Specification

Title of the Invention:

Amine-Based Curing Agent, said Curing Agent-Containing Curable Resin Composition and said Curing Agent-Containing Corrosion-Resistant Coating Composition

Field of the Invention

The present invention relates to an amine-based curing agent useful as a curing agent for an epoxy resin, having good curing properties particularly at low temperature and having good compatibility with a petroleum resin widely used in a corrosion-resistant coating composition, a curable resin composition containing the curing agent, and a corrosion-resistant coating composition containing the curing agent and having good low-temperature curing properties, particularly to a tar-free corrosion-resistant coating composition useful in coating of an interior of a ship such as a ballast tank.

Background Art

An amine-based curing agent is known as a curing agent for an epoxy resin in the art. A resin composition containing the above curing agent and the epoxy resin is curable at room temperature so as to be widely used in a heavy-duty corrosion-resistant coating composition for ships, steel structures and the like. However, the above resin composition shows poor curing properties at such a low temperature as in winter, resulting in making it

impossible to show original properties of the epoxy resin.

For the purpose of improving curing properties at low temperature, the following methods (1) to (4), that is, (1) use of a curing promotor, (2) use of a mercaptan-based curing agent, (3) use of an acrylate-containing resin and (4) use of an epoxy-urethane curing system, have been proposed in the art.

The above method (1) has such drawbacks that use of a catalyst such as a tertiary amine, phenols or the like for ring opening of epoxy group as used in the curing promotor results a unsatisfactory promoting effect at low temperature, and that a remaining catalyst in a cured film may result a cured film showing poor properties in water resistance and film performances.

The above method (2) has such drawbacks that use of the curing agent shows good low-temperature curing properties, but results a cured film showing poor properties in water resistance and chemical resistance as well as troubles of odor development.

The above method (3) has such drawbacks that a Michel addition reaction between an acrylate group and the amine may improve low temperature curing properties, but many ester linkages remaining in a cured film may result a cured film showing poor properties in water resistance and alkali resistance.

The above method (4) is such that a curing system consisting of a combination of an epoxy resin as epoxy

polyol with isocyanates as a curing agent is used, and provides good low temperature curing properties to be practically used. However, the above curing system has such drawbacks that the isocyanate may be expanded under high humidity, that a long-term corrosion-resistant property is unsatisfactory, that compatibility thereof with a petroleum based resin used in the corrosion-resistant coating composition is poor, and that design in the heavy-duty corrosion-resistant coating composition is difficult.

A tar-epoxy resin coating composition has been used in the art as the corrosion-resistant coating composition for use in ships and steel structures. The above coating composition shows good properties in corrosion resistance, water resistance, chemical resistance, etc., but had such drawbacks that a problem from the standpoints of safety and health is a matter of concern because of containing tar, and that a black color of tar makes difficult maintenance and control after the application of the coating composition, and makes a closed space dark, resulting in making operations therein dangerous.

Various proposals for the preparation of a coating composition which makes possible a light color finishing and is useful for coating of an interior of a ship such as a ballast tank have been made by use of a petroleum-based resin in place of tar. The present applicant also proposed a corrosion-resistant coating composition containing a petroleum resin having particular properties (see Japanese

Patent Application Laid-Open Nos. 263713/97 and 302276/97).

The above corrosion-resistant coating compositions contain a petroleum resin having a comparatively good compatibility with an amine based curing agent, and are capable of forming a light color coating film showing good properties in corrosion resistance, water resistance, adhesion properties and the like. However, at low temperature, the coating film shows unsatisfactory curing properties due to the amine based curing agent used therein, resulting in that a coating film showing good film performances can not be obtained as the case may be.

Disclosure of the Invention

The present inventors made intensive studies for the purpose of solving the above problems to find out that an amine based curing agent can be prepared by modifying a Mannich reaction product having a specified composition with an epoxy resin, and shows good low temperature curing properties and good compatibility with a petroleum based resin widely used in the corrosion-resistant coating composition, and that use of the amine based curing agent makes it possible to obtain a tar-free corrosion-resistant coating composition showing a good low temperature curing properties and to form a light color coating film showing good properties in corrosion resistance, water resistance, adhesion properties, and the like, resulting in achieving the present invention.

In a first embodiment, the present invention provides

an amine based curing agent prepared by reacting a condensation reaction product of (a) an amine, (b) phenol and (c) formaldehyde with (d) an epoxy resin containing at least two epoxy groups in one molecule, said amine (a) being a mixture of xylenediamine with an aliphatic polyamine, and said phenol (b) being a mixture of at least one selected from the group consisting of bisphenol A, bisphenol F and carbolic acid with an alkyl phenol having an alkyl chain of 9 or more carbon atoms.

In a second embodiment, the present invention provides a curable resin composition comprising (A) an epoxy resin and (B) an amine based curing agent prepared by reacting a condensation reaction product of (a) a mixture of xylenediamine with an aliphatic polyamine, (b) a mixture of at least one selected from the group consisting of bisphenol A, bisphenol F and carbolic acid with an alkyl phenol having an alkyl chain of 9 or more carbon atoms and (c) formaldehyde with (d) an epoxy resin containing at least two epoxy groups in one molecule.

In a third embodiment, the present invention provides a corrosion-resistant coating composition comprising (A) an epoxy resin, (B) an amine based curing agent and (C) a petroleum based resin, said amine based curing agent (B) being prepared by reacting a condensation product of (a) a mixture of xylenediamine with an aliphatic polyamine, (b) a mixture of at least one selected from the group consisting of bisphenol A, bisphenol F and carbolic acid with an alkyl

phenol having an alkyl chain of 9 or more carbon atoms and (c) formaldehyde with (d) an epoxy resin containing at least two epoxy groups in one molecule, said petroleum based resin (C) being contained in an amount of 20 to 150 parts by weight per 100 parts by weight of a curable resin solid content.

Preferred Embodiment of the Invention

The amine based curing agent in the first embodiment of the present invention or the amine based curing agent (B) in the second and third embodiments of the present invention (hereinafter may be referred to as the amine based curing agent of the present invention) is a curing agent prepared by reacting a condensation product of (a) an amine, (b) phenol and (c) formaldehyde with (d) an epoxy resin containing at least two epoxy groups in one molecule.

The amine (a) in the present invention is a mixture of xylenediamine with an aliphatic polyamine. Preferable examples of the aliphatic polyamine may include diethylenetriamine, triethylenetetramine and the like.

A mixing ratio of xylenediamine to the aliphatic polyamine is preferably in the range of 2:1 to 1:2 ratio by weight. Too much xylenediamine beyond the above ratio results a coating film showing poor adhesion properties. On the other hand, too much aliphatic polyamine causes poor low temperature curing properties and poor compatibility with the petroleum based resin.

The phenol (b) in the present invention is a mixture of

at least one selected from the group consisting of bisphenol A, bisphenol F and carbolic acid with an alkyl phenol having an alkyl chain of 9 or more carbon atoms. The alkyl phenol has an alkyl chain having 9 or more carbon atoms. Use of alkyl chain having less than 9 carbon atoms undesirably reduces compatibility with a petroleum based resin. Examples of the alkyl phenol may include nonyl phenol, dodecyl phenol, cardanol and the like.

A mixing ratio of at least one selected from the group consisting of bisphenol A, bisphenol F and carbolic acid to the alkyl phenol in the phenol (b) is preferably in the range of 2:1 to 1:2 by weight ratio. Too much amount of at least one selected from the group consisting of bisphenol A, bisphenol F and carbolic acid reduces compatibility with the petroleum based resin. On the other hand, too much amount of the alkyl phenol undesirably reduces low temperature curing properties and water resistance.

The epoxy resin (d) used in the present invention may include ones having at least two epoxy groups in one molecule, and preferably ones having an epoxy equivalent of 150 to 600. Of the epoxy resin (d), the bisphenol type epoxy resin is particularly preferable from the standpoints of water resistance and low temperature curing properties.

The amine based curing agent of the present invention may be prepared by a conventional process which comprises mixing the above components (a), (b) and (c), followed by heating and dephydrolyzing at 50 to 180℃ to obtain a

condensation reaction product according to Mannich reaction, adding the component (d), and heating at 20 to 200 ℃ for reacting an amino group in the condensation reaction product with an epoxy group.

Mixing molar ratios of the above components (a), (b), (c) and (d) are such that the component (b) is in the range of 0.7 to 1.3 moles, the component (c) is in the range of 0.7 to 1.3 moles and the component (d) is in the range of 0.2 to 0.5 mole per one mole of the component (a) respectively. When an amount of the component (a) is above the above molar ration range, the low temperature curing properties may be reduced, and bleeding of unreacted products may take place from the coating film surface. On the other hand, when an amount of the component (a) is below the above molar ratio range, curing properties may be reduced, and an unreacted component (b) may remain in the coating film, resulting in reducing water resistance.

The amine based curing agent obtained as above in the present invention is useful as a curing agent for the epoxy resin, shows good curing properties under low temperature atmosphere, and can shorten a drying and curing time at normal temperature.

The epoxy resin (A) used in the second and third embodiments of the present invention may include ones having at least two epoxy groups in one molecule, and preferably has an epoxy equivalent of 150 to 600, preferably 180 to 300. Examples of the epoxy resin (A) may include known

epoxy resins such as bisphenol type epoxy resin, aliphatic epoxy resin, glycidyl ester based epoxy resin, glycidyl amine based epoxy resin, phenol movolak type epoxy resin, cresol type epoxy resin, dimer acid-modified epoxy resin and the like. These resins may be used alone or in combination.

In the second and third embodiments of the present invention, a mixing ratio of the component (A) to the component (B) may arbitrarily be varied depending on kinds of the components (A) and (B) to be used, but may preferably be such that an equivalent ratio of an active hydrogen equivalent in the component (B) to an epoxy equivalent in the component (A) may be in the range of 0.5 to 1.0.

The curable resin composition in the second embodiment of the present invention may optionally include a petroleum based resin, other liquid modifier and reactive or non-reactive diluent; pigments such as extender pigment, anticorrosion pigment, color pigment and the like; and known additives such as organic solvent, anti-settling agent, anti-sagging agent, wetting agent, reaction promoting agent, adhesion properties-imparting agent, dehydrating agent, and the like.

The petroleum based resin (C) in the third embodiment of the present invention may preferably include a petroleum resin which is solid at normal temperature and has a softening point in the range of 50 to 150℃ , preferably 80

to 100℃. Examples of the above petroleum resin may include aromatic based petroleum resins prepared by polymerizing C_9 fractions such as styrene derivatives, indene and the like, obtained from heavy oil by produced during petroleum naphtha cracking; copolymer based petroleum resins prepared by copolymerizing the above C_5 fraction and the C_9 fraction, aliphatic based petroleum resins prepared by subjecting conjugated dienes in the C_5 fraction, for example, cyclopentadiene, 1,3-pentadiene and the like to partial cyclic polymerization; resins prepared by subjecting the aromatic based petroleum resin to hydrogenation, alicyclic based petroleum resins prepared by polymerizing cyclopentadiene, and the like.

When the softening point of the petroleum based resin (C) is lower than 50℃, water resistance of the coating film may be reduced and the component (C) may bleed onto the surface of the coating film, so that adhesion properties may remain. On the other hand, when higher than 150℃, viscosity of the coating composition may be increased, resulting in reducing workability and physical properties of the coating film.

Particularly, the petroleum based resin (C) may preferably include a hydroxyl group-containing petroleum resin containing hydroxyl group in an amount of 0.5 to 1.5 moles in one molecule and having a softening point in the range of 50 to 150℃. The hydroxyl group-containing petroleum resin may be prepared by introducing hydroxyl

group into the above petroleum resins. Of these resins, the hydroxyl group-containing aromatic based petroleum resin is preferable from the standpoints of water resistance and compatibility with the components (A) and (B).

When an amount of hydroxyl group contained in the hydroxyl group-containing petroleum resin is less than 0.5 mole in one molecule, compatibility with the amine based curing agent may be reduced and give an adverse effect on coating film performances. When more than 1.5 moles, water resistance may be reduced.

The corrosion-resistant coating composition in the third embodiment of the present invention may contain the petroleum based resin (C) in an amount of 20 to 150 parts by weight, preferably 50 to 150 parts by weight per 100 parts by weight of a cured resin solid content. When the above amount is less than 20 parts by weight, a satisfactory water resistance can not be obtained. On the other hand, when more than 150 parts by weight, a brittle coating film makes it impossible to obtain good physical properties, and seriously reduces low temperature curing properties.

The corrosion-resistant coating composition in the third embodiment of the present invention may optionally contain other liquid modifier or diluent; pigments such as extender pigment, anti-corrosion pigment, color pigment and the like; a reactive diluent; additives usually used in the coating composition, for example, organic solvent, anti-settling agent, anti-sagging agent, wetting agent, reaction-

promoting agent, adhesion properties-imparting agent, dephydrating agent and the like.

The corrosion-resistant coating composition in the third embodiment of the present invention is a two-pack type coating composition comprising a base material containing the epoxy resin (A) and the petroleum based resin (C), and the amine based curing agent (B), and is usually coated onto a primary anticorrosive coating film such as a zinc primer. The above coating composition may be coated by the known coating methods such as air spray coating, airless spray coating, brushing, roller coating and the like so as to be a dry film thickness in the range of 150 to 500μm.

Example

The present invention will be explained more in detail by the following Examples, in which "part" and "%" represent "part by weight" and "% by weight" respectively.

Preparation of Amine-Based Curing Agent

Example 1

A reactor equipped with a stirrer and a thermometer was charged with 68 g (0.5 mole) of xylenediamine, 52 g (0.5 mole) of diethylenetriamine, 114 g (0.5 mole) of bisphenol A and 110 g (0.5 mole) of nonyl phenol, followed by stirring thoroughly, adding 81 g (one mole) of 37% formalin to carry out reaction, heating up to 100℃ and carrying out reaction for 2 hours, and dehydrating to obtain a condensation reaction product, adding 95 g (0.25 mole) of Epon #828

(Trade name, epoxy resin, epoxy equivalent: 190, marketed by Yuka Shell Epoxy Co., Ltd.), reacting at 80 ℃ for 2 hours, and diluting with a toluene: isopropanol = 1:1 mixed solvent to obtain an amine based curing agent (B-1) having a non-volatile matter content of 60%. The curing agent solution showed a viscosity of 900 cps (measured under 25 ℃ /60 r.p.m. by use of a B-type viscometer).

Examples 2-4 and Comparative Examples 1-6

Example 1 was duplicated except for respective compositions shown in Table 1 to obtain respective amine based curing agents (B-2) to (B-9). Comparative Example 6 was such that a high viscosity made preparation of a curing agent impossible. In Table 1, composition is represented by a molar ratio, (Note 1) and (Note 2) are as shown below.

(Note 1) Epon #1001: epoxy resin, epoxy equivalent: 475, marketed by Yuka Shell Epoxy Co., Ltd., trade name.

(Note 2) Epiclon #520: trade name, monoepoxy compound, marketed by Dainippon Ink and Chemicals, Inc.

Table 1

			Examples				Comparative Examples					
			1	2	3	4	1	2	3	4	5	6
Amine based curing agent			B-1	B-2	B-3	B-4	B-5	B-6	B-7	B-8	B-9	-
Composition	a	methaxylenediamine	0.5	0.6	0.5	0.5	1.0	-	0.5	0.5	0.5	0.5
		diethylenetriamine	0.5	0.6	0.5	0.5	-	1.0	0.5	0.5	0.5	0.5
	b	bisphenol A	0.5	0.5	0.6	0.5	0.5	0.5	-	0.5	0.5	1.0
		nonyl phenol	0.5	0.5	0.6	0.5	0.5	0.5	1.0	0.5	0.5	-
	c	formaldehyde	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	d	Epon #828	0.25	0.25	0.25		0.25	0.25	0.25	-		0.25
		Epon #1001 (Note 1)				0.25						
		Epiclon #520 (Note 2)									0.25	
Non-volatile matter content			60	60	60	60	60	60	60	60	60	-
Viscosity (cps/25 ℃)			900	400	400	2000	600	1000	400	400	700	-
Active hydrogen equivalent			150	122	165	198	187	124	149	102	127	-

Preparation of Curable Resin Composition

Examples 5-8 and Comparative Examples 7-12

A one-liter reactor was charged with 100 parts of Epon #828, and respective amine-based curing agents as obtained above according to formulations as shown in Table 2, followed by mixing and stirring to obtain respective curable resin compositions. Respective compositions were subjected to the following performance tests. Test results are shown in Table 2. In Table 2, (Note 3) represents as follows.

(Note 3) Versamin F20: trade name, Mannich-modified m-xylene diamine, active hydrogen equivalent: 80, marketed by Henkel Japan Ltd., non-volatile matter content: 100%, viscosity: 3000 cps.

Performance Test

(*1) Compatibility:

Immediately after mixing, respective samples were coated onto a glass plate to be a dry film thickness of about 250 μm by use of an applicator, followed by drying under the conditions of 5℃ and 65% RH atmosphere for 24 hours to visually evaluate a coating film appearance as follows.

3: No changes; 2: haze developed; 1: separated.

(*2) Low temperature curing properties:

Immediately after mixing, respective samples were coated onto a degreased, polished mild steel sheet (0.8 × 70 × 150 mm) so as to be a dry film thickness of about 250 μm by use of an applicator, followed by drying under the

conditions of 5℃ and 65% RH for 16 hours, and pressing the surface of a coating film with the finger to visually evaluate a coating film appearance as follows. 3: Strong pressing with the finger develops no slippage of the coating film; 2: strong pressing with the finger develops slippage of the coating film; 1: soft pressing with the finger develops stippage of the coating film.

(*3) Adhesion properties:

Immediately after mixing, respective samples were coated onto a shot blasted steel sheet (2 × 70 × 150 mm) so as to be a dry film thickness of about 250 μm by use of an applicator, followed by drying under the conditions of 5℃ and 65% RH for 7 days to obtain respective coating test panels, which were subjected to the cross cut tape adhesion test by forming cross cuts on the test panels, followed by adhering thereonto an adhesive cellophane tape, and separating the tape to visually evaluate the coating film appearance as follows. 3: Good; 2: separation takes place partly; 1: separation takes place all over the surface.

Table 2

		Examples				Comparative Examples					
		5	6	7	8	7	8	9	10	11	12
Epon #828		100	100	100	100	100	100	100	100	100	100
Amine based curing agent	(B-1)	100									
	(B-2)		100								
	(B-3)			100							
	(B-4)				100						
	(B-5)					100					
	(B-6)						100				
	(B-7)							100			
	(B-8)								100		
	(B-9)									100	
Amine based curing agent for comparison (Note 3)											40
Performance test	compatibility	3	3	3	3	3	3	3	3	3	3
	low temperature curing properties	3	3	3	3	3	2	2	2	2	3
	adhesion properties	3	3	3	3	3	3	3	2	3	2

Preparation of Corrosion-Resistant Coating Composition

Example 9

A one-liter reactor was charged with 100 parts of Epon #828, 70 parts of titanium white, 100 parts of talc, 100 parts of a hydroxyl group-containing petroleum resin (Note 4), 10 parts of an antisagging agent (Note 5) and 10 parts of xylene, followed by mixing and stirring in a disper to form a dispersion as a base material, adding thereinto 100 parts of the amine based curing agent (B-1) just before coating, and mixing and stirring to obtain a corrosion-resistant coating composition.

Examples 10-14 and Comparative Examples 13-21

Example 9 was duplicated except for compositions and formulations shown in Table 3 to obtain respective corrosion-resistant coating compositions. In Table 3, (Note 4), (Note 5) and (Note 6) are explained as follows.

(Note 4) Neopolymer K-2: Trade name, divinyl toluene-indene copolymer containing 1 to 1.1 moles of hydroxyl group in one molecule, softening point: 100℃ , marketed by Nippon Petrochemicals Co., Ltd.

(Note 5) Disparlon A630-20XN: trade name, polyamide wax, marketed by Kusumoto Chemicals Ltd.

(Note 6) Coronate L: trade name, isocyanate curing agent, tolylene diisocyanate-modified product, NCO content: 13%, marketed by Nippon Polyurethane Industry Co., Ltd.

Performance Test

Respective corrosion-resistant coating compositions

obtained as above were subjected to the following performance tests. Results are shown in Table 4.

(*4) Compatibility:

The above (*1) was duplicated except that the corrosion-resistant coating compositions were used in place of the resin compositions in the above (*1).

(*5) Low temperature curing properties:

The above (*2) was duplicated except that the corrosion-resistant coating compositions were used in place of the resin compositions in the above (*2).

(*6) Flexibility:

Respective corrosion-resistant coating compositions were coated onto a degreased, polished mild steel sheet (150 × 70 × 0.8mm) so as to be a dry film thickness of about 250 μm by the airless spray coating method, followed by drying under the conditions of 20℃ and 65% RH for 7 days to prepare respective coating test panels respectively. Respective coating test panels were folded at a folding angle of 90° at 20℃ with a coating film surface facing outside followed by visually evaluating cracks developed on the coating film of a folded portion as follows. 3: No cracks developed; 2: few cracks developed; many cracks developed.

(*7) Water Resistance to Temperature Difference:

Respective corrosion-resistant coating compositions obtained as above were coated onto a shot blasted steel sheet (300 × 100 × 3.2mm), i.e. test panel I, and onto a

test panel II prepared by coating SD Zinc 1000 HA (Trade name, marketed by Kansai Paint Co., Ltd., silicate zinc primer) onto the above steel sheet so as to be a dry film thickness of about 25 μm, followed by drying for one day, by the airless spray coating so as to be a dry film thickness of about 250 μm, followed by drying under an atmosphere of 20℃ and 65% RH for 7 days to obtain coating test panels respectively.

Respective coating test panels were dipped for 14 days into such a dipping vessel that a coating surface of the coating test panel may contact with a hot water at 40℃ and the back surface of the coating test panel may contact with water at 20℃, followed by visually evaluating conditions of the coating surface as follows.

3: Nothing abnormal; 2: little development of blisters and rust; 1: remarkable development of blisters and rust.

(*8) Seawater Resistance:

Respective coating test panels obtained in the same manner as in the above (*7) were dipped into seawater at 50℃ for 3 months, followed by visually evaluating conditions of the coating surface as follows. 3: Nothing abnormal; 2: little development of blisters; 1: remarkable development of blisters.

Table 3

			Examples						Comparative Examples								
			9	10	11	12	13	14	13	14	15	16	17	18	19	20	21
Base material	Epon #828		100	100	100	100	100		100	100	100	100	100	100	100	100	100
	Epon #1001							100									
	titanium white		70	70	70	70	70	70	70	70	70	70	70	70	70	70	70
	talc		100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
	hydroxyl group-containing petroleum resin (Note 4)		100	100	100	100	50	100	100	100	100	100	100	100	100	200	
	antisagging agent (Note 5)		10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
	xylene		10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
Curing agent	amine based curing agent	(B-1)	100				100	100								100	100
		(B-2)		100													
		(B-3)			100												
		(B-4)				100											
		(B-5)							100								
		(B-6)								100							
		(B-7)									100						
		(B-8)										100					
		(B-9)											100				
	amine based curing agent for comparison (Note 3)													40			
	isocyanate curing agent (Note 6)														50		

Table 4

		Examples						Comparative Examples								
		9	10	11	12	13	14	13	14	15	16	17	18	19	20	21
Compatibility		3	3	3	3	3	3	3	2	3	3	3	2	1	3	3
Low temperature curing properties		3	3	3	3	3	3	3	2	1	2	2	1	3	1	3
Flexibility		3	3	3	3	3	3	3	3	3	3	3	2	2	3	1
Water Resistance to Temperature Difference	test panel I	3	3	3	3	3	3	2	3	1	3	2	2	2	2	1
	test panel II	3	3	3	3	3	3	2	3	1	3	2	2	2	2	1
Seawater Resistance	test panel I	3	3	3	3	3	3	3	3	2	3	2	2	2	2	2
	test panel II	3	3	3	3	3	3	3	3	2	3	2	2	2	2	2

Effect of the Invention

The present invention makes it possible to provide an amine based curing agent prepared by modifying a Mannich reaction product having a specified composition with an epoxy resin and showing good low temperature curing properties and good compatibility with a petroleum based resin, and also to provide a curable resin composition containing the amine based curing agent, showing good low temperature curing properties and capable of forming a coating film having good corrosion resistance and adhesion properties.

The present invention makes it possible to provide a tar-free corrosion-resistant coating composition showing good low temperature curing properties without problems from the standpoints of safety and health by use of the amine based curing agent prepared by modifying a Mannich reaction product having a specified composition with an epoxy resin and showing good compatibility with a petroleum based resin. The corrosion-resistant coating composition of the present invention is capable of forming a coating film having a light color and good properties in corrosion resistance, water resistance and adhesion properties.

Industrial Applicability

The corrosion-resistant coating composition of the present invention is very useful as the heavy-duty corrosion-resistant coating composition for use in ships and steel structures.

Claims

1. An amine based curing agent prepared by reacting a condensation reaction product of (a) an amine, (b) phenol and (c) formaldehyde with (d) an epoxy resin containing at least two epoxy groups in one molecule, said amine (a) being a mixture of xylenediamine with an aliphatic polyamine, and said phenol (b) being a mixture of at least one selected from the group consisting of bisphenol A, bisphenol F and carbolic acid with an alkyl phenol having an alkyl chain of 9 or more carbon atoms.

2. An amine based curing agent as claimed in claim 1, wherein a mixing ratio of xylenediamine to the aliphatic polyamine in the amine (a) is in the range of 2:1 to 1:2 by a weight ratio.

3. An amine based curing agent as claimed in claim 1, wherein a mixing ratio of at least one selected from the group consisting of bisphenol A, bisphenol F and carbolic acid to the alkyl phenol in the phenol (b) is in the range 2:1 to 1:2 by a weight ratio.

4. An amine based curing agent as claimed in claim 1, wherein a molar ratio of components (a), (b), (c) and (d) to be used is such that the component (b) is in the range of 0.7 to 1.3 moles, the component (c) is in the range of 0.7 to 1.3 moles and component (d) is in the range of 0.2

* C L M S *

to 0.5 mole per one mole of component (a) respectively.

5. A curable resin composition containing (A) an epoxy resin and (B) an amine based curing agent prepared by reacting a condensation reaction product of (a) a mixture of xylenediamine with an aliphatic polyamine, (b) a mixture of at least one selected from the group consisting of bisphenol A, bisphenol F and carbolic acid with an alkyl phenol having an alkyl chain of 9 or more carbon atoms and (c) formaldehyde with (d) an epoxy resin containing at least two epoxy groups in one molecule.

6. A curable resin composition as claimed in claim 5, wherein the epoxy resin (A) has at least two epoxy groups in one molecule and an epoxy equivalent of 150 to 600.

7. A curable resin composition as claimed in claim 5, wherein a mixing ratio of the component (A) and component (B) is such that an equivalent ratio of an active hydrogen equivalent in the component (B) to an epoxy equivalent in the component (A) is in the range of 0.5 to 1.0.

8. A corrosion-resistant coating composition comprising (A) an epoxy resin, (B) an amine based curing agent and (C) a petroleum based resin, said amine based curing agent (B) being prepared by reacting a condensation reaction product of (a) a mixture of xylenediamine with an aliphatic

polyamine, (b) a mixture of at least one selected from the group consisting of bisphenol A, bisphenol F and carbolic acid with an alkyl phenol having an alkyl chain of 9 or more carbon atoms and (c) formaldehyde with (d) an epoxy resin containing at least two epoxy groups in one molecule, said petroleum based resin (C) being contained in an amount of 20 to 150 parts by weight per 100 parts by weight of a cured resin solid content.

9. A corrosion-resistant coating composition as claimed in claim 8, wherein said epoxy resin (A) has at least two epoxy groups in one molecule and an epoxy equivalent of 150 to 600.

10. A corrosion-resistant coating composition as claimed in claim 8, wherein the petroleum based resin (C) is a petroleum resin having hydroxyl group in the range of 0.5 to 1.5 moles in one molecule and a softening point in the range of 50 to 150℃.

11. A corrosion-resistant coating composition as claimed in claim 8, wherein a mixing ratio of component (A) and component (B) is such that an equivalent ratio of an active hydrogen equivalent in component (B) to an epoxy equivalent in component (A) is in the range of 0.5 to 1.0.