

COATING COMPOSITION FOR CORROSION PROOFING

Technical Field

This invention relates to a coating composition used as a substitute for
5 tar-based epoxy paint. More particularly, the invention relates to a coating
composition for corrosion proofing that is useful for coating the portions
exposed to seawater such as the internal walls of ballast tanks of ships.

Background Art

10 In the prior art, tar-based epoxy paint has been used as an
anticorrosive coating for ships, steel structures and the like. Although the
coating material of this kind exhibits good corrosion resistance, water
resistance and chemical resistance, it is injurious to the health due to its tar
content and its safekeeping is not easy because of its black color. In addition,
15 when the coating work is done in an enclosed room, the working is dangerous
because the working space becomes dark.

In recent years, tar-free epoxy coating material that is made by using
petroleum resin in place of the tar, has been proposed. This is proposed, for
example, in Japanese Patent Publication No. 59-52656 and Japanese Laid-
20 Open Patent Publication No. 9-263713. The resin that is disclosed in the
former Japanese Patent Publication No. 59-52656 contains hydroxyl groups.
In examples of the invention, there is described a resin having a softening
point of 93°C, which is prepared by polymerization in the co-existence of
phenol using a fraction containing unsaturated components obtained by
25 cracking of naphtha. Furthermore, Japanese Laid-Open Patent Publication
No. 9-263713 discloses, in its example, an epoxy resin-based anticorrosive
coating composition which is made by using divinyltoluene-indene copolymer
(softening point: 100°C) containing 1 to 1.1 mole of hydroxyl group per one
molecule thereof.

However, the epoxy based coating materials disclosed in the above patents present a problem in the compatibility of petroleum resin with cured resin comprising an epoxy resin and a curing agent, particularly, amine-based curing agent. Therefore, they are not suitable for applying as a coating onto
5 portions exposed directly to seawater such as internal walls of ballast tanks of ships, with which corrosion resistance and water resistance are severely required.

Disclosure of Invention

10 As a result of intensive study for the purpose to solve the above-described problems, the present invention has been accomplished by using a resin made from an aromatics fraction containing a specified content ratio of indenenes together with a resin, in which the content of phenolic hydroxyl groups is reduced to a relatively low level. The thus produced coating
15 composition of the invention exhibits excellent compatibility with an epoxy resin or a curing agent, particularly an amine-based curing agent. As a result, it is possible to obtain a coating composition for corrosion proofing (hereinafter referred to as "anticorrosive coating composition") that is excellent in anticorrosiveness, water resistance and adhesive property
20 without causing hygiene problems and, in addition, the color of obtained coating film is bright.

Accordingly, a first aspect of the present invention relates to an anticorrosive coating composition comprising an epoxy resin (A), a curing agent (B) preferably an amine-based curing agent, and an aromatic petroleum
25 resin (C) having 0.1 or more but less than 1.0 of phenolic hydroxyl group per one molecule. The aromatic petroleum resin is prepared by polymerizing a cracked oil fraction of 60 to 90% by weight in content ratio of indenenes, in the coexistence of phenols and a Friedel-Crafts catalyst. The cracked oil fraction is the one obtained by distillation of a fraction of 140 to 220°C in boiling point

which is derived from the cracked oil obtained by thermal cracking of petroleum resources. Furthermore, the anticorrosive coating composition of the invention is characterized in that it contains 1 to 500 parts by weight of the aromatic petroleum resin (C) per 100 parts by weight of the epoxy resin.

5 A second aspect of the present invention relates to an anticorrosive coating composition as described in the first aspect of the invention, wherein an content ratio of conjugated dienes in the cracked oil fractions is not more than 5% by weight.

The present invention will be described in more detail.

10 The epoxy resin (A) used in the present invention has at least two epoxy groups per one molecule and its suitable epoxy equivalent is 150 to 600, preferably 180 to 500. Exemplified as such epoxy resins are conventionally known resins such as bisphenol-type epoxy resins, aliphatic epoxy resins, glycidyl ester epoxy resins, glycidyl amine epoxy resin, phenol-novolak-type
15 epoxy resins, cresol-type epoxy resins, and dimer acid-modified epoxy resins. These resins can be used alone or in a mixture of two or more.

As the curing agent (B) used in the present invention, any of well known curing agents used for epoxy resins can be employed. They are exemplified by various aliphatic or aromatic amines, polyamide resins, acid
20 anhydrides, phenol resins, and polyisocyanates. These curing agents may be used alone or in a mixture of two or more.

Particularly preferable curing agents are amine-based curing agents. Their examples include aliphatic polyamines such as m-xylene diamine, isophorone diamine, diethylene triamine, triethylene tetramine, and
25 diaminodiphenyl methane; cycloaliphatic polyamines; aromatic polyamines; adducts of these polyamines with epoxy resins; polyamide amines; and polyamide resins. These compounds may be used alone or in a mixture of two or more of them.

The mixing ratio of the epoxy resins (A) with curing agents (B) is

arbitrarily selected depending on the types of both components to be used. In general, the curing agent in the range of 1 to 200 parts by weight is selected to 100 parts by weight of the epoxy resin. When an amine-based curing agent is used as a preferable curing agent (B), its use quantity is
5 generally selected such that the equivalent weight ratio defined by the active hydrogen equivalent weight in the curing agent (B)/the epoxy equivalent weight of the epoxy resin (A) falls in the range of 0.5 to 1.0.

The aromatic petroleum resin (C) used in the present invention is a petroleum resin which is solid at ordinary temperatures, contains phenolic
10 hydroxyl groups, and has a softening point of 50 to 150°C, preferably 80 to 110°C.

For producing the above-mentioned petroleum resins, a fraction containing main components having boiling points in the range of 140 to 220°C is used as the starting material, wherein the fraction is derived from
15 the cracked oils obtained as by-products in the process of the cracking of hydrocarbons such as naphtha and butane in order to produce ethylene, propylene and the like. In these fractions, unsaturated compounds such as styrene, α - or β -methylstyrene, vinyltoluene, indene, methyindene, dicyclopentadiene, and dimethylcyclopentadiene and saturated compounds such as
20 ethylbenzene, trimethylbenzene, indane, methyindane and naphtharene are involved. Further, there are included conjugated dienes such as cyclopentadiene and methylcyclopentadiene formed during the distillation process by the thermal cracking of dicyclopentadiene, dimethylcyclopentadiene and the like.

25 In the present invention, a fraction obtained by the distillation of the above-mentioned cracked oil is used as a starting material. The content ratio of indenenes in the fraction is in the range of 60 to 90% by weight. The use of a fraction containing indenenes in the amount other than the above range, is not preferable because it results in an anticorrosive coating composition

with poor performance. The content ratio (% by weight) of indenenes in the fraction is defined by the following equation:

$$\frac{\text{Total qty. of alkylindenenes such as indene and methylinene}}{\text{Total qty. of unsaturated components in cracked oil fraction}} \times 100$$

It is preferable to use a fraction of a content ratio of 5% by weight or less of conjugated dienes such as cyclopentadiene or methylcyclopentadiene.

- 5 It is thus possible to improve further the anticorrosive performance of the anticorrosive coating composition by reducing the content ratio of conjugated dienes contained in the fraction to a level of 5% by weight or less. The content ratio of conjugated dienes (% by weight) is defined by the following equation:

$$\frac{\text{Total qty. of conjugated dienes}}{\text{Total qty. of unsaturated components in cracked oil fraction}} \times 100$$

- 10 The analysis of above-mentioned components can be easily done by well known gas chromatography.

Furthermore, it is possible to obtain the cracked oil fraction having the above-described composition without difficulty by treating cracked oil of a thermal cracking by-product with the appropriate combination of known
15 distillation methods.

The raw material resin used in the present invention can be prepared through the polymerization of the above-mentioned cracked oil fraction in the presence of 1.0 to 10.0 parts by weight of phenols to 100 parts by weight of the cracked oil fraction using 0.01 to 3% by weight of Friedel-Crafts catalyst
20 relative to the amount of the cracked oil fraction at reaction temperatures in the range of 10 to 100°C.

Phenols used in the present invention are exemplified by phenol itself, alkyl group-substituted phenols such as cresol, xylenol, tert-butyl phenol, and nonyl phenol. These compounds can also be used in a mixture. Among
25 them, preferable one is phenol. Although phenols can exist in the reaction

system as one component contained in the Friedel-Crafts catalyst, a predetermined amount of phenol is frequently fed into the reaction system separately from the catalyst.

Examples of Friedel-Crafts catalyst used in the present invention
5 include metal halides, preferably boron trifluoride, or its complex with oxygen-containing compound such as phenol, ethyl ether, butyl ether, butyl alcohol or methyl alcohol.

The duration of polymerization can be selected from the range of 0.5 to 10 hours in the case of batch type operation.

10 A resin having a desired softening point can be obtained by feeding predetermined quantities of above-mentioned cracked oil fraction, phenols, Friedel-Crafts catalyst and then carrying out the polymerization through any of known methods. After the polymerization, the catalyst is deactivated using an alkaline material or the like followed by the removal and separation
15 of unreacted oils or low molecular polymers by means of distillation or the like to obtain an intended resin.

The petroleum resin (C) used for preparing the coating composition according to the present invention contains 0.1 or more but less than 1.0 of phenolic hydroxyl group per resin molecule. It is preferably 0.5 to 0.9.
20 Furthermore, the resin containing phenolic hydroxyl groups within the above-mentioned range can be obtained by appropriately regulating the amount of each starting material and polymerization conditions in the polymerization process.

If above-described petroleum resin (C) used in the present invention
25 contains more than 1.0 phenolic hydroxyl group per one molecule of the resin, it is not suitable as a resin for anticorrosive coating composition. Furthermore, if it contains less than 0.1 phenolic hydroxyl group, it is not desirable either because the compatibility with epoxy resin is not good. Still further, the amount of hydroxyl group contained in the resultant resins can be

measured by the method described, for example, in I. E. 17 C. Anal. Ed. (1945) p. 394.

In addition, the softening point of the above-described resins should be in the range of 50 to 150°C, preferably 80 to 110°C. In the case that the softening point is below 50°C, the obtainable anticorrosive coating film will exhibit a low water resistance and occasionally exhibit sticky property due to the bleeding of resin component on its surface. On the other hand, in the case that the softening point exceeds 150°C, the work efficiency in coating operation becomes worse due to the increase in the viscosity of coating composition, and the physical properties of the coating film may be undesirably deteriorated. By the way, the number average molecular weight of the resin used in the present invention is in the range of 500 to 3000.

In order to prepare the anticorrosive coating composition of the present invention, 1 to 500 parts, preferably, 10 to 300 parts by weight of the foregoing petroleum resin (C) containing phenolic hydroxyl groups is added to 100 parts by weight of the epoxy resin (A). In the case that the amount of the petroleum resin (C) is less than 1 part by weight, the water resistance of the obtained composition is not good enough. On the other hand, if the quantity exceeds 500 parts by weight, the obtained coating film may be brittle. So that, both the cases are not preferable.

Furthermore, in order to impart flexibility, 50 parts by weight or less of other liquid modifiers of reactive diluents such as xylene resin, toluene resin, and epoxy compounds such as butyl glycidyl ether can be add to 100 parts by weight (as cured solid content) of the anticorrosive coating composition. Among them, aromatic resins or compounds are preferably used in order to maintain the water resistance.

Still further, as occasion demands, pigments such as extender pigments, anticorrosive pigments, coloring pigments; reactive diluents; and other ordinary additives such as organic solvents, anti-settling agents, anti-

sagging agents, wetting agents, reaction promoters, adhesion improvers and dehydrating agents can be optionally added to the composition of the present invention.

The anticorrosive coating composition of the present invention is a two-part liquid system composition which comprises a main component containing an epoxy resin and a curing agent preferably amine-based curing agents. It is usually applied to a primary anticorrosive coating such as zinc primer. More particularly, the mill scale on a steel plate is removed by applying shot blasting in the first place. An inorganic zinc shop primer of ethyl silicate type one or the like is then applied thereon. After that, the anticorrosive coating composition according to the present invention is applied onto the under coating. As the primer coating material, various kinds of primers as well as the zinc silicate can be used. Furthermore, it is possible to apply directly the coating composition of the invention onto a steel plate without any primer coating with ensuring satisfactory anticorrosive effect.

As the method for applying the composition, various conventionally known coating methods can be employed, for example, air spraying, airless spraying, brushing, and roller painting. The above-mentioned anticorrosive coating composition is applied so as to form a coating film having a thickness of 150 to 500 μm .

Best Method to Carry Out the Embodiment of the Invention

The present invention will be described in more detail with reference to the following examples. In the description, "part" and "%" indicate "parts by weight" and "% by weight", respectively.

<Preparation Example>

A fraction having a boiling range of 140 to 220°C was fractionated to obtain a cracked oil fraction. The starting fraction was derived from cracked

oil obtained by thermal cracking of petroleum naphtha. The obtained cracked oil fraction was adjusted to the values such that whole unsaturated components: 51%, content ratio of indenenes: 70%, and content ratio of conjugated dienes: 0.5%.

5 In the next place, 5g of phenol was added to 100g of the above cracked oil fraction and 0.5g of boron trifluoride-phenol complex was further added. This reaction mixture was subjected to polymerization at 30°C for 3 hours. After that, the catalyst was removed using an aqueous solution of sodium hydroxide and rinsed with water. Unreacted oil and low polymers were
10 distilled off to obtain 56 g of a petroleum resin (A).

The softening point of the obtained resin was 103°C and it was confirmed by analysis that the content of phenolic hydroxyl groups was 0.8 per one molecule.

<Comparative Preparation Example>

15 The same procedure as in the above Preparation Example was done to obtain a cracked oil fraction of the content ratio of indenenes of 20% and the content ratio of conjugated dienes 6%.

This fraction was then subjected to polymerization in the like manner as in the foregoing Preparation Example to obtain a petroleum resin (B)
20 having a softening point of 85°C and 0.8 of phenolic hydroxyl groups per one molecule.

<Example 1>

To a mixing tank were added 100 parts of epoxy resin, 30 parts of titanium white, 100 parts of talc, 100 parts of the petroleum resin (A)
25 obtained in Preparation Example, 20 parts of hydrocarbon plasticizer, 5 parts of anti-sagging agent and 150 parts of solvent mixture consisting of equal amounts of xylene, MIBK and cyclohexane and the contents were dispersed by mixed together using a mixer to obtain a main component. Then, 80 parts (as solid basis) of polyamide resin was added as a curing agent and it was

subjected to mixing to obtain an anticorrosive coating composition.

Their compositions and test results are shown in Table 1.

<Example 2, Comparative Example>

Compositions were similarly prepared with the formulae shown in
 5 Table 1. In Comparative Example, the petroleum resin (B) prepared in
 Comparative Preparation Example was used. The results are also shown in
 Table 1.

Table 1

	Example		Comparative Example
	1	2	3
Composition of Coating Material (parts by weight)			
Epoxy Resin ⁽¹⁾	100	100	100
Titanium White	30	30	30
Talc	100	100	100
Petroleum Resin (A) ⁽²⁾	100	200	---
Petroleum Resin (B) ⁽³⁾	---	---	150
Plasticizer ⁽⁴⁾	10	10	10
Anti-Sagging Agent ⁽⁵⁾	5	5	5
Mixed Solvent	150	150	150
Curing Agent (as solid content) ⁽⁶⁾	80	80	80
Impact Resistance : 500 g×30 cm	Good	Good	Cracked
Resistance to Cooling/Heating Cycles (-20°C×1 hr⇄60°C×1 hr): 3 cycles	Good	Good	Cracked
Seawater Resistance	○	○	△

10

- (1) Epoxy equivalent: 475; made by Yuka Shell Epoxy Co., Ltd.;
 trade name: Epon #1001.

- (2) Petroleum Resin (A) prepared in Preparation Example.
- (3) Petroleum Resin (B) prepared in Comparative Preparation Example.
- (4) Hydrocarbon plasticizer; made by Nippon Oil Co., Ltd.;
trade name: Hysol SAS LH.
- 5 (5) Aliphatic acid derivative; made by Ito Seiyu K. K.;
trade name: ASA T-55-20BX.
- (6) Curing agent for polyamide resin; made by Henkel Hakusui K. K.;
trade name: Versamid 115, used as a 50% solution of a mixed solvent
comprising equal amounts of xylene, MIBK and cyclohexane.

10 The following tests were carried out to evaluate the performance of
the anticorrosive coating composition.

(1) Test for Impact Resistance (du Pont method)

A degreased polished soft steel plate ($200 \times 100 \times 0.6$ mm) was coated
with each coating composition using an applicator to form a film of about 250
15 μm in thickness on dry basis and it was subjected to drying under the
atmosphere of $20^\circ\text{C} \times 65\%$ R. H. for 7 days to obtain each test plate.

The du Pont type impact resistance test as defined in JIS K5400-1990
was performed under the atmosphere of 20°C with the above test plates.

(2) Cooling/Heating Cycle Resistance Test

20 A degreased polished soft steel plate was coated with a silicate zinc
primer to form a film of about $25 \mu\text{m}$ in thickness on dry basis and it was dried
for one day. The thus formed plate was further coated with each test
composition to form a film of about $250 \mu\text{m}$ in thickness on dry basis and it
was subjected to drying under the atmosphere of $20^\circ\text{C} \times 65\%$ R. H. for 7 days
25 to obtain each test plate.

Repeated cooling/heating cycle resistance test was done in accordance
with JIS K5400-1990 on these test plates.

(3) Seawater Resistance Test

The same test pieces as those prepared in the above (2) Repeated

Cooling/Heating Cycle Resistance Test were immersed in seawater at 50°C for a period of 6 months and then the appearance of coated surfaces was evaluated by visual observation. Evaluation standards were as follows:

- 5 ○ : No change was observed.
 △ : Slight blistering was observed.
 × : Conspicuous blistering was observed.

Industrial Applicability

An anticorrosive coating composition of the present invention is prepared by using a petroleum resin containing phenolic hydroxyl groups having a specific content ratio of indenenes. Therefore, the compatibility of the petroleum resins with epoxy resins and curing agents, especially amine-based curing agents, is good. So that the obtained coating film causes no hygiene problem and is excellent in anticorrosiveness, water resistance and adhesiveness. In addition, the color of coating film is bright, so that it is very useful as an anticorrosive coating material for ships and steel structures.



What is Claimed is:

1. An anticorrosive coating composition comprising an epoxy resin (A), a curing agent (B), preferably an amine-based curing agent, and an aromatic petroleum resin (C) having 0.1 or more but less than 1.0 of phenolic hydroxyl groups per one molecule, wherein said aromatic petroleum resin is prepared by polymerizing a cracked oil fraction of 60 to 90% by weight in the content ratio of indenenes in the coexistence of phenols with a Friedel-Crafts catalyst. said cracked oil fraction being obtained by distilling a fraction principally containing components having boiling point in the range of 140 to 220°C, said fraction being derived from a cracked oil obtained by thermal cracking of petroleum resources, and said composition containing 1 to 500 parts by weight of said aromatic petroleum resin (C) per 100 parts by weight of said epoxy resin.
2. The anticorrosive coating composition in Claim 1, wherein the content ratio of conjugated dienes in said cracked oil fraction is less than 5% by weight.

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REPLACED