

[Document Type] Specification

[Title of the Invention] RESIN COATED STEEL AND MANUFACTURING
METHOD THEREFOR

[Technical Field of the Invention]

[0001]

The present invention relates to a steel coated with a urethane resin (resin coated steel), and a manufacturing method therefor.

Priority is claimed on Japanese Patent Application No. 2016-052696, filed on March 16, 2016, the content of which is incorporated herein by reference.

[Related Art]

[0002]

From a viewpoint of reliability of corrosion resistance, heavy anticorrosive coating using a thick urethane resin coating having a thickness of 2 mm or greater is applied to steel pipe piles, steel pipe sheet piles, and steel sheet piles used in a severe oceanic corrosive environment. Generally, a urethane resin coating is formed by spray coating a two-liquid solventless polyurethane resin composition, which is prepared by mixing a main agent including various kinds of polyol and a hardener having aromatic isocyanate as a main composition. Since this urethane elastomer composition has high viscosity and a high hardening rate, it is possible to perform thick coating having a thickness of 2 mm or greater with single coating. Therefore, the urethane resin composition can be applied not only to steel pipe piles but also to steels having a complicated shape, for example, steel pipe sheet piles and steel sheet piles. In a highly reliable anticorrosive layer, even in a case where a defect occurs in the anticorrosive layer, it is required that the defect does not reach the steel. Highly reliable anticorrosive layers include a thick urethane resin coating having excellent

shock resistance, and a heavy anticorrosive coating method using the urethane resin coating is a standard anticorrosive method in Japan. Since base material treatment, coating equipment, and a coating technique are required, urethane resin coated steels are mainly produced in factories.

[0003]

Generally, urethane resins are not resins having favorable weather resistance. Therefore, it is difficult to use a urethane resin which is colored other than black in a corrosive environment. If carbon black is added to a urethane resin, a black urethane resin is obtained, and the carbon black restrains the urethane resin from deteriorating due to ultraviolet rays. Therefore, even if a urethane resin has deteriorated due to ultraviolet rays and a urethane resin coating has worn down, the ratio of the depth of wear to the overall thickness of a urethane resin film is sufficiently small. Therefore, in the related art, it has been assumed that if even a black urethane resin coating is applied to a surface of a steel, the urethane resin coating can sufficiently protect the steel against corrosion. However, it has also been found that in a tidal zone or a splash zone of a structure in an actual environment in the ocean, there are cases where the amount of wear is larger than an amount estimated through a laboratory test in the related art. In addition, as in a tropical environment, there is an increasing need for an oceanic structure in an environment in which severe deterioration of resin is estimated. Therefore, countermeasures to prevent deterioration of resin are newly required.

[0004]

Generally, in order to enhance weather resistance of a urethane resin, an ultraviolet absorber or an oxidant inhibitor is added to the urethane resin. However, since urethane resins are thermosetting resins, an additive is unlikely to move inside

the resin. Therefore, the additive has a small effect of preventing deterioration of the urethane resin.

[0005]

In the field of general coating, a coating on a steel is used for not only protecting the steel against corrosion but also for applying a predetermined design (external appearance) to the steel. In order to apply a design, a topcoat colored in a color different from that of a lower layer is likely to be used. In order to maintain a design over a long period of time, a topcoat is required not to change in color due to ultraviolet rays. Therefore, since intermolecular bonds are unlikely to be cut due to ultraviolet rays in fluorine-based topcoats or silicon-based topcoats, the fluorine-based topcoats or the silicon-based topcoats are perceived as excellent topcoats having less color changes.

[0006]

As another kind of topcoats, Patent Document 1 discloses a method of coating a surface of a colored urethane resin with an acrylic urethane resin colored in the same color as that of the colored urethane resin in order to maintain its design over a long period of time. In the method of Patent Document 1, both the resins are colored in a color other than black, and weather resistance (discoloring resistance) is regarded as important. Therefore, a polyurethane elastomer coated layer includes aliphatic isocyanate having high weather resistance while being poor in anticorrosive properties.

[0007]

In addition, Patent Document 2 discloses a method of forming an acrylic urethane resin layer on an anticorrosive layer including a urethane resin in order to prevent a color change of the resin. In Patent Document 2, weather resistance of acrylic urethane resin coating is checked through an accelerated weathering test using a

sunshine weather meter. In addition, polymer polyol such as polybutadiene having hydroxyl groups at its terminals is used as an essential element of a polyurethane resin.

[0008]

Patent Document 3 discloses a method of applying a coating film colored other than black on a black urethane elastomer layer at a position higher than a tidal zone. In the method of Patent Document 3, it is possible to maintain an excellent external appearance over a long period of time by using the colored coating film.

[0009]

However, in topcoats disclosed in Patent Documents 1 to 3, in a case where a resin coated steel is used as a material of an oceanic structure, a resin coating cannot protect the steel against corrosion for a long period of time.

[Prior Art Document]

[Patent Document]

[0010]

[Patent Document 1] Japanese Unexamined Patent Application, First Publication No. S63-183838

[Patent Document 2] Japanese Examined Patent Application, Second Publication No. S63-13826

[Patent Document 3] Japanese Unexamined Patent Application, First Publication No. H8-27826

[Disclosure of the Invention]

[Problems to be Solved by the Invention]

[0011]

An object of the present invention is to provide a urethane resin coated steel in which deterioration and wear of a urethane resin coating are prevented and a urethane

resin can continuously protect the steel against corrosion even in a case of being used as a material of a structure in the ocean for a long period of time. In addition, another object of the present invention is to provide a method of manufacturing a urethane resin coated steel having such heavy anticorrosive properties.

[Means for Solving the Problem]

[0012]

The gist of the present invention is as follows.

[0013]

(1) According to an aspect of the present invention, there is provided a resin coated steel including a steel, a primer layer that is provided on a surface of the steel, a urethane resin layer that is provided on a surface of the primer layer, and a top coating layer that is provided on a surface of the urethane resin layer. The urethane resin layer includes an inorganic pigment including carbon black, and a urethane resin having a urethane bond including constituent atoms of a hydroxyl group of polyol and an isocyanate group of isocyanate. The top coating layer includes carbon black and an acrylic urethane resin. The polyol includes a castor oil derivative having 2.7 or more hydroxyl groups per molecule, and an organic composition having 2.0 hydroxyl groups per molecule. The isocyanate includes at least one selected from the group consisting of diphenylmethane diisocyanate, toluene diisocyanate, a diphenylmethane diisocyanate derivative, and a toluene diisocyanate derivative. In the urethane resin layer, when a mass obtained by subtracting a mass of the isocyanate from a mass of the urethane resin layer is defined as a mass of the main agent, a mass of the carbon black ranges from 0.2% to 5.0% of the mass of the main agent, a mass obtained by subtracting the mass of the carbon black from a mass of the inorganic pigment ranges from 10% to 60% of the mass of the main agent, and a mass of the castor oil derivative

ranges from 10% to 70% of the mass of the main agent. In the top coating layer, the mass of the carbon black ranges from 0.2% to 5.0% of a mass of the top coating layer.

[0014]

(2) According to another aspect of the present invention, there is provided a method of manufacturing a resin coated steel including forming a primer layer by applying a primer onto a surface of a steel, forming a urethane resin layer by applying a liquid mixture including a main agent and a hardener onto a surface of the primer layer and hardening the liquid mixture, and forming a top coating layer by applying an acrylic urethane resin coating material including carbon black onto a surface of the urethane resin layer and hardening the acrylic urethane resin coating material. The main agent includes an inorganic pigment including carbon black, and polyol. The hardener includes at least one selected from the group consisting of diphenylmethane diisocyanate, toluene diisocyanate, a diphenylmethane diisocyanate derivative, and a toluene diisocyanate derivative. The polyol includes a castor oil derivative having 2.7 or more hydroxyl groups per molecule, and an organic composition having 2.0 hydroxyl groups per molecule. In the main agent, a mass of the carbon black ranges from 0.2% to 5.0% of a mass of the main agent, a mass obtained by subtracting the mass of the carbon black from a mass of the inorganic pigment ranges from 10% to 60% of the mass of the main agent, and a mass of the castor oil derivative ranges from 10% to 70% of the mass of the main agent. In the acrylic urethane resin coating material, the mass of the carbon black ranges from 0.2% to 5.0% of a mass of the acrylic urethane resin coating material.

[Effects of the Invention]

[0015]

According to the aspects of the present invention, even in an environment

exposed to ultraviolet rays and water, such as the ocean, since the top coating layer protects the urethane resin layer against ultraviolet rays and water, the urethane resin layer can prevent corrosion of the steel over a long period of time. Therefore, according to the aspects of the present invention, it is possible to provide a resin coated member having high durability even under a condition of being exposed to water, such as the ocean, particularly with respect to a region from a tidal zone to an underwater part affected by both ultraviolet rays and moisture. Therefore, according to the aspects of the present invention, it is possible to configure a low-cost structure having high durability under a condition of being exposed to water, such as the ocean.

[Brief Description of the Drawings]

[0016]

FIG. 1 is a schematic view of a part of a cross section of a resin coated steel according to an embodiment of the present invention.

FIG. 2 is a view showing a relationship between a ratio of a mass of a castor oil derivative (first polyol) having 2.7 or more hydroxyl groups per molecule to a mass of a main agent, and a combined cycle test result.

[Embodiments of the Invention]

[0017]

The inventor has investigated a method for preventing wear of a urethane resin due to ultraviolet rays, water, and the like and maintaining durability of a heavy anticorrosive coating over a long period of time. First, as a way thereof, the inventor formed a protective thin-film layer for enhancing weather resistance on a surface of a urethane resin layer. As the protective thin-film layer, the inventor used an acrylic urethane resin assumed to have high adhesion to the urethane resin layer. Since the urethane resin layer had a high hardening rate, the urethane resin layer was coated with

a topcoat (protective thin-film layer) after being hardened. However, in a urethane resin coated steel obtained by this method, the resin could not protect the steel against corrosion over a long period of time. The inventor has investigated the reason thereof. As a result, the inventor has found that it is difficult to stably achieve sufficient adhesion of a top coating layer to a urethane resin layer in a urethane coated steel.

[0018]

In addition, as described above, since the purpose of topcoats in the related art is to apply a design to a steel, there has been little investigation on adhesion of topcoats to a urethane resin. Particularly, the relationship between a plurality of factors (for example, ultraviolet rays and water) and adhesion in an actual environment has not been perceived. For example, fluorine-based modified resins or silicon-based modified resins have lower adhesion to urethane resins compared to general acrylic urethane resins. However, adhesion of these modified resins in the atmosphere during a short period of time is sufficient for ordinary use, so that adhesion has seldom been discussed.

[0019]

The inventor has investigated the reason that adhesion of a top coating layer to a urethane resin layer is not sufficient even if the top coating layer includes an acrylic urethane resin. An acrylic urethane resin mainly adheres to a lower layer due to a hydrogen bond by a molecular polarity or an anchoring effect of unevenness on a surface. Therefore, the number of chemical bonds between the acrylic urethane resin and the lower layer is comparatively small. In this case, moisture is likely to infiltrate into a space between the acrylic urethane resin and the lower layer. Therefore, even though the acrylic urethane resin has sufficient adhesion to the lower layer in the atmosphere, an adhesion force of the acrylic urethane resin to the lower layer is easily

degraded under the water. Therefore, in regard to the chemical composition of a urethane resin, the inventor has investigated a method in which a chemical bond with an acrylic urethane resin can be formed on a surface of a urethane resin layer even after the urethane resin layer is hardened.

[0020]

A urethane bond is formed due to hydroxyl groups (-OH) of polyol in a main agent and isocyanate groups (-NCO) of a hardener. Therefore, the inventor has investigated a method of causing these functional groups, which are assumed to be able to make an acrylic urethane resin come into tight contact with a urethane resin layer by means of urethane bonds, to remain on a surface of the urethane resin layer. Since isocyanate groups are likely to react with water in the air, it is difficult for isocyanate groups to remain on a surface of a urethane resin layer. Although a few hydroxyl groups (-OH) are generally present on a surface of a urethane resin after the urethane resin is hardened, they do not react with water in the air. Therefore, the inventor has investigated a method of causing hydroxyl groups of polyol in a main agent to remain on a surface of a urethane resin layer, particularly from an aspect of a chemical composition. As a result, the inventors have found that if a urethane resin including a proper amount of castor oil-based polyol having 2.7 or more hydroxyl groups per molecule is used, adhesion of an acrylic urethane resin to a urethane resin layer can be sufficiently ensured. Since adhesion of a top coating layer including an acrylic urethane resin to a urethane resin layer has become sufficient by this method, the inventor has further investigated a method of causing ultraviolet rays to be unlikely to reach an interface between a top coating layer and a urethane resin layer.

[0021]

Hereinafter, a resin coated steel according to an embodiment of the present

invention will be described in detail.

[0022]

FIG. 1 is a schematic view of a part of a cross section (one surface) of a resin coated steel according to the present embodiment. As shown in FIG. 1, a resin coated steel 5 includes a steel 1, a primer layer 2 provided on a surface of the steel 1, a urethane resin layer 3 provided on a surface of the primer layer 2, and a top coating layer 4 provided on a surface of the urethane resin layer 3. A resin layer 6 including the primer layer 2, the urethane resin layer 3, and the top coating layer 4 is formed on at least one surface of the steel 1. That is, the resin layer 6 may be formed on both surfaces of the steel 1. In addition, the resin layer 6 may be formed on the entire surface of the steel 1.

[0023]

(Steel 1)

The kind (chemical composition), the shape, the dimensions, and the product category of the steel 1 are not particularly limited. As described below, since the resin layer 6 has excellent durability particularly in a severely corrosive environment such as the ocean, it is preferable that the steel 1 is a product required to be anticorrosive over a long period of time. For example, it is preferable that the steel 1 is a large-sized steel product, such as a steel pipe, a steel pipe pile, a steel pipe sheet pile, and a steel sheet pile. For example, the steel 1 may have a thickness ranging from 5 mm to 50 mm. In regard to the kind of steel, the steel 1 may be a common steel or a high alloy steel. The resin layer 6 can be applied to any kind of steel 1. For example, the steel 1 may have a surface layer of a common steel, a high alloy steel, or a nonferrous metal such as a plated metal.

[0024]

(Primer layer 2)

The resin coated steel 5 includes the primer layer 2 in order to cause the resin layer 6 to firmly adhere to the steel 1. Therefore, as long as the primer layer 2 has affinity with respect to both the steel 1 and the urethane resin layer 3, the chemical composition and the thickness of the primer layer 2 are not particularly limited. For example, the primer layer 2 may include at least one selected from the group consisting of a urethane resin and an epoxy resin. In addition, for example, the thickness of the primer layer 2 may range from 10 to 200 μm .

[0025]

(Urethane resin layer 3)

In order to prevent corrosion of the steel 1 against corrosion, the resin coated steel 5 includes the urethane resin layer 3. The urethane resin layer 3 includes an inorganic pigment including carbon black, and a urethane resin. The urethane resin has urethane bonds ($-\text{NHCOO}-$) including constituent atoms of hydroxyl groups ($-\text{OH}$) of polyol (for example, $\text{HO-R}_1-\text{OH}$) and isocyanate groups ($-\text{NCO}$) of isocyanate [diisocyanate] (for example, $\text{OCN-R}_2-\text{NCO}$) (that is, one nitrogen atom, one carbon atom, one hydrogen atom, and two oxygen atoms per urethane bond). Due to the urethane bonds, in the urethane resin, molecular skeletons (R_1) of polyol and molecular skeletons (R_2) of isocyanate are bonded to each other. In the present embodiment, in order to clarify the standard of the mass in the urethane resin layer 3, the mass obtained by subtracting the mass of isocyanate (entire mass of atoms supplied from isocyanate) from the mass of the urethane resin layer 3 is defined as the mass of the main agent (main resin).

[0026]

(Carbon black in urethane resin 3)

The urethane resin layer 3 includes carbon black (CB) as one of inorganic pigments. Since carbon black favorably absorbs ultraviolet rays, carbon black protects the urethane resin layer 3 against ultraviolet rays and enhances weather resistance of the urethane resin layer 3. In order to cause carbon black to uniformly disperse in the urethane resin layer 3 and to sufficiently protect the urethane resin layer 3 against ultraviolet rays, the mass of the carbon black is required to range from 0.2% to 5.0% of the mass of the main agent. If the mass of the carbon black is less than 0.2% of the mass of the main agent, weather resistance of the urethane resin layer 3 becomes insufficient. In addition, if the mass of the carbon black exceeds 5.0% of the mass of the main agent, carbon black is flocculated in the urethane resin layer 3.

[0027]

(Inorganic pigment (excluding carbon black) in urethane resin layer 3)

Excluding carbon black, the material of the inorganic pigment is not particularly limited. The inorganic pigment is selected in accordance with characteristics required for the urethane resin layer 3. For example, if the inorganic pigment is selected as an extender pigment, the inorganic pigment includes oxide minerals such as clay, pearlite, kaolin, kaolin clay, montmorillonite, talc, and alumina ore. Clay and pearlite include silicon oxide (silica). Kaolin, kaolin clay, and montmorillonite include aluminum silicate. Talc includes magnesium silicate. Therefore, for example, the inorganic pigment may include oxide, and the oxide may be silicon oxide (silica) or silicate (silicate). If the inorganic pigment includes oxide minerals, strength of the urethane resin layer 3 increases, and anticorrosive performance of the urethane resin layer 3 is enhanced. On the other hand, adhesion of the urethane resin layer 3 to the top coating layer 4 is degraded. Therefore, the mass of the inorganic pigment excluding carbon black (mass obtained by subtracting

the mass of the carbon black from the mass of the inorganic pigment) is required to range from 10% to 60% of the mass of the main agent. It is preferable that the mass ranges from 15% to 50% of the mass of the main agent. If the mass of the inorganic pigment excluding carbon black is less than 10% of the mass of the main agent, strength of the urethane resin layer 3 becomes insufficient. In addition, if the mass of the inorganic pigment excluding carbon black exceeds 60% of the mass of the main agent, adhesion of the urethane resin layer 3 to the top coating layer 4 becomes insufficient. For example, in a case where the inorganic pigment mainly includes silica, the specific gravity of the inorganic pigment often ranges from 2.6 to 2.7. In addition, the shape of the inorganic pigment is also not particularly limited. For example, inorganic minerals may be crushed oxide minerals.

[0028]

(Urethane resin in urethane resin layer 3)

The urethane resin includes the molecular skeletons (R_1) of polyol, the molecular skeletons (R_2) of isocyanate, and urethane bonds ($-NHCOO-$). In addition, the urethane resin may optionally include at least one selected from the group consisting of unreacted hydroxyl groups ($-OH$), unreacted isocyanate groups ($-NCO$), functional groups derived from hydroxyl groups other than urethane bonds, and functional groups derived from isocyanate groups other than urethane bonds. The molecular skeletons of polyol are partial structures (skeleton portions) resulted after the hydroxyl groups are excluded from the polyol. The molecular skeletons of isocyanate are partial structures (skeleton portions) resulted after the isocyanate groups are excluded from the isocyanate. These partial structures vary in accordance with the kind of polyol and isocyanate.

[0029]

If three or more hydroxyl groups bonded to one polyol molecule is used for a urethane bond, a three-dimensional network structure is formed around the molecular skeleton of the polyol molecule. Therefore, the polyol molecule having three or more hydroxyl groups is likely to supply hydroxyl groups to a surface of the urethane resin layer 3. As a result, if there are a large number of polyol molecules having three or more hydroxyl groups, the number of hydroxyl groups in an interface between the urethane resin layer 3 and the top coating layer 4 (hereinafter, an upper interface) increases. Meanwhile, the three-dimensional network structure makes the urethane resin layer 3 brittle. Therefore, embrittlement caused due to an increase in the number of bonds is offset by ductility (flexibility) of the molecular structure (molecular skeleton). A castor oil derivative having 2.7 or more hydroxyl groups (functional groups) per molecule includes a sufficient amount of polyol molecules having a flexible molecular structure to the extent that sufficient hydroxyl groups can be supplied to a surface of the urethane resin layer 3. Therefore, the polyol according to the present embodiment is required to include a castor oil derivative (hereinafter, first polyol) having 2.7 or more hydroxyl groups (functional groups) per molecule. If the mass of the first polyol is less than 10% of the mass of the main agent, a sufficient amount of hydroxyl groups cannot be supplied to the upper interface. In addition, if the mass of the first polyol exceeds 70% of the mass of the main agent, the urethane resin layer 3 becomes brittle due to excessive hydroxyl groups. Therefore, as shown in FIG. 2, the mass of the first polyol ranges from 10% to 70% of the mass of the main agent. It is particularly preferable that the mass of the first polyol ranges from 30% to 60% of the mass of the main agent. In addition, it is preferable that the polyol consists of only the first polyol and second polyol (will be described below).

[0030]

The first polyol is classified as castor oil-based polyol, and the castor oil-based polyol includes castor oil, an ester exchange reaction product of castor oil and polyol, an ester compound of castor oil and polyol, and an addition compound of those and alkylene oxide. That is, the castor oil-based polyol is polyol which can be generated with castor oil (including castor oil-based fatty acids) as a main raw material.

[0031]

Commercially available castor oil-based polyol can be used as the first polyol. For example, URIC H-series manufactured by Itoh Oil Chemicals Co., Ltd. are commercially available. As the URIC H-series corresponding to the first polyol, there are URIC H-30 (having a hydroxyl value ranging from 155 to 165 mgKOH/g and 2.7 functional groups), URIC H-52 (having a hydroxyl value ranging from 195 to 205 mgKOH/g and three functional groups), URIC H-57 (having a hydroxyl value ranging from 85 to 115 mgKOH/g and three functional groups), URIC H-73X (having a hydroxyl value ranging from 260 to 280 mgKOH/g and three functional groups), URIC H-81 (having a hydroxyl value ranging from 330 to 350 mgKOH/g and three functional groups), URIC H-102 (having a hydroxyl value ranging from 300 to 340 mgKOH/g and five functional groups), URIC H-420 (having a hydroxyl value ranging from 300 to 340 mgKOH/g and three functional groups), URIC H-854 (having a hydroxyl value ranging from 205 to 225 mgKOH/g and three functional groups), URIC H-870 (having a hydroxyl value ranging from 264 to 276 mgKOH/g and three functional groups), POLYCASTOR #10 (having a hydroxyl value ranging from 155 to 165 mgKOH/g and five or six functional groups), and POLYCASTOR #30 (having a hydroxyl value ranging from 150 to 160 mgKOH/g and five to six functional groups). The aforementioned examples of castor oil-based polyol have 2.7 or more functional groups (hydroxyl groups), flexible molecular structures, and excellent mechanical

strength. In addition, the upper limit for the number of functional groups of the URIC H-series is approximately six. In this manner, since castor oil-based polyol having 6.0 or less functional groups is likely to come to hand, the upper limit for the number of functional groups may be 6.0. The number of functional groups (the number of hydroxyl groups) of polyol denotes the number of hydroxyl groups stipulated in JIS K 1557 or ISO 14900 and 15063.

[0032]

Castor oil-based polyol includes a chemical composition or a derivative derived from castor oil in the molecular skeleton of each molecule. The main composition of the castor oil is glyceride of fatty acids. In this glyceride, fatty acids are bonded to hydroxyl groups of glycerin via ester bonds. Most of the fatty acids are ricinoleic acids, and the rest of the fatty acids are, for example, oleic acids, linoleic acids, linolenic acids, palmitic acids, stearic acids, and dihydroxy acids. Since castor oil-based polyol has such a chemical composition derived from castor oil, the molecular skeleton of the castor oil-based polyol makes a resin flexible.

[0033]

If only two hydroxyl groups bonded to one polyol molecule are used for urethane bonds, chain structures are formed around the molecular skeletons of the polyol molecules. Therefore, a polyol molecule having two hydroxyl groups is not much restricted in movement by other molecules, so that elongation of the urethane resin layer 3 is enhanced. Therefore, the polyol according to the present embodiment is required to include an organic composition (hereinafter, the second polyol) having 2.0 hydroxyl groups (functional groups) per molecule. The second polyol includes a polyol product marked with 2 as the number of hydroxyl groups (the number of functional groups), and a diol compound. The amount of second the polyol is not

particularly limited. In order to enhance elongation of the urethane resin layer 3, it is preferable that the mass of the second polyol ranges from 10% to 80% of the mass of the main agent and it is more preferable to range from 20% to 60%. The second polyol can be suitably selected in accordance with characteristics additionally applied to the urethane resin layer 3. Examples of such characteristics include flexibility and heat resisting properties. A specific mass of the second polyol can be determined in accordance with the additionally applied characteristics. For example, as the second polyol, it is possible to use at least one selected from the group of the following (a) to (d).

[0034]

(a) As the second polyol, castor oil-based polyol can be used. As the castor oil-based polyol corresponding to the second polyol, for example, there are URIC H-62, URIC Y-202, URIC Y-403, URIC Y-406, and URIC Y-332. These products are manufactured by Itoh Oil Chemicals Co., Ltd. and have two functional groups (hydroxyl groups).

[0035]

(b) As the second polyol, amine polyol can be used. As the amine polyol corresponding to the second polyol, for example, there is polyol obtained by adding alkylene oxide having two to four carbons to amines. In addition, amines are classified into aromatic amine and aliphatic amine. As the aromatic amine, for example, there are aniline, toluenediamine, diethyltoluenediamine, and 4,4'-diamino-3,3'-diethyldiphenylmethane. The aromatic amine may be aromatic monoamine or aromatic polyamine. As the aliphatic amine, there are ethylenediamine, hexamethylenediamine, and diethylenetriamine. The aliphatic amine may be aliphatic polyamine. As the alkylene oxide having two to four carbons, for example,

there are ethylene oxide and propylene oxide. As a compound of amines and alkylene oxide having two to four carbons, for example, there is N,N-bis (2-hydroxypropyl) aniline.

[0036]

(c) As the second polyol, polybutadiene polyol can be used. As the polybutadiene polyol corresponding to the second polyol, for example, there are Poly bdTM R-45HT and Poly bdTM R-15HT. These products are manufactured by Idemitsu Kosan Co., Ltd. and have two functional groups (hydroxyl groups).

[0037]

(d) As the second polyol, alkylene diol can be used. For example, the alkylene diol corresponding to the second polyol may have branched chain saturated hydrocarbon or linear chain saturated hydrocarbon. Examples of specific alkylene diol having branched chain saturated hydrocarbon include 2-methyl-1,3-propanediol (solidifying point: -91°C), 2-methyl-1,4-butanediol (solidifying point: -30°C or lower), 3-methyl-1,5-pentanediol, and 2,4-diethyl-1,5-pentanediol. In addition, examples of specific alkylene diol having linear chain saturated hydrocarbon include 1,3-propanediol.

[0038]

The second polyol according to the present embodiment may be at least one selected from the group consisting of (a) castor oil-based polyol, (b) amine polyol, (c) polybutadiene polyol, and (d) alkylene diol. That is, a single compound, a single product, or a mixture can be used as the second polyol according to the present embodiment.

[0039]

The isocyanate according to the present embodiment may be at least one

selected from the group consisting of diphenylmethane diisocyanate (MDI), toluene diisocyanate (TDI), a diphenylmethane diisocyanate derivative (MDI derivative), and a toluene diisocyanate derivative (TDI derivative). The MDI and the TDI are aromatic diisocyanate and have two isocyanate groups. In addition, the MDI derivative and the TDI derivative include an oligomer of MDI or an oligomer of TDI. Examples of the isocyanate according to the present embodiment include monomeric MDI, polymeric MDI, modified isocyanate, a pure TDI isomer, an isomer mixture of TDI, and blended isocyanate. In addition, as products manufactured by Tosoh Corporation, there are Millionate MT-series (monomeric MDI products), Millionate MR-series (polymeric MDI products), Coronate series (polyol modified isocyanate products), Millionate MTL-series (carbodiimide modified products of MDI), Coronate T-80/T-65/T-100 (TDI products), and blended isocyanate thereof (mixed product of MDI and TDI). In addition, as products manufactured by BASF INOAC polyurethane Ltd., there are Luplanate MS and MI (monomeric MDI products); Luplanate M20S, M11S, and M5S (polymeric MDI products); MM-103, MP-102, and MB-301 (modified MDI products); and Luplanate T-80 (TDI product). A mixture of the above-described products may be used as the isocyanate according to the present embodiment.

[0040]

The ratio of the amount of the isocyanate according to the present embodiment to the amount of the polyol according to the present embodiment is defined based on the number of isocyanate groups (total number) included in isocyanate with respect to the number of hydroxyl groups (total number) included in polyol. It is preferable that the ratio (-NCO/-OH) of the number of isocyanate groups (-NCO) to the number of hydroxyl groups (-OH) ranges from 0.9 to 1.2. If the ratio is 0.9 or higher, the urethane resin layer 3 has sufficient hardness. In addition, if the

ratio (-NCO/-OH) is 1.2 or lower, the urethane resin layer 3 has favorable quality in density. The ratio (-NCO/-OH) preferably ranges from 1.0 to 1.1.

[0041]

(Other chemical compositions in urethane resin layer 3)

As other chemical compositions, the urethane resin layer 3 may include a chemical composition derived from at least one selected from the group consisting of a reaction accelerator, a water absorbent (moisture absorbent), a thixotropy imparting agent, a flame retardant, and a plasticizer.

[0042]

For example, an amine compound or a metal catalyst can be used as the reaction accelerator. As the amine compound, there are triethylenediamine, bis (2-dimethylaminoethyl) ether, and N,N,N',N'-tetramethylhexamethylenediamine. In addition, as the metal catalyst, there are dioctyltin dilaurate and stannous octoate.

[0043]

It is preferable that a zeolite compound is used as the water absorbent. For example, as the powdery zeolite compound, there are Zeoram A-3, A-4, and F-9 manufactured by Tosoh Corporation.

[0044]

For example, Aerosil which is dry silica manufactured by Nippon Aerosil Co., Ltd. can be used as the thixotropy imparting agent.

[0045]

It is possible to use antimony trioxide, aluminum hydroxide, tetrabromophenyl ether, tris (chloropropyl) phosphate (TCPP), or the like as the flame retardant.

[0046]

It is possible to use carboxylic ester such as phthalate ester, adipate ester, and sebacate ester as the plasticizer. Examples of such carboxylic ester include dibutyl phthalate (DBP), dioctyl phthalate (DOP), diisodecyl phthalate (DIDP), dicetyl adipate (DOA), trioctyl trimate (TOTM), and tricresyl phosphate (TCP). Particularly, it is preferable that the plasticizer is diisononyl adipate (DINA) or diisononyl phthalate (DINP).

[0047]

(Thickness of urethane resin layer 3)

The thickness of the urethane resin layer 3 is not particularly limited. If the thickness of the urethane resin layer 3 is 2 mm or greater, the urethane resin layer 3 has sufficient defect resistance and anticorrosive properties. In addition, if the thickness of the urethane resin layer 3 is 5 mm or lower, internal stress in the urethane resin layer 3 can be reduced, so that peeling resistance at a low temperature can be applied to the urethane resin layer 3. Therefore, it is preferable that the thickness of the urethane resin layer 3 ranges from 2 to 5 mm.

[0048]

(Essential constituent according to chemical composition of urethane resin layer 3)

Therefore, the urethane resin layer 3 according to the present embodiment includes an inorganic pigment including carbon black (CB), and a urethane resin having urethane bonds including constituent atoms of hydroxyl groups of polyol and isocyanate groups of isocyanate. In the present embodiment, polyol includes the castor oil derivative (first polyol) having 2.7 or more hydroxyl groups (functional groups) per molecule, and the organic composition (second polyol) having 2.0 hydroxyl groups (functional groups) per molecule. In addition, in the present

embodiment, isocyanate includes at least one selected from the group consisting of diphenylmethane diisocyanate, toluene diisocyanate, a diphenylmethane diisocyanate derivative, and a toluene diisocyanate derivative. Moreover, in the urethane resin layer 3 according to the present embodiment, when a mass obtained by subtracting the mass of isocyanate from the mass of the urethane resin layer 3 is defined as the mass of the main agent, the mass of the carbon black ranges from 0.2% to 5.0% of the mass of the main agent, the mass obtained by subtracting the mass of the carbon black from the mass of the inorganic pigment ranges from 10% to 60% of the mass of the main agent, and the mass of the castor oil derivative ranges from 10% to 70% of the mass of the main agent.

[0049]

(Top coating layer 4)

In order to protect the urethane resin layer 3 against ultraviolet rays and water, the resin coated steel 5 includes the top coating layer 4. The top coating layer 4 includes carbon black and an acrylic urethane resin. The acrylic urethane resin has urethane bonds (-NHCOO-) including constituent atoms of hydroxyl groups (-OH) of acrylic polyol (for example, HO-R₃-OH) and isocyanate groups (-NCO) of isocyanate (for example, OCN-R₄-NCO). In the urethane resin, molecular skeletons (R₃) of polyol and molecular skeletons (R₄) of isocyanate are bonded to each other by means of the urethane bonds.

[0050]

(Carbon black in top coating layer 4)

The top coating layer 4 includes carbon black. Since carbon black favorably absorbs ultraviolet rays, carbon black protects the urethane resin layer 3 and the top coating layer 4 against ultraviolet rays and enhances weather resistance of the urethane

resin layer 3 and the top coating layer 4. In order to sufficiently protect the urethane resin layer 3 against ultraviolet rays, the mass of the carbon black is required to range from 0.2% to 5.0% of the mass of the top coating layer 4. If the mass of the carbon black is less than 0.2% of the mass of the top coating layer 4, ultraviolet rays are transmitted through the top coating layer 4 and reach the upper interface. Therefore, the urethane resin layer 3 in the vicinity of the upper interface cannot be restrained from deteriorating. In addition, if the mass of the carbon black exceeds 5.0% of the mass of the top coating layer 4, carbon black is flocculated in the top coating layer 4. In this case, even if the mass of the carbon black is further increased, intensity of ultraviolet rays transmitted through the top coating layer 4 seldom changes. In addition, since the top coating layer 4 includes carbon black, the surface of the resin coated steel 5 is black.

[0051]

(Acrylic urethane resin in top coating layer 4)

An acrylic urethane resin includes the molecular skeletons (R_3) of acrylic polyol, the molecular skeletons (R_4) of isocyanate, and urethane bonds ($-NHCOO-$). In addition, the acrylic urethane resin may optionally include at least one selected from the group consisting of unreacted hydroxyl groups ($-OH$), unreacted isocyanate groups ($-NCO$), functional groups derived from hydroxyl groups other than urethane bonds, and functional groups derived from isocyanate groups other than urethane bonds. The molecular skeletons of acrylic polyol are partial structures (skeleton portions) resulted after the hydroxyl groups are excluded from the acrylic polyol. The molecular skeletons of isocyanate are partial structures (skeleton portions) resulted after the isocyanate groups are excluded from the isocyanate. These partial structures vary in accordance with the kind of acrylic polyol and isocyanate.

[0052]

The molecular skeletons of acrylic polyol apply weather resistance to the top coating layer 4. A copolymer of a methacrylate monomer or acrylic ester, and an unsaturated monomer (unsaturated ethylene monomer) having hydroxyl groups and double bonds can be used as the acrylic polyol of the present embodiment. As the methacrylate monomer, there are methyl methacrylate, ethyl methacrylate, and the like. As the acrylic ester, there are methyl acrylate, ethyl acrylate, and the like. As the unsaturated monomer having hydroxyl groups and double bonds, there are hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxyethyl acrylate, hydroxypropyl acrylate, and the like. The method of copolymerization may be a known method.

[0053]

Commercially available acrylic polyol can be used as the acrylic polyol. For example, as the acrylic polyol manufactured by Takeda Pharmaceutical Co., Ltd., there are TAKELAC UA-702, TAKELAC UA-902, and TAKELAC UA-905.

[0054]

The isocyanate groups of isocyanate are chemically bonded to the hydroxyl groups of the urethane resin layer 3 in the upper interface. Adhesion between the urethane resin layer 3 and the top coating layer 4 is enhanced due to the chemical bonds (urethane bonds) thereof. The isocyanate according to the present embodiment may be a prepolymer manufactured from aliphatic isocyanate. Examples of the aliphatic isocyanate include xylylene diisocyanate (XDI), isophorone diisocyanate (IPDI), and hexamethylene diisocyanate (HDI). In addition, for example, in the prepolymer, there may be a compound which is obtained by adding aliphatic isocyanate to polyether polyol. Moreover, for example, the polyether polyol may be

polyalkylene polyol which has two or three active hydrogen groups (hydroxyl groups) in one molecule and is able to be obtained by polymerizing alkylene oxide in polyol while an alkali catalyst or the like is present. Examples of the polyol used for the polymerization include propylene glycol, butanediol, neopentyl glycol, hexanediol, glycerin, and trimethylolpropane. In addition, examples of the alkylene oxide used for the polymerization include propylene oxide, ethylene oxide, and butylene oxide. It is possible to manufacture a urethane prepolymer having aliphatic isocyanate at its terminals by adding aliphatic isocyanate to polyalkylene polyol. In the present embodiment, such a urethane prepolymer can be utilized. In addition, in the present embodiment, it is possible to utilize a 1,6-hexamethylene diisocyanate homopolymer which can be manufactured from HDI. If the top coating layer 4 includes molecular skeletons of a compound derived from aliphatic isocyanate (aliphatic isocyanate derivative), the color of the top coating layer 4 is unlikely to change into yellow due to ultraviolet rays. Therefore, in the top coating layer 4, it is preferable that there are more molecular skeletons of aliphatic isocyanate than the molecular skeletons of aromatic isocyanate. Examples of the aromatic isocyanate include diphenylmethane diisocyanate (MDI) and toluene diisocyanate (TDI).

[0055]

In order to further enhance weather resistance, the top coating layer 4 may include an ultraviolet absorber or a light stabilizer. For example, a hindered amine-based light stabilizer can be used as the light stabilizer. Examples of the hindered amine-based light stabilizer include bis (1,2,2,6,6-pentamethyl-4-piperidyl) sebacate, bis (2,2,6,6-tetramethyl-4-piperidyl) sebacate, and 8-benzyl-7,7,9,9-tetramethyl-3-octyl 1,3,8-triazaspiro [4,5] undecane-2,4-dione.

[0056]

SANOL LS-292 and SANOL LS-765 manufactured by Sankyosha Co., Ltd. can be utilized as products including the bis (1,2,2,6,6-pentamethyl-4-piperidyl) sebacate. In addition, SANOL LS-770 manufactured by Sankyosha Co., Ltd. can be utilized as a product including the bis (2,2,6,6-tetramethyl-4-piperidyl) sebacate. Moreover, SANOL LS-1114 manufactured by Sankyosha Co., Ltd. can be utilized as a product including the 8-benzyl-7,7,9,9-tetramethyl-3-octyl 1,3,8-triazaspiro [4,5] undecane-2,4-dione.

[0057]

(Thickness of top coating layer 4)

The thickness of the top coating layer 4 is not particularly limited. If the thickness of the top coating layer 4 is 30 μm or greater, the top coating layer 4 has sufficient strength, so that it is possible to more reliably enhance weather resistance of the resin coated steel 5. In addition, in order to reduce the cost, the thickness of the top coating layer 4 may be 100 μm or smaller. Therefore, it is preferable that the thickness of the top coating layer 4 ranges from 30 to 100 μm .

[0058]

(Essential constituent according to chemical composition of top coating layer 4)

Therefore, the top coating layer 4 according to the present embodiment includes carbon black and an acrylic urethane resin. In addition, in the top coating layer according to the present embodiment, the mass of the carbon black ranges from 0.2% to 5.0% of the mass of the top coating layer 4.

[0059]

(Effect of resin coated steel 5 according to present embodiment)

In the resin coated steel 5 according to the present embodiment, since there

are a number of chemical bonding points (a number of strong bonds) in an interface between the urethane resin layer 3 and the top coating layer 4, water can be prevented from infiltrating into the interface, so that it is possible to maintain adhesion between the urethane resin layer 3 and the top coating layer 4 even under a condition of being exposed to water, such as the ocean. In addition, since the top coating layer 4 protects the urethane resin layer 3 against ultraviolet rays and water, the urethane resin layer 3 can prevent corrosion of the steel 1 over a long period of time. Therefore, there is no need to form the extremely thick urethane resin layer 3. As a result, by means of the resin coated steel 5 according to the present embodiment, it is possible to provide a low-cost structure having high durability under a condition of being exposed to water, such as the ocean.

[0060]

In addition, in a case where steel pipe piles are actually installed, the driving depth generally varies every time a pile is installed. At a position higher than a splash zone, adhesion between resins is easily maintained for a long period of time. However, at a position lower than a tidal zone, adhesion between resins is degraded in a short period of time. In the resin coated steel 5 according to the present embodiment, even at a position lower than the tidal zone, adhesion between the urethane resin layer 3 and the top coating layer 4 can be maintained. Therefore, in the resin coated steel 5 according to the present embodiment, since there is no need to consider an area for applying the resin layer 6 or the top coating layer 4, the resin coated steel 5 according to the present embodiment can be preferably used as a steel pipe pile.

[0061]

Hereinafter, a method of manufacturing a resin coated steel according to

another embodiment of the present invention will be described in detail.

[0062]

(Applying of primer)

First, a primer layer is formed by applying a primer onto a surface of a steel (base material treatment). For example, a urethane resin or an epoxy resin of two-liquid mixed type can be used as the primer. If the viscosity of the primer is lowered, the primer is likely to be adapted to the unevenness of a steel surface. Therefore, it is preferable that the primer is a solvent-type primer having low viscosity. Spray coating may be employed as an applying method. In addition, it is preferable that the primer is applied onto a surface of a steel such that the thickness of the primer layer ranges from 10 to 200 μm . In order to enhance adhesion between the primer layer and a urethane resin layer as much as possible, blast treatment using sand, alumina, grid, or shot may be performed before the primer is applied to a surface of a steel. Scale, contaminants, and the like on a steel surface can be removed through the blast treatment. In addition, the steel disclosed in the embodiment related to the resin coated steel can be used as the steel according to the present embodiment.

[0063]

(Applying of main agent and hardener)

Next, a liquid mixture including a main agent and a hardener is applied onto a surface of the primer layer, and the liquid mixture is hardened, thereby forming a urethane resin layer. For example, a liquid mixture may be prepared by mixing a main agent and a hardener in advance, and the liquid mixture may be applied onto a surface of the primer layer by being sprayed. In addition, it is preferable that the liquid mixture is applied onto a surface of the primer layer such that the thickness of the urethane resin layer ranges from 2 to 5 mm. In this case, the liquid mixture has a

thickness of several millimeters. The liquid mixture is a two-liquid solventless coating material.

[0064]

The liquid mixture according to the present embodiment is a two-liquid polyurethane resin composition including a main agent and a hardener, and urethane polymerization starts by mixing two liquids. The main agent includes an inorganic pigment including carbon black (CB), and polyol. The polyol includes a castor oil derivative (hereinafter, a first polyol) having 2.7 or more hydroxyl groups (functional groups) per molecule, and an organic composition having 2.0 hydroxyl groups per molecule (hereinafter, a second polyol). The first polyol is polyol which can be induced while having castor oil as a raw material. In addition, the mass of the first polyol ranges from 10% to 70% of the mass of the main agent (total mass). The mass of the inorganic pigment excluding carbon black ranges from 10% to 60% of the mass of the main agent. The mass of the carbon black ranges from 0.2% to 5.0% of the main agent. It is preferable that the polyol consists of only the first polyol and the second polyol. The hardener includes at least one selected from the group consisting of diphenylmethane diisocyanate (MDI), toluene diisocyanate (TDI), a diphenylmethane diisocyanate derivative (MDI derivative), and a toluene diisocyanate derivative (TDI derivative).

[0065]

In the present embodiment, the inorganic pigment disclosed in the embodiment related to the resin coated steel can be used as the inorganic pigment. In the present embodiment as well, the mass of the inorganic pigment excluding carbon black ranges from 10% to 60% of the mass of the main agent. If the mass of the inorganic pigment is reduced, viscosity of the main agent can be lowered. Therefore,

applying efficiency can be enhanced. In addition, if the mass of the inorganic pigment is increased, strength of the urethane resin layer can be enhanced. Therefore, the mass of the inorganic pigment excluding carbon black may range from 15% to 50% of the mass of the main agent.

[0066]

In the present embodiment, the first polyol disclosed in the embodiment related to the resin coated steel can be used as the first polyol. In the present embodiment as well, the mass of the first polyol ranges from 10% to 70% of the mass of the main agent. It is particularly preferable that the mass of the first polyol ranges from 30% to 60% of the mass of the main agent. In addition, the upper limit for the number of hydroxyl groups of the first polyol may be 6.0. The number of functional groups (the number of hydroxyl groups) of polyol denotes the number of hydroxyl groups stipulated in JIS K 1557 or ISO 14900 and 15063.

[0067]

In the present embodiment, the second polyol disclosed in the embodiment related to the resin coated steel can be used as the second polyol. In the present embodiment as well, it is preferable that the mass of the second polyol ranges from 10% to 80% of the mass of the main agent and it is more preferable to range from 20% to 60% of the mass of the main agent.

[0068]

In the present embodiment, the isocyanate in the urethane resin layer 3 disclosed in the embodiment related to the resin coated steel can be used as the isocyanate. In the present embodiment as well, it is preferable that the main agent and the hardener (that is, isocyanate) are mixed such that the ratio (-NCO/-OH) of the number of isocyanate groups (-NCO) derived from isocyanate to the number of

hydroxyl groups (-OH) derived from polyol ranges from 0.9 to 1.2. If the amount of the hardener increases, a foaming amount in the liquid mixture increases. Meanwhile, if the amount of the hardener is reduced, there is a possibility that a hardening amount becomes insufficient in a case where isocyanate reacts with moisture in the air. Therefore, in order to further enhance productivity or a yield, the ratio (-NCO/-OH) may range from 1.0 to 1.1.

[0069]

In the present embodiment, other chemical compositions disclosed in the embodiment related to the resin coated steel can be used as other chemical compositions in the main agent. That is, the main agent may include a chemical composition derived from at least one selected from the group consisting of a reaction accelerator, a water absorbent, a thixotropy imparting agent, a flame retardant, and a plasticizer.

[0070]

(Applying of acrylic urethane resin coating material)

Lastly, an acrylic urethane resin coating material including carbon black (CB) is applied onto a surface of the urethane resin layer, and the acrylic urethane resin is hardened, thereby forming a top coating layer. For example, an acrylic urethane resin coating material may be adjusted by mixing solvent-type acrylic polyol (main agent of the acrylic urethane resin coating material) including carbon black and isocyanate (hardener of the acrylic urethane resin coating material) in advance, and the acrylic urethane resin coating material may be applied onto a surface of the urethane resin layer by being sprayed. In addition, it is preferable that the acrylic urethane resin coating material is applied onto a surface of the urethane resin layer such that the thickness of the top coating layer ranges from 30 to 100 μm . In the acrylic urethane

resin coating material, the mass of the carbon black ranges from 0.2% to 5.0% of the mass of the acrylic urethane resin coating material. The smaller the amount of carbon black, the higher the dispersibility of carbon black in the acrylic urethane resin coating material.

[0071]

In addition to carbon black, the acrylic resin coating material includes acrylic polyol and isocyanate. In the present embodiment, the acrylic polyol disclosed in the embodiment related to the resin coated steel can be used as the acrylic polyol. In addition, the isocyanate in the top coating layer 4 disclosed in the embodiment related to the resin coated steel can be used as the isocyanate. In addition, the acrylic resin coating material may include an ultraviolet absorber or a light stabilizer as an optional chemical composition. In the present embodiment, the light stabilizer disclosed in the embodiment related to the resin coated steel can be used as the light stabilizer.

[0072]

In urethane polymerization, since no by-product is generated, the mass of the main agent in the present embodiment is equal to the mass of the main agent of the embodiment related to the resin coated steel. In addition, the mass of the acrylic urethane resin coating material in the present embodiment is equal to the mass of the top coating layer 4 of the embodiment related to the resin coated steel. In both the embodiments described above, it can be considered that the weight of each chemical composition does not change due to urethane polymerization.

[0073]

In the method of manufacturing a resin coated steel according to the present embodiment, it is possible to provide a resin coated steel in which a urethane resin layer can prevent corrosion of a steel over a long period of time even under a condition

of being exposed to water, such as the ocean.

[Examples]

[0074]

1) Production procedure and evaluation method for test sheets

Test sheets No. 1 to 22 were produced through the following procedure and were evaluated.

Grit blasting was performed on a surface of a steel plate (6×100×150 mm), and rust was removed until the derusting degree becomes Sa 2·1/2 or higher. As a commercially available primer having a urethane resin composition, PG331 Urethane Primer manufactured by DKS Co., Ltd. was used for base material treatment. A surface of the steel plate was coated with the urethane primer using a spray, and a primer layer having a thickness of 30 µm was formed on the surface of the steel plate. After three hours therefrom, the surface of the primer layer was coated with a urethane resin coating material using a high-pressure spray coater, and a urethane resin layer having a thickness ranging from 2 to 5 mm was formed. A urethane resin coating material, which was prepared by mixing a main agent and a hardener (hardener/main agent) using a mixer such that the ratio of the number of -NCO to the number of -OH (-NCO/-OH) became 1.1, was supplied to the high-pressure spray coater. On the next day, the urethane resin layer was coated with a top coating material using a cup gun (spray), and a top coating layer having a thickness ranging from 30 to 100 µm was formed. The top coating material was prepared by mixing a main agent and a hardener in advance using an agitator.

[0075]

After an obtained test sheet was cured for one week, the test sheet was cut into pieces having a size of 75×150 mm. The rear surface and the side surfaces of the cut

test sheet was sealed with an epoxy resin. A cut test piece was subjected to a sea water immersion test at 40°C stipulated in ISO 20340, and a combined cycle test for 175 days. In the combined cycle test, a combination (cycle) of a wet weather resistance test using QUV for three days, cooling to -20°C for one day, and salt spraying for three days was repetitively performed. In each of the test pieces before the test (initial adhesion), after the sea water immersion test, and after the combined cycle test, an adhesion force of the top coating layer with respect to the urethane resin layer was evaluated with a pull-off tester manufactured by Elcometer Ltd., by using a dolly (test cylinder) having a diameter of 20 mm. In the evaluation result, a test piece having an adhesion force of 5 MPa or higher was determined to be favorable, and a test piece having an adhesion force lower than 5 MPa was determined to be poor.

[0076]

2) Main agent of urethane resin coating material

In No. 1 to 17, as one of the main agent compositions of the urethane resin layer (urethane resin coating material), castor oil-based polyol (hereinafter, a first polyol) having 2.7 or more hydroxyl groups per molecule was used. In No. 1 to 14, as the first polyol, URIC H-30 (having a hydroxyl value ranging from 155 to 165 mgKOH/g and 2.7 functional groups) manufactured by Itoh Oil Chemicals Co., Ltd. was used. In No. 15 to 17, as the first polyol, URIC H-57 (having a hydroxyl value ranging from 85 to 115 mgKOH/g and three functional groups) manufactured by Itoh Oil Chemicals Co., Ltd. was used. In No. 1 to 17, the mass of the first polyol ranged from 5% to 80% of the mass of the main agent.

[0077]

In addition, in No. 1 to 18, as one of the main agent compositions of the urethane resin layer, polyol having 2.0 hydroxyl groups per molecule (hereinafter, a

second polyol) was used. In No. 1 to 5 and 18, as the second polyol, URIC Y-403 (having a hydroxyl value ranging from 150 to 170 mgKOH/g and two functional groups) which is manufactured by Itoh Oil Chemicals Co., Ltd. and is a representative example of castor oil-based polyol was used. In No. 7 to 11, as the second polyol, 3-methyl-1,5-pentanediol which is a representative example of diol-based polyol was used. In No. 12 to 14, as the second polyol, N,N-bis (2-hydroxypropyl) aniline which is a representative example of aromatic amine-based polyol was used. In No. 15 to 18, as the second polyol, Poly bdTM R-15HT which is manufactured by Idemitsu Kosan Co., Ltd. and is a representative example of polybutadiene-based polyol was used. In No. 1 to 5 and 7 to 18, the mass of the second polyol ranged from 11% to 81% of the mass of the main agent. In No. 18, two kinds of the second polyols were used.

[0078]

Moreover, in No. 1 to 18, as one of the main agent compositions of the urethane resin layer, an inorganic pigment was used. In No. 1 to 11 and 13 to 18, as one of the inorganic pigments (UV resistant color pigment), carbon black (CB) was used. The mass of the carbon black ranged from 0.5% to 5.0% of the mass of the main agent. In No. 1 to 6 and 8 to 18, as one of the inorganic pigments (inorganic extender pigment), clay was used. The mass of the clay ranged from 10% to 60% of the mass of the main agent. In No. 1 to 18, Zeoram A-4 (zeolite) manufactured by Tosoh Corp. was used as a moisture absorbent, hexabromobenzene was used as a flame retardant, and diisononyl phthalate was used as a plasticizer. In addition, as other chemical compositions, a hardening catalyst (dioctyltin dilaurate) and a thixotropy imparting agent (Aerosil #200 manufactured by Nippon Aerosil Co., Ltd.) were used.

The main agent was prepared by mixing the main agent compositions.

[0079]

3) Hardener of urethane resin coating material

In No. 1 to 14 and 18, as polymeric MDI (Cr-MDI) (hardener), Millionate MR-200 manufactured by Tosoh Corporation was used. In addition, in No. 15 to 17, as TDI (hardener), Coronate T-100 manufactured by Tosoh Corporation was used.

[0080]

6) Top coating material

In No. 1 to 6, as the top coating layer (top coating material), NAX MIGHTYLAC G-2 (acrylic urethane (1)) manufactured by Nippon Paint Co., Ltd. was used. In No. 7 to 15 and 18, as the top coating layer, Hardtop XP (acrylic urethane (2)) manufactured by Jotun Group was used. These two kinds of coating materials are general acrylic urethane resin coating materials, in which acrylic polyol (main agent), 1,6-hexamethylene diisocyanate homopolymer (HDI-based isocyanate hardener), a colored coating material, and a light stabilizer were mixed. In No. 1 to 15 and 18, carbon black was used as the colored coating material, and the mass of the carbon black was 0.5% of the top coating material. In addition, in No. 16, as the top coating layer, Hardtop XP (acrylic urethane (3)) manufactured by Jotun Group was used. In No. 16, as the colored coating material, a blue coating material was used. In No. 17, Duflon 100 (fluorine-based coating material) manufactured by Nippon Paint Co., Ltd. was used.

[0081]

7) No. 19 to 22

No. 19 is a simulation test corresponding to the example of the invention (line 2 in Table 1) disclosed in Patent Document 1. No. 20 is a simulation test corresponding to Example 1 disclosed in Patent Document 2. No. 21 is a test in which carbon black is added to an acrylic urethane coating material of Example 1

disclosed in Patent Document 2. No. 22 is a simulation test corresponding to Example disclosed in Patent Document 3.

[0082]

In No. 19 to 22, the following polyol was used as the main agent composition. In No. 19, as polyester polyol, NIPPOLLAN 141 (having a hydroxyl value ranging from 102 to 108 KOHmg/g) manufactured by Tosoh Corp. was used. In No. 20 to 22, as the polybutadiene polyol, Poly bdTM R-45HT manufactured by Idemitsu Kosan Co., Ltd. was used. In No. 20 and 21, as the aromatic amine-based polyol, N,N bis (2-hydroxypropyl) aniline was used.

In addition, in No. 19 to 22, as the hardener, the following MDI was used. In No. 19 and 22, as the MDI, Millionate MT manufactured by Tosoh Corp. was used. In No. 20 and 21, as coarse MDI (Cr-MDI), Millionate MR-100 manufactured by Tosoh Corp. was used.

Moreover, in No. 19 to 22, Zeoram A-4 manufactured by Tosoh Corp. was used as the zeolite, and dioctyl phthalate was used as the plasticizer.

In regard to the top coating material, in No. 19 to 21, as the acrylic urethane coating material (acrylic urethane), Hypon 50 topcoat manufactured by Nippon Paint Co., Ltd. was used. In No. 22, Duflon 100 was used as the fluorine-based coating material (fluorine). As described above, in No. 21, carbon black was added to Hypon 50 topcoat.

[0083]

Tables 1 to 3 show the experimental conditions and the evaluation results of No. 1 to 18. Underlined numbers or letters in the columns of Table 1 and Table 3 indicate that the conditions according to the present invention are not satisfied.

In No. 2 to 5, 8 to 10, and 13 to 15, since the conditions according to the

present invention were satisfied, even if the test sheets were in an aqueous environment, adhesion of the top coating layer with respect to the urethane resin layer was excellent. Therefore, the test sheets had excellent initial adhesion, and the test sheets maintained a sufficient adhesion force even after both the tests in an aqueous environment and a combined environment of ultraviolet rays and water. Meanwhile, in No. 7, the test sheet did not have sufficient initial adhesion. In No. 1, 11, 17, and 18, the test sheets could not maintain a sufficient adhesion force after the immersion test and the combined cycle test. In No. 6, 12, and 16, the test sheets could not maintain a sufficient adhesion force after the combined cycle test. In No. 7, it is assumed that physical properties of the urethane resin have degraded while being cured. In No. 1, 11, 17, and 18, it is assumed that water has infiltrated into the interface between the top coating layer and the urethane resin layer so that the bonds in the interface between the urethane resin layer and the top coating layer are cut. In addition, in No. 6, 12, and 16, it is assumed that ultraviolet rays have been transmitted through the top coating layer so that the interface between the top coating layer and the urethane resin layer has noticeably deteriorated.

[0084]

Tables 4 and 5 show the experimental conditions and the evaluation results of No. 19 to 22. In addition, in No. 19 to 22, since the urethane resin layer did not include the chemical composition based on castor oil-based polyol having 2.7 or more hydroxyl groups per molecule, the test sheets could not maintain a sufficient adhesion force after the immersion test and the combined cycle test. Particularly, in No. 20, since neither a color pigment nor carbon black was added to the top coating layer, the surface of the urethane resin layer significantly deteriorated, and the top coating layer easily peeled from the urethane resin layer.

[0085]

[Table 1]

No.	Urethane resin layer (liquid mixture)							
	Main compositions of main agent							
	Layer thickness (mm)	Castor oil-based derivative		Polyol having two hydroxyl groups		Inorganic pigment		
Number of hydroxyl groups		Mass %	Kind	Mass %	CB mass%	Clay mass%		
1	2	2.7	<u>5</u>	Castor oil-based	76	1.0	10	Comparative Example
2	2	2.7	10	Castor oil-based	71	1.0	10	Example
3	2	2.7	30	Castor oil-based	51	1.0	10	Example
4	2	2.7	50	Castor oil-based	31	1.0	10	Example
5	2	2.7	70	Castor oil-based	11	1.0	10	Example
6	2	2.7	<u>80</u>	-	0	1.0	11	Comparative Example
7	3	2.7	10	Diol-based	81	1.0	<u>0</u>	Comparative Example
8	3	2.7	10	Diol-based	61	1.0	20	Example
9	3	2.7	10	Diol-based	41	1.0	40	Example
10	3	2.7	10	Diol-based	21	1.0	60	Example
11	3	2.7	10	Diol-based	11	1.0	<u>70</u>	Comparative Example
12	4	2.7	40	Aromatic amine-based	20	<u>0.0</u>	30	Comparative Example
13	4	2.7	40	Aromatic amine-based	19.5	0.5	30	Example
14	4	2.7	40	Aromatic amine-based	15	5.0	30	Example
15	5	3.0	40	Polybutadiene-based	19	1.0	30	Example
16	5	3.0	40	Polybutadiene-based	19	1.0	30	Comparative Example
17	5	3.0	40	Polybutadiene-based	19	1.0	30	Comparative Example
18	5	<u>2.0</u>	40	Polybutadiene-based	19	1.0	30	Comparative Example

[0086]

[Table 2]

No.	Urethane resin layer (liquid mixture)					
	Optional compositions of main agent				Hardener	
	Moisture absorbent	Flame retardant	Plasticizer	Others		
	Mass%	Mass%	Mass%	Mass%		
1	1	2	4	1	Cr-MDI	Comparative Example
2	1	2	4	1	Cr-MDI	Example
3	1	2	4	1	Cr-MDI	Example
4	1	2	4	1	Cr-MDI	Example
5	1	2	4	1	Cr-MDI	Example
6	1	2	4	1	Cr-MDI	Comparative Example
7	1	2	4	1	Cr-MDI	Comparative Example
8	1	2	4	1	Cr-MDI	Example
9	1	2	4	1	Cr-MDI	Example
10	1	2	4	1	Cr-MDI	Example
11	1	2	4	1	Cr-MDI	Comparative Example
12	1	2	6	1	Cr-MDI	Comparative Example
13	1	2	6	1	Cr-MDI	Example
14	1	2	6	1	Cr-MDI	Example
15	1	2	6	1	TDI	Example
16	1	2	6	1	TDI	Comparative Example
17	1	2	6	1	TDI	Comparative Example
18	1	2	6	1	Cr-MDI	Comparative Example

[0087]

[Table 3]

No.	Top coating layer (acrylic urethane resin coating material)			Evaluation test			
				Initial adhesion force	ISO 20340		
	Layer thickness (μm)	Kind	Color	Strength (MPa)	Immersion (MPa)	Combined cycle (MPa)	
1	30	Acrylic urethane (1)	Black	14	3	4	Comparative Example
2	30	Acrylic urethane (1)	Black	15	9	7	Example
3	30	Acrylic urethane (1)	Black	15	11	10	Example
4	30	Acrylic urethane (1)	Black	15	13	12	Example
5	30	Acrylic urethane (1)	Black	15	13	11	Example
6	30	Acrylic urethane (1)	Black	16	14	4	Comparative Example
7	30	Acrylic urethane (2)	Black	7	6	3	Comparative Example
8	30	Acrylic urethane (2)	Black	12	8	7	Example
9	30	Acrylic urethane (2)	Black	13	9	8	Example
10	30	Acrylic urethane (2)	Black	14	10	9	Example
11	30	Acrylic urethane (2)	Black	16	4	4	Comparative Example
12	100	Acrylic urethane (2)	Black	18	17	3	Comparative Example
13	100	Acrylic urethane (2)	Black	18	17	15	Example
14	100	Acrylic urethane (2)	Black	18	17	16	Example
15	30	Acrylic urethane (2)	Black	13	15	13	Example
16	30	Acrylic urethane (3)	<u>Blue</u>	13	16	4	Comparative Example
17	30	<u>Fluorine-based Duflon</u>	Black	13	4	2	Comparative Example
18	30	Acrylic urethane (2)	Black	12	4	3	Comparative Example

[0088]

[Table 4]

No.	Urethane resin layer (liquid mixture)								
	Layer thickness (mm)	Main compositions of main agent							
		Polyol 1		Polyol 2		Inorganic pigment (excluding CB)		CB parts by mass	
		Kind	Parts by mass	Kind	Parts by mass	Kind	Parts by mass		
19	2.5	Polyester polyol	100					3	Comparative Example
20	2.5	Polybutadiene polyol	100	Aromatic amine-based polyol	56	Calcium carbonate	50	0	Comparative Example
21	2.5	Polybutadiene polyol	100	Aromatic amine-based polyol	56	Calcium carbonate	50	1	Comparative Example
22	3	Polybutadiene polyol	100			Clay	30	1	Comparative Example

[0089]

[Table 5]

No.	Urethane resin layer (liquid mixture)			Top coating layer (resin coating material)			Evaluation test			
	Optional compositions of main agent		Hardener				Initial adhesion force	ISO 20340		
	Zeolite parts by mass	Plasticizer parts by mass	Kind	Layer thickness (μm)	Coating material		Strength (MPa)	Immersion (MPa)	Combined cycle (MPa)	
					Kind	Color				
19			MDI	50	Acrylic urethane	Blue	12	5	4	Comparative Example
20	3	40	Cr-MDI	30	Acrylic urethane	Colorless	11	4	Has Peeled	Comparative Example
21	3	40	Cr-MDI	30	Acrylic urethane	Black	11	3	1	Comparative Example
22			MDI	40	Fluorine	Blue	10	4	3	Comparative Example

[Industrial Applicability]

[0090]

There is provided a resin coated steel in which a resin coating can protect the steel against corrosion over a long period of time even in a severely corrosive environment such as the ocean, and a manufacturing method therefor.

[Brief Description of the Reference Symbols]

[0091]

- 1 steel
- 2 primer layer
- 3 urethane resin layer
- 4 top coating layer
- 5 resin coated steel
- 6 resin layer

[Document Type] CLAIMS

What is claimed is:

1. A resin coated steel comprising:
 - a steel;
 - a primer layer that is provided on a surface of the steel;
 - a urethane resin layer that is provided on a surface of the primer layer; and
 - a top coating layer that is provided on a surface of the urethane resin layer,wherein the urethane resin layer includes an inorganic pigment including carbon black, and a urethane resin having a urethane bond including constituent atoms of a hydroxyl group of polyol and an isocyanate group of isocyanate,
 - wherein the top coating layer includes carbon black and an acrylic urethane resin,
 - wherein the polyol includes a castor oil derivative having 2.7 or more hydroxyl groups per molecule, and an organic composition having 2.0 hydroxyl groups per molecule,
 - wherein the isocyanate includes at least one selected from the group consisting of diphenylmethane diisocyanate, toluene diisocyanate, a diphenylmethane diisocyanate derivative, and a toluene diisocyanate derivative,
 - wherein in the urethane resin layer, when a mass obtained by subtracting a mass of the isocyanate from a mass of the urethane resin layer is defined as a mass of a main agent, a mass of the carbon black ranges from 0.2% to 5.0% of the mass of the main agent, a mass obtained by subtracting the mass of the carbon black from a mass of the inorganic pigment ranges from 10% to 60% of the mass of the main agent, and a mass of the castor oil derivative ranges from 10% to 70% of the mass of the main agent, and

wherein in the top coating layer, the mass of the carbon black ranges from 0.2% to 5.0% of a mass of the top coating layer.

2. A method of manufacturing a resin coated steel comprising:

forming a primer layer by applying a primer onto a surface of a steel;

forming a urethane resin layer by applying a liquid mixture including a main agent and a hardener onto a surface of the primer layer and hardening the liquid mixture; and

forming a top coating layer by applying an acrylic urethane resin coating material including carbon black onto a surface of the urethane resin layer and hardening the acrylic urethane resin coating material,

wherein the main agent includes an inorganic pigment including carbon black, and polyol,

wherein the hardener includes at least one selected from the group consisting of diphenylmethane diisocyanate, toluene diisocyanate, a diphenylmethane diisocyanate derivative, and a toluene diisocyanate derivative,

wherein the polyol includes a castor oil derivative having 2.7 or more hydroxyl groups per molecule, and an organic composition having 2.0 hydroxyl groups per molecule,

wherein in the main agent, a mass of the carbon black ranges from 0.2% to 5.0% of a mass of the main agent, a mass obtained by subtracting the mass of the carbon black from a mass of the inorganic pigment ranges from 10% to 60% of the mass of the main agent, and a mass of the castor oil derivative ranges from 10% to 70% of the mass of the main agent, and

wherein in the acrylic urethane resin coating material, the mass of the carbon

black ranges from 0.2% to 5.0% of a mass of the acrylic urethane resin coating material.