0.3	0.3	0.2
Adeca Hardener EH350			
Mixing ratio in coating process	93:	95:	90.5:
Main agent: hardener (by weight)	7.3	12.3	10.2

The starting materials shown in Table 1 are as follows.

(1) Epikote 828 (trade name)

available from Shell Chemical Co., bisphenol A type,
liquid epoxy resin (epoxy equivalent: 180 - 190)

(2) Epikote 834-85x (trade name)

available from Shell Chemical Co., bisphenol A type,
semi-solid epoxy resin (epoxy equivalent: 290 - 310,
solvent: xylene, non-volatile content (NV): 85 %)

(3) Epikote 1001-70 (trade name)

available from Shell Chemical Co., bisphenol A type,
solid epoxy resin (epoxy equivalent: 660 - 690, solvent:
xylene/toluene/MIBK, NV: 70 %)

(4) Laroflex MP-25 (trade name)

available from BASF Co., vinyl chloride/vinyl isobutyl
ether copolymer (Mw: 28,000 - 30,000)

(5) TCP

available from Mitsubishi Gas Kagaku K.K., tricresyl
phosphate

(6) Talc NKK (trade name)

available from Fuji Talc K.K.

(7) Tar solution

available from BO Chemical Co., bojuntan varnish
(solvent: xylene, NV: 70 %)

(8) Disparon 6600 (trade name)

available from Kusumoto Kasei K.K., thixotropic agent
of powdered polyamide type

(9) Red iron oxide

trade name: Bengara Tsubame, available from Nippon
Bengara Kogyo K.K.

(10) Alpaste 1900xS (trade name)

available from Toyo Aluminum K.K., non-leaving type
aluminum (NV: 75 %, solvent: xylene/terpene)

(11) Luckamide TD-966 (trade name)

available from Dainippon Ink & Chemicals Inc.,
polyamide (amine value: 150 - 190, NV: 60 %, solvent:
xylene/1-butanol)

(12) Adeca Hardener EH350 (trade name)

available from Asahi Denka Kogyo K.K., modified
polyamine (amine value: 330 - 380, NV: 100 %)

(13) TAP (trade name)

available from Kayaku Aquezo K.K., tertiary amine
(amine value: 620)

(14) MIBK (methyl isobutyl ketone)

Discoloration resistance test of top coat

One surface of a steel plate (70 × 150 × 2.3 mm) having been subjected to sandblasting was coated with a non-tar type epoxy resin heavy-duty coating composition (primer) for testing by an air spray in such an amount that the dry film thickness would be 200 μ m, followed by drying at 20 °C for 24 hours. Then, the surface of the resulting paint film was coated with a polyolefin chloride type white top coat (trade name: Ravax Top Coat White, available from Chugoku Marine Paints Ltd.) by an air spray in such an amount that the dry film thickness would be 50 μ m, followed by drying at 20 °C for 24 hours, to obtain a test plate. The test plate was mounted on an outdoor exposure stand (in accordance with JIS K5400 9. 9) placed in Ohtake Research Center of Chugoku Marine Paints Ltd. (Ohtake-shi, Hiroshima Prefecture) so that the surface of the paint film was exposed outside, to perform an outdoor exposure test for 30 days. Thereafter, degree of discoloration of the top coat film was evaluated by visual observation.

The results are set forth in Table 2.

Table 2

Heavy-duty coating composition (primer)	Discoloration of top coat film
OT-1	not observed
OT-2 (A)	not observed
OT-2 (B)	not observed
OT-3	not observed
OT-4	not observed
OT-5	not observed
OT-6	not observed
OT-7	not observed
H-1	seriously browned
H-2	not observed
E-2	not observed

As is clear from the above results, the heavy-duty coating compositions OT-1 to OT-7 provides excellent discoloration resistance of the top coat films, so that appearance of the top coat films on the topside and the boot topping is not deteriorated.

Anticorrosive test

A steel plate (70 × 150 × 2.3 mm) having been subjected to sandblasting was coated with the test paint by an air spray in such an amount that the dry film thickness

would be 200 μm , followed by drying at 20 °C for 7 days, to obtain a test plate.

The test plate was immersed in a 3 % saline solution at 40 °C for 180 days. Then, degree of blistering and degree of rusting were evaluated by visual observation in accordance with ASTM D714-56 and ASTM D610-85, respectively, and adhesive strength was evaluated by a cross-cut adhesive test in accordance with JIS K5400 8. 5. 2.

The results are set forth in Table 3.

Evaluation marks of blister test

10: No blister is observed.

9: The area of blisters having a diameter of 0.5 mm is less than 0.2 % of the whole area of the test plate.

8: The area of blisters having a diameter of 0.5 mm is about 0.5 % of the whole area of the test plate.

7: The area of blisters having a diameter of 0.5 to 1 mm is about 0.5 % of the whole area of the test plate.

6: The area of blisters having a diameter of 1 to 2 mm is about 0.5 to 1 % of the whole area of the test plate.

5: The area of blisters having a diameter of 2 to 3 mm is about 1 to 5 % of the whole area of the test plate.

4: The area of blisters having a diameter of 3 to 5 mm is about 5 to 10 % of the whole area of the test plate.

3: The area of blisters having a diameter of 3 to 5 mm is about 10 to 15 % of the whole area of the test plate.

2: The area of blisters having a diameter of 3 to 5 mm is about 15 to 30 % of the whole area of the test plate.

1: The area of rusting-blisters is not less than 30 % of the whole area of the test plate.

Evaluation marks of rusting test (ASTM D610-85)

10: No rusting is observed, or the rusted area is less than 0.03 % of the whole area of the test plate.

9: The rusted area is not less than 0.03 % and less than 0.1 % of the whole area of the test plate.

8: The rusted area is not less than 0.1 % and less than 0.3 % of the whole area of the test plate.

7: The rusted area is not less than 0.3 % and less than 1 % of the whole area of the test plate.

6: The rusted area is not less than 1 % and less than 3 % of the whole area of the test plate.

5: The rusted area is not less than 3 % and less than 10 % of the whole area of the test plate.

4: The rusted area is not less than 10 % and less than 16 % of the whole area of the test plate.

3: The rusted area is not less than 16 % and less than 33 % of the whole area of the test plate.

2: The rusted area is not less than 33 % and less than 50 % of the whole area of the test plate.

1: The rusted area is not less than 50 % of the whole area of the test plate.

Evaluation marks of cross-cut adhesive test

10: Each cut line is fine; both sides of each cut line are smooth; and peeling is not observed at any intersection point of the cut lines and any square.

9: Each cut line is a little thick.

8: Slight peeling is observed at the intersection points of the cut lines; peeling of square is not observed; and the area of defective portion is not more than 5 % of the total area of all squares.

7: Peeling is observed at the both sides and the intersection points of the cut lines; and the area of defective portion is not more than 5 % of the total area of all squares.

6: Peeling is observed at the both sides and the intersection points of the cut lines; and the area of defective portion is 5 to 15 % of the total area of all squares.

5: The width of peeling caused by cutting is wider than that of "6"; and the area of defective portion is 15 to 25 % of the total area of all squares.

4: The width of peeling caused by cutting is wide; and the area of defective portion is 25 to 35 % of the total area of all squares.

3: Peeling of square is observed; and the area of defective portion is not more than 35 % of the total area of all squares.

2: The width of peeling caused by cutting is wider than that of "3"; and the area of defective portion is 35 to 50 % of the total area of all squares.

1: The width of peeling caused by cutting is wider than that of "2"; and the area of defective portion is 50 to 70 % of the total area of all squares.

0: The area of defective portion is not less than 70 % of the total area of all squares.

Table 3

Heavy-duty coating composition	Anticorrosive test		
	Blister	Rusting	Adhesion
OT-1	10	10	10
OT-2 (A)	10	10	10
OT-2 (B)	10	10	10
OT-3	10	10	10
OT-4	10	10	10
OT-5	10	10	10
OT-6	10	10	10
OT-7	10	10	10
H-1	10	10	10
H-2	10	10	10
E-2	5	7	9

As is clear from the results set forth in Table 3, the heavy-duty coating compositions OT-1 to OT-7 exhibit anticorrosive properties equal to or higher than those of the tar type epoxy resin heavy-duty coating compositions.

Overcoatability test

Adhesive test to various top coats

A steel plate (70 × 150 × 2.3 mm) having been subjected to sandblasting was coated with the test paint (primer) by an air spray in such an amount that the dry film thickness would be 200 μm . Then, the plate was mounted on an outdoor exposure stand (in accordance with JIS K5400 9. 9) placed in Ohtake Research Center of Chugoku Marine Paints Ltd. (Ohtake-shi, Hiroshima Prefecture) so that the surface of the test paint film was exposed outside, to perform an outdoor exposure test for 10 days. Thereafter, the plate was coated with each of various top coats shown in Table 4 by an air spray in such an amount that the dry film thickness would be 50 μm , followed by drying at 20 °C for 7 days, to obtain a test plate.

The test plate was immersed in a 3 % saline solution at 20 °C for 90 days, and adhesive strength to the top coat film was evaluated by the cross-cut adhesive test (in accordance with JIS K5400 8. 5. 2) in the same manner as described above.

The results are set forth in Table 4.

Table 4

Primer	Top Coat		
Heavy-duty coating composition	Ravax Top Coat White *1	Uny Marine White *2	Epicon Marine Top Coat White *3
OT-1	10	10	10
OT-2 (A)	10	10	10
OT-2 (B)	10	10	10
OT-3	10	10	10
OT-4	10	10	10
OT-5	10	10	10
OT-6	10	10	10
OT-7	10	10	10
H-1	2 **	2 **	4 **
H-2	6	4	8
E-2	6	4	8

** In the H-1 paint system of Table 4, discoloration (browning) of the top coat was observed.

*1: chlorinated polyolefin top coat (one-pack type), available from CHUGOKU MARINE PAINTS, LTD.

*2: isocyanate crosslinked two-pack type urethane top coat, available from CHUGOKU MARINE PAINTS, LTD.

*3: modified polyamide crosslinked two-pack type epoxy top coat, available from CHUGOKU MARINE PAINTS, LTD.

As is clear from the results set forth in Table 4, the heavy-duty coating compositions OT-1 to OT-7 exhibit excellent overcoatability with various top coats.

Preparation of organotin-free hydrolyzable antifouling paint

Antifouling paint compositions having the compounding ratios shown in Table 5 were prepared. In Table 5, the amount of each component is expressed by "part(s) by weight".

In the preparation of each antifouling paint composition having the compounding ratio shown in Table 5, the components were shaken for 2 hours in a paint shaker containing glass beads, followed by aging at room temperature for 12 hours. Then, the resulting mixture was filtered through a filter of 100 mesh, to obtain a desired organotin-free hydrolyzable antifouling paint composition.

Table 5

Component	Organotin-Free Hydrolyzable Antifouling Paint	
	AF-1	AF-2
S-3 Varnish	19	21
BL-1 Varnish	9	11
Toyoparax 150	3	1
Mica Shiratama	2	1
Red iron oxide	1	1
Titanium white	1	1
Copper suboxide	42	42
Zinc pyrithione	2	0
Copper pyrithione	0	2
Zinc white	6	6
Molecular Sieve 4A	1	1
Disparon 305	0.5	0.5
Disparon 4200-20	1	1
Xylene	12.5	11.5
Total Amount	100	100

The components shown in Table 5 are as follows.

(1) S-3 Varnish

trialkylsilyl ester copolymer solution, monomer ratio in the polymer: tributylsilyl methacrylate/methyl methacrylate = 50/50 (by weight), solvent: xylene, heating residue: 49.6 % by weight, viscosity: 259 cPs/25°C

(2) BL-1 Varnish

styrene acrylic ester copolymer solution, monomer ratio in the polymer: isobutyl methacrylate/t-butyl methacrylate/styrene/stearyl methacrylate = 30/30/30/10 (by

weight), heating residue: 50 % by weight, viscosity: A₄
(Gardner/25°C)

(3) Toyoparax 150 (trade name)

available from Tosoh K.K., chlorinated paraffin,
average number of carbon atoms: 14.5, chlorine content: 50
%, viscosity: 12 poise/25°C, specific gravity: 1.25/25°C

(4) Mica Shiratama (trade name)

available from Wakimoto Unmo, leafing type pigment,
mean particle diameter: 15 μ m, aspect ratio: 40

(5) Molecular Sieve 4A (trade name)

dehydrating agent, available from Union Showa K.K.,
synthetic zeolite powder

(6) Disparon 305 (trade name)

available from Kusumoto Chemicals, Ltd., hydrogenated
caster oil anti-sagging agent

(7) Disparon 4200-20 (trade name)

available from Kusumoto Chemicals, Ltd., polyethylene
oxide anti-settling agent, 20 % xylene paste

Adhesive test to antifouling paint

A steel plate (70 × 150 × 2.3 mm) having been
subjected to sandblasting was coated with the test paint
(primer) by an air spray in such an amount that the dry
film thickness would be 200 μ m. Then, the plate was
mounted on an outdoor exposure stand (in accordance with
JIS K5400 9. 9) placed in Ohtake Research Center of Chugoku
Marine Paints Ltd. (Ohtake-shi, Hiroshima Prefecture) so
that the surface of the test paint film was exposed

outside, to perform an outdoor exposure test for 10 days. Thereafter, the plate was coated with the organotin-free paint (AF-1 or AF-2) by an air spray in such an amount that the dry film thickness would be 100 μm , followed by drying at 20 °C for 7 days, to obtain a test plate.

The test plate was immersed in natural seawater for 180 days, and adhesive strength to the organotin-free hydrolyzable antifouling paint was evaluated by the cross-cut adhesive test (in accordance with JIS K5400 8. 5. 2).

The results are set forth in Table 6.

Table 6

Heavy-duty coating composition	Adhesion of Organotin-Free Hydrolyzable Antifouling Paint	
	AF-1	AF-2
OT-1	10	10
OT-2 (A)	10	10
OT-2 (B)	10	10
OT-3	10	10
OT-4	10	10
OT-5	10	10
OT-6	10	10
OT-7	10	10
H-1	0	0
H-2	2	2
E-2	2	2

Antifouling properties and degree of consumption in the antifouling paint system

A sandblasted plate (70 × 20 × 3 mm) was bent so as to be fit onto the side of a rotating drum placed in seawater in Hiroshima Bay.

The sandblasted plate was coated with a non-tar type epoxy resin heavy-duty coating composition (a test primer) by an air spray in such an amount that the dry film thickness would be 200 μm , followed by drying at 20 °C for 2 days. Then, the plate was coated with an organotin-free hydrolyzable antifouling paint by an applicator in such an amount that the dry film thickness would be 200 μm , followed by drying at 20 °C for 7 days, to obtain a test plate.

For comparison with the above painting method of the invention, a conventional painting method is performed in the following manner. The sandblasted plate was coated with a two-pack type tar epoxy heavy-duty coating composition (trade name: Viscon AC, available from Chugoku Marine Paints, Ltd.) by an air spray in such an amount that the dry film thickness would be 150 μm , followed by drying at 20 °C for 2 days. Then, the plate was further coated with a vinyl type binder coat (trade name: Silvax SQK, available from Chugoku Marine Paints, Ltd.) by an air spray in such an amount that the dry film thickness would be 50 μm , followed by drying at 20 °C for 2 days. Thereafter, the plate was furthermore coated with an organotin-free

hydrolyzable antifouling paint by an applicator in such an amount that the dry film thickness would be 200 μm , followed by drying at 20 °C for 7 days, to obtain a test plate.

Each of the test plates prepared above was fit onto the rotating drum, and a ship running simulation was conducted at a peripheral speed of 15 knots under 50 % working conditions (alternation of 12-hour working at night and 12-hour rest in the day time) for 12 months, to evaluate antifouling properties (dynamic antifouling properties, proportion (%) of an area of the test plate fouled with various aquatic organisms) and degree of consumption (decrease (μm) of film thickness).

The results are set forth in Table 7 and Table 8.

Table 7

Heavy-duty coating composition (Primer)	Antifouling properties: fouled area (%)	
	AF-1	AF-2
OT-1	0	0
OT-2 (A)	0	0
OT-2 (B)	0	0
OT-3	0	0
OT-4	0	0
OT-5	0	0
OT-6	0	0
OT-7	0	0
H-1	20	20
H-2	0	0
E-2	0	0
Conventional paint system (Tar epoxy heavy-duty coating composition and binder coat)	0	0

Remarks: AF-1 and AF-2 are organotin-free hydrolyzable antifouling paints shown in Table 5.

Table 8

Heavy-duty coating composition (Primer)	Degree of consumption: μm	
	AF-1	AF-2
OT-1	55	59
OT-2 (A)	56	56
OT-2 (B)	56	56
OT-3	53	54
OT-4	55	59
OT-5	53	56
OT-6	54	55
OT-7	53	54
H-1	34	31
H-2	50	54
E-2	52	55
Conventional paint system (Tar epoxy heavy-duty coating composition and binder coat)	51	53

Remarks: AF-1 and AF-2 are organotin-free hydrolyzable antifouling paints shown in Table 5.

As is clear from the results set forth in Table 7 and Table 8, the heavy-duty coating compositions OT-1 to OT-7 can provide a paint system having antifouling properties and consumption equal to or higher than those of the conventional paint system, even if any binder coat which is necessary in the conventional paint system is not used.

Effect of decrease in number of painting times, number of kinds of paints and number of kinds of thinners

With respect to the number of painting times, the number of kinds of paints and the number of kinds of thinners, the painting method of the invention is compared with the conventional painting method.

Comparison on the saving of labor in the painting process between the painting method of the invention and the conventional painting method was made by applying an organotin-free hydrolyzable antifouling paint to the bottom and the boot topping of a bulk carrier of 75,000 tons newly built, as shown in Table 9 (lifetime of paint film: 2 years).

Table 9-I

	Painting Method Using Paint of the Invention	
	Type of Paint	Number of painting times
Bottom and Boot topping	Non-tar type epoxy resin heavy-duty coating composition	2
	Organotin-free hydrolyzable antifouling paint	2
Topside	Non-tar type epoxy resin heavy-duty coating composition	1
	Urethane top coat	1
Total number of kinds of paints	3	
Total number of painting times	6	
Total number of kinds of thinners	3	

Table 9-II

	Painting Method-1 Using Conventional Paint	
	Type of Paint	Number of painting times
Bottom and Boot topping	Tar type epoxy resin heavy-duty coating composition	1
	Vinyl resin binder coat	2
	Organotin-free hydrolyzable antifouling paint	2
Topside	Chlorinated rubber heavy-duty coating composition	2
	Chlorinated rubber top coat	2
Total number of kinds of paints	5	
Total number of painting times	9	
Total number of kinds of thinners	4 (Use of thinner in common for organotin-free hydrolyzable anti-fouling paint and for chlorinated rubber coating composition and top coat:3)	

Table 9-III

	Painting Method-2 Using Conventional Paint	
	Type of Paint	Number of painting times
Bottom and Boot topping	Tar type epoxy resin heavy-duty coating composition	2
	Vinyl resin binder coat	1
	Organotin-free hydrolyzable antifouling paint	2
Topside	Epoxy resin heavy-duty coating composition	2
	Epoxy resin top coat	2
Total number of kinds of paints	5	
Total number of painting times	9	
Total number of kinds of thinners	3 (The same thinner is employable for the tar type epoxy resin heavy-duty coating composition and for the epoxy resin coating composition and top coat in common)	

Rationalization of painting process by the method of the invention

In the painting of the outside shell of a bulk carrier of 75,000 tons newly built, the aforesaid painting method according to the invention was compared with the conventional painting method-1 to evaluate degree of rationalization in the following items.

With respect to the degree of rationalization, the painting method of the invention was evaluated based on the conventional painting method-1 being 100.

1. Time for painting work

The period of time necessary for applying a paint with an airless spray was evaluated. This period of time does not include time for preparing painting equipment but includes time for moving of workers at the scaffold or by vehicle for high lift work.

2. Non-effective work

The following non-effective work was evaluated.

(1) Changing of paints, and washing of painting machines or painting tools associated with the changing of paints.

(2) Control of spray overlapping or protection necessary for application of different paints in the paint-change zone.

(3) Moving of workers, preparation of painting, and cleaning or rearrangement after painting.

3. Failure in painting

Painting failures caused by mischoice of paints, failure of spraying on the paint-change zone and mischoice of thinners were evaluated.

4. Process control

The labor necessary for controlling painting intervals, labor for controlling fitting of the painting process with other processes (building or transferring of

blocks) and labor for controlling disposition of workers were evaluated.

5. Storage and stock management of paint

The work relating to ordering, warehousing, classification and rearrangement of paints and thinners was evaluated.

6. Loss of paint and thinner, disposal of waste paint and waste thinner

The loss of paints and thinners produced by changing paints, loss of paints caused by excess use in the spray overlapping for application of different paints, increase of unusable paints caused by pot life over of the residual paints, and disposal of waste paints and thinners were evaluated.

The results are set forth in Table 10

Table 10

	Degree of rationalization	
	Painting method using paint of the invention	Painting method-1 using conventional paint
1. Time for painting work	70	100
2. Non-effective work	70	100
3. Painting failure	90	100
4. Process control	80	100
5. Storage and stock management of paint	80	100
6. Loss of paint and thinner, Disposal of waste paint and waste thinner	50	100

As is clear from the above results, the rationalization of painting of the outside shell of a ship's hull is feasible by the use of the painting method using the paint of the invention.

As is clear from the above results, the rationalization of the painting of the outside shell of a ship's hull is feasible by the use of the painting method of the invention.

Further, the rationalization can be promoted by the use of the non-tar type epoxy resin heavy-duty coating composition of the invention as a primer for other ship parts than the outside shell.

Moreover, because the area of the same paint can be widened to thereby stabilize the painting technique required for the painting workers, uniform and high-quality paint films can be easily obtained, and besides other immeasurable advantages such as improvement of working efficiency can be provided.

What is claimed is:

1. A non-tar type epoxy resin paint composition comprising:
 - (a) a bisphenol epoxy resin,
 - (b) a vinyl chloride copolymer, and
 - (c) a hardener comprising polyamide or its modified product.
2. The paint composition as claimed in claim 1, wherein the bisphenol epoxy resin (a) has an epoxy equivalent of 100 to 500.
3. The paint composition as claimed in claim 1 or claim 2, wherein said paint composition further contains (d) an aluminum powder in addition to the components (a), (b) and (c).
4. The paint composition as claimed in any one of claims 1 to 3, wherein the vinyl chloride copolymer is a vinyl chloride/alkyl vinyl ether copolymer.
5. The paint composition as claimed in any one of claims 1 to 4, wherein said paint composition contains tricresyl phosphate.
6. The paint composition as claimed in any one of claims 1 to 5, wherein a mixture of the polyamide or its



modified product and another hardener component is contained as the hardener.

7. The paint composition as claimed in any one of claims 1 to 6, wherein said paint composition is used as a heavy-duty coating composition.

8. A heavy-duty coating film formed from the paint composition as claimed in any one of claims 1 to 7.

9. A painting method of an outside shell of a ship's hull, comprising the steps of:

coating (i) a bottom of a ship's hull or (ii) a bottom and a boot topping of a ship's hull with a non-tar type epoxy resin heavy-duty coating composition as a primer to form a primer film; and

further coating the surface of the primer film with an organotin-free hydrolyzable antifouling paint.

10. A painting method of an outside shell of a ship's hull, comprising the steps of:

coating the whole outside shell of a ship's hull including a bottom, a boot topping and a topside with a non-tar type epoxy resin heavy-duty coating composition as a primer to form a primer film; and

further coating the surface of the primer film provided on (i) the bottom or (ii) the bottom and the boot



topping out of the thus primer-treated outside shell with an organotin-free hydrolyzable antifouling paint.

11. A painting method of an outside shell of a ship's hull, comprising the steps of:

coating the whole outside shell of a ship's hull including a bottom, a boot topping and a topside with a non-tar type epoxy resin heavy-duty coating composition to form a primer film;

further coating the surface of the primer film provided on (i) the bottom or (ii) the bottom and the boot topping out of the thus primer-treated outside shell with an organotin-free hydrolyzable antifouling paint, and coating the surface of the primer film provided on the topside with a topside top coat;

and optionally

furthermore coating the boot topping with a boot topping top coat.

12. The painting method of an outside shell of a ship's hull as claimed in any one of claims 9 to 11, wherein the non-tar epoxy resin heavy-duty coating composition further contains a thermoplastic resin.

13. The painting method of an outside shell of a ship's hull as claimed in claim 12, wherein the thermoplastic resin is at least one resin selected from a



chlorinated polyolefin, an acrylic resin, a vinyl acetate resin, a styrene resin and a vinyl chloride resin.

14. The painting method of an outside shell of a ship's hull as claimed in claim 13, wherein the vinyl chloride resin is a vinyl chloride/vinyl isobutyl ether copolymer.

15. The painting method of an outside shell of a ship's hull as claimed in any one of claims 9 to 14, wherein the non-tar type epoxy resin heavy-duty coating composition contains an aluminum powder.

16. The painting method of an outside shell of a ship's hull as claimed in claim 11, wherein the topside top coat is an urethane paint, an epoxy paint, an acrylic paint or a chlorinated polyolefin paint, and the boot topping top coat is an urethane paint, an epoxy paint, an acrylic paint, a chlorinated polyolefin paint or an organotin-free antifouling paint.

17. The painting method of an outside shell of a ship's hull as claimed in any one of claims 9 to 16, wherein the organotin-free hydrolyzable antifouling paint contains a trialkylsilyl ester copolymer containing 20 to 65 % by weight of constituent units derived from a trialkylsilyl ester of a polymerizable unsaturated



carboxylic acid and having a number-average molecular weight (Mn) of 1,000 to 50,000.

18. The painting method of an outside shell of a ship's hull as claimed in any one of claims 9 to 17, wherein the organotin-free hydrolyzable antifouling paint contains a vinyl resin in which an organic acid is linked to at least one side chain terminal through a metallic ester linkage.

19. A painted ship's hull having:

a non-tar type epoxy resin heavy-duty coating primer film applied on (i) a bottom of the ship's hull or (ii) a bottom and a boot topping of the ship's hull, and

an organotin-free hydrolyzable antifouling film applied on the primer film.

20. A painted ship's hull having:

a non-tar type epoxy resin heavy-duty coating primer film applied on the whole outside shell of the ship's hull including a bottom, a boot topping and a topside, and

an organotin-free hydrolyzable antifouling film applied on the primer film provided on (i) the bottom or (ii) the bottom and the boot topping out of the whole primer film.

21. A painted ship's hull having:



a non-tar type epoxy resin heavy-duty coating primer film applied on the whole outside shell of the ship's hull including a bottom, a boot topping and a topside,

an organotin-free hydrolyzable antifouling film applied on the primer film provided on (i) the bottom or (ii) the bottom and the boot topping, and a topside top coat film applied on the primer film provided on the topside,

and optionally

a boot topping top coat film further applied on the boot topping.

22. The painted ship's hull as claimed in any one of claims 19 to 21, wherein the non-tar type epoxy resin heavy-duty coating primer film further contains a thermoplastic resin.

23. The painted ship's hull as claimed in claim 22, wherein the thermoplastic resin is at least one resin selected from a chlorinated polyolefin, an acrylic resin, a vinyl acetate resin, a styrene resin and a vinyl chloride resin.

24. The painted ship's hull as claimed in claim 23, wherein the vinyl chloride resin is a vinyl chloride/vinyl isobutyl ether copolymer.



25. The painted ship's hull as claimed in any one of claims 19 to 24, wherein the non-tar type epoxy resin heavy-duty coating film contains an aluminum powder.

26. The painted ship's hull as claimed in claim 21, wherein the topside top coat film is formed by applying an urethane paint, an epoxy paint, an acrylic paint or a chlorinated polyolefin paint, and the boot topping top coat film is formed by applying an urethane paint, an epoxy paint, an acrylic paint, a chlorinated polyolefin paint or an organotin-free antifouling paint.

27. The painted ship's hull as claimed in any one of claims 19 to 26, wherein the organotin-free hydrolyzable antifouling film contains a trialkylsilyl ester copolymer containing 20 to 65 % by weight of constituent units derived from a trialkylsilyl ester of a polymerizable unsaturated carboxylic acid and having a number-average molecular weight (Mn) of 1,000 to 50,000.

28. The painted ship's hull as claimed in any one of claims 19 to 27, wherein the organotin-free hydrolyzable antifouling film contains a vinyl resin in which an organic acid is linked to at least one side chain terminal through a metallic ester linkage.

