ZINC-FREE PRIMER, SHIPPING CONTAINER, POWDER PROTECTIVE COATING, AND CONSTRUCTION PROCESS THEREFOR

The present disclosure claims the priority of the Chinese patent application filed with the China National Intellectual Property Administration on August 16, 2023, with the application number CN2023110390474 and the title "Shipping Container, Powder Protective Coating for Shipping Container and Construction Process Thereof", the entire contents of which are incorporated into the present disclosure by reference.

TECHNICAL FIELD

The present disclosure relates to the field of material technology, in particular to a zinc-free primer, a shipping container, a powder protective coating and a construction process thereof.

BACKGROUND

Traditional container protection using water-based paint coating consumes a large amount of organic solvents and generates a large amount of wastewater and waste residue, and the pollution problem has been plaguing the industry.

In the container field, GENUIN has successfully developed powder coatings for containers in 2022. After the official announcement in August 2022, nearly 30,000 TEU containers have been produced, and a group standard has been formed. At present, the protective coating system for cold-rolled steel plates of containers used by the applicant comprises a first layer of zinc-rich primer with a thickness of more than 35 microns, followed by spraying of a base coat and a top coat.

Specifically, when producing containers using metal plates such as cold-rolled steel plates, the surface of the cold-rolled steel plates has a small amount of oil stains due to process reasons when leaving the factory. Therefore, the cold-rolled steel plates must undergo pre-treatment before cold working: first, degrease the surface of the steel plates (acid or alkali

degreasing), then clean, dry (air-dry or hot air), perform shot blasting, and pre-coat with zinc-rich primer. After the pre-treatment is completed, enter cold working (punching, shearing and pressing forming), perform steel structure assembly and welding, and after shot blasting cleaning of the welded seams, perform the entire container coating operation (comprising painting, powder spraying, and the like).

In practical use, although the performance of the containers produced by the above spraying method is superior to that of the containers produced by the previous water-based paint method, the pre-treatment process of cold-rolled steel plates before cold working has the following problems: 1. There is the problem of sewage treatment; 2. The zinc-rich primer is an oil-based paint (non-water-based), which has the problem of VOC emissions. The above two points bring hidden dangers of non-compliance with environmental protection standards. At the same time, the applicant found that for containers with high corrosion resistance requirements for maritime transportation, once corrosion occurs, the corrosion spread is serious.

Therefore, a new coating system and coating process are needed to solve the above problems.

SUMMARY

To alleviate or solve at least one aspect or at least one point of the above problems, the present disclosure is proposed.

The present disclosure provides a powder protective coating for a shipping container, the container comprises an inner surface of the container and an outer surface of the container; at least part of the container is processed from a metal plate. The metal plate forming the inner surface of the container is provided with at least a three-layer coating structure of A1 layer, A2 layer and A3 layer. The material of the A1 layer comprises a high-solid oil paint and a non-metallic conductive material; the A1 layer does not contain metallic zinc; the material of the A2 layer is epoxy powder; the material of the A3 layer is epoxy powder.

And/or, the metal plate forming the outer surface of the container is provided with at least a three-layer coating structure of B1 layer, B2 layer and B3 layer. The material of the B1 layer comprises a high-solid oil paint and a non-metallic conductive material; the B1 layer

does not contain metallic zinc; the material of the B2 layer is epoxy powder; the material of the B3 layer is polyester powder.

Optionally, the A1 layer does not contain zinc; the B1 layer does not contain zinc.

Optionally, the A1 layer is formed by roller coating before the metal plate forms the container, and the A2 layer and the A3 layer are formed by spraying after forming the container body; and/or, the B1 layer is formed by roller coating before the metal plate forms the container, and the B2 and B3 layers are formed by spraying after forming the container body.

Optionally, the thickness of the A1 layer is less than the thickness of the A2 layer and the A3 layer; and/or, the thickness of the B1 layer is less than the thickness of the B2 and B3 layers. Optionally, the thickness of the A1 layer is less than 20 microns, more optionally less than 12 microns.

Optionally, the thickness of the A1 layer is 8-12 microns, the thickness of the A2 layer is 37-43 microns, and the thickness of the A3 layer is 38-43 microns; and/or, the thickness of the B1 layer is 8-12 microns, the thickness of the B2 layer is 37-43 microns, and the thickness of the B3 layer is 44-46 microns.

Optionally, the solid content ratio of the high-solid oil paint in the A1 layer is not less than 60%, and the content of the non-metallic conductive material ranges from 0.5% to 10% by weight of the high-solid oil paint; and/or, the solid content ratio of the high-solid oil paint in the B1 layer is not less than 60%, and the content of the non-metallic conductive material ranges from 0.5% to 10% by weight of the high-solid oil paint.

Optionally, the zinc content in the A1 and B1 layers is zero, and the thickness of the A1 layer and the B1 layer are approximately the same.

Optionally, the non-metallic conductive material in the A1 and B1 layers is graphite, and the content of graphite is approximately 2%.

Optionally, the solid content ratio of the high-solid oil paint in the A1 and B1 layers is 70%, and the content of the non-metallic conductive material is 5% by weight of the high-solid oil paint.

In addition, the present disclosure also provides a construction process of a protective coating for the shipping container, comprising the following steps:

Performing derusting and/or abrasive blasting treatment on the metal sheet;

Performing hot coating application: applying the A1 layer and the B1 layer after heating the coating material or the plate;

Drying or air-drying, wherein the air-drying utilizes hot air;

Processing the metal sheet, followed by welding, to form the container body;

Performing abrasive blasting treatment on welded seams of the entire container;

Spraying the A2 layer and B2 layer; spraying the A3 layer and B3 layer;

Curing and cooling.

Optionally, when air-drying with hot air, the temperature of the thick plate with a thickness of more than 4mm after hot air heating is not lower than 85 °C.

Optionally, before performing hot coating application, it also comprises the process of uniformly mixing the high-solid oil paint and the non-metallic conductive material.

Optionally, after performing derusting and/or abrasive blasting treatment on the metal plate, the surface roughness is between 15-35 microns.

The present disclosure also provides a shipping container, comprising the protective coating described in any one of the foregoing, or adopting the construction process described in the foregoing.

Optionally, the materials forming the A1 layer and the B1 layer each comprise, by mass percentage: 25-30% of modified epoxy resin, 10-15% of anti-rust pigment, 3-5% of cyclohexanone, 8-10% of xylene, 3-6% of n-butanol, 8-20% of curing agent, and 0.5-10% of the non-metallic conductive material, the remainder being color filler.

Optionally, the non-metallic conductive material comprises at least one of graphite, graphene and conductive mica.

Optionally, by mass percentage, the epoxy powder of the A2 layer and the B2 layer each comprises: 25-50% of polyester resin, 22-45% of epoxy resin, 1-10% of phenolic curing agent, 0.1-2.4% of accelerator, 0.5-2% of leveling agent, 0.1-2% of degassing agent, 5-30% of composite filler and 0.2-2% of toughening agent, the remainder being color filler.

Optionally, the acid value of the polyester resin is 34-76 mg KOH/g, and the viscosity is 3000-6000 mPa·s; and/or, the epoxy value of the epoxy resin is 0.090-0.165 eq/100g, and the softening point is 87-105 °C.

Optionally, the epoxy powder of the A3 layer comprises, by mass percentage: 30-60% of polyester resin, 20-36% of epoxy resin, 0.5-1% of leveling agent, 0.1-1% of defoamer, 0.2-2% of antioxidant and 0.5-3% of toughening agent, the remainder being color filler.

Optionally, the acid value of the polyester resin is 34-76 mg KOH/g, and the viscosity is 3000-6000 mPa·s; and/or, the epoxy value of the epoxy resin is 0.090-0.165 eq/100g, and the softening point is 87-105 °C.

Optionally, the polyester powder of the B3 layer comprises, by mass percentage: 30-45% of high weather-resistant polyester resin, 22-35% of ultra-weather-resistant polyester resin, 0-3.5% of triglycidyl isocyanurate, 0-2.5% of hydroxyalkylamide, 14-24% of blocked polyisocyanate, 0.5-1.5% of leveling agent, 0.1-3% of accelerator, 0.1-1% of defoamer, 0.5-3.2% of toughening agent, 0.2-2% of antioxidant and 2-25% of composite filler, the remainder being color filler.

Optionally, the acid value of the high weather-resistant polyester is 29-34 mg KOH/g, and the viscosity is 4500-6000 mPa·s; the hydroxyl value of the ultra-weather-resistant polyester is 100-120 mg KOH/g, and the viscosity is 3200-4200 mPa·s.

The present disclosure also provides a zinc-free primer applied to containers, which comprises, by mass percentage: 25-30% of modified epoxy resin, 10-15% of anti-rust pigment, 3-5% of cyclohexanone, 8-10% of xylene, 3-6% of n-butanol, 8-20% of curing agent, and 0.5-10% of the non-metallic conductive material, the remainder being color filler.

The present disclosure further improves and optimizes the powder coating system and develops a zinc-free pre-treatment primer. A high-solid oil paint is used, and a non-metallic conductive material is used instead of metallic zinc. Through the above settings, compared with the prior art, since no metallic zinc is contained, the corrosion spread phenomenon can be reduced.

Since the first layer uses high-solid oil paint and non-metallic conductive material, and the non-metallic conductive material is used instead of metallic zinc, on the one hand, the conductivity can be guaranteed, which is beneficial to the subsequent spraying. At the same time, the corrosion spread phenomenon can be reduced. At the same time, since the non-metallic conductive material and the high-solid oil paint are mixed more fully, the first layer can be made thinner, and its corrosion resistance is more excellent. Since the A1 layer is

formed before the container is assembled, and subsequent welding and assembly are required to form the container, the weldability must be guaranteed. Adding non-metallic conductive material improves the conductivity of the A1 layer to avoid affecting the welding.

Since it does not contain metallic materials, the adhesion of the powder is better, which is more conducive to subsequent spraying. Through practical verification, the zinc-free pre-treatment primer fully meets the requirements of rust prevention between processes. The adhesion between the zinc-free pre-treatment primer and the powder is better, the corrosion spread is superior to that of water-based paint, and the welding performance is consistent with that of the zinc-rich primer. At the same time, the cost of the zinc-free pre-treatment primer is lower than that of the zinc-rich primer, and the weight is lighter.

In the construction process of the present disclosure, laser derusting is adopted for pre-treatment, which avoids sewage discharge. High-solid oil paint is used, which effectively reduces VOC emissions. Compared with the prior art, its thickness is greatly reduced, saving materials, and its environmental protection effect is good.

The present disclosure breaks the tradition of using zinc-rich primer in the current container field, creatively adopts zinc-free primer, so that the A1 layer and the B1 layer do not contain zinc, and uses non-metallic conductive materials to ensure conductivity. Therefore, when corrosion occurs, there is no generation of zinc salts, thereby avoiding the separation phenomenon between the bottom layer and the substrate caused by volume expansion, thereby reducing the corrosion spread phenomenon and prolonging the service life.

Other characteristics and advantages of the present disclosure will become apparent through the following detailed description, or partly learned through the practice of the present disclosure.

It should be understood that the above general description and the following detailed description are only exemplary and explanatory, and cannot limit the present disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

In order to make the content of the present disclosure easier to understand clearly, the present disclosure will be further described in detail below according to specific

embodiments of the present disclosure and in conjunction with the accompanying drawings, wherein:

The accompanying drawings herein are incorporated into the specification and constitute a part of the specification, show embodiments consistent with the present disclosure, and are used together with the specification to explain the principle of the present disclosure. Obviously, the drawings in the following description are only some embodiments of the present disclosure. For those of ordinary skill in the art, other drawings can also be obtained according to these drawings without creative work.

FIG. 1 is an anti-propagating corrosion performance test sample according to Example 1 of the present disclosure.

FIG. 2 is an anti-propagating corrosion performance test sample according to Example 2 of the present disclosure.

FIG. 3 is an anti-propagating corrosion performance test sample according to Example 2 of the present disclosure.

FIG. 4 is an anti-propagating corrosion performance test sample according to Comparative Example 1.

FIG. 5 is an anti-propagating corrosion performance test sample according to Example 5 of the present disclosure.

FIG. 6 is an anti-propagating corrosion performance test sample according to Example 6 of the present disclosure.

FIG. 7 is an anti-propagating corrosion performance test sample according to Example 7 of the present disclosure.

FIG. 8 is an anti-propagating corrosion performance test sample according to Example 11 of the present disclosure.

FIG. 9 is an anti-propagating corrosion performance test sample according to Example 12 of the present disclosure.

FIG. 10 is an anti-propagating corrosion performance test sample according to Example 13 of the present disclosure.

FIG. 11 is an anti-propagating corrosion performance test sample according to Comparative Example 2.

FIG. 12 is an anti-propagating corrosion performance test sample according to Comparative Example 3.

DETAILED DESCRIPTION

The following description of the embodiments of the present disclosure with reference to the accompanying drawings is intended to explain the overall concept of the present disclosure, and should not be construed as a limitation to the present disclosure. In the present disclosure, the same reference numerals denote the same or similar components.

The features described herein can be implemented in different forms and should not be construed as being limited to the examples described herein. On the contrary, the examples described herein are provided only to show some of the many feasible ways to implement the methods, devices and/or systems described herein, which will be clear after understanding the disclosure of the present disclosure.

Although terms such as "first", "second" and "third" may be used herein to describe various components, components, regions, layers or parts, these components, components, regions, layers or parts should not be limited by these terms. On the contrary, these terms are only used to distinguish one component, component, region, layer or part from another component, component, region, layer or part.

The terms used herein are only for describing various examples and are not intended to limit the disclosure. Unless the context clearly indicates otherwise, the singular form is also intended to comprise the plural form. The terms "comprising", "including" and "having" indicate the presence of the described features, quantities, operations, components, elements and/or their combinations, but do not exclude the presence or addition of one or more other features, quantities, operations, components, elements and/or their combinations.

In order to enable those skilled in the art to use the content of the present disclosure, the following exemplary embodiments may be given in combination with specific present disclosure scenarios, specific system parameters, device and component parameters, and specific connection methods. However, for those skilled in the art, these embodiments are only examples, and the general principles defined herein can be applied to other embodiments and present disclosure scenarios without departing from the spirit and scope of the present

disclosure.

The present disclosure provides a powder protective coating for a shipping container. The container comprises an inner surface of the container and an outer surface of the container. At least part of the container is processed from a metal plate.

The metal plate forming the inner surface of the container is provided with at least a three-layer coating structure of A1 layer, A2 layer and A3 layer: the material of the A1 layer comprises a high-solid oil paint and a non-metallic conductive material; the A1 layer does not contain metallic zinc; the material of the A2 layer is epoxy powder; the material of the A3 layer is epoxy powder.

And/or, the metal plate forming the outer surface of the container is provided with at least a three-layer coating structure of B1 layer, B2 layer and B3 layer: the material of the B1 layer comprises a high-solid oil paint and a non-metallic conductive material; the B1 layer does not contain metallic zinc; the material of the B2 layer is epoxy powder; the material of the B3 layer is polyester powder.

It should be noted that existing container manufacturing enterprises, primer suppliers and powder suppliers are all upstream and downstream supply relationships, and generally the three are different production enterprises. At present, containers in the prior art generally use zinc-rich primer as the bottom coating, and powder suppliers basically do not improve or research the zinc-rich primer for containers. The main function of the primer is to provide temporary protection for the intermediate plates used in container production before the powder coating is applied. The corrosion resistance of the terminal container products basically relies on the intermediate paint and topcoat to achieve corrosion protection. Therefore, when corrosion problems occur in the terminal container products, container manufacturing enterprises generally think that the corrosion is caused by the intermediate paint or topcoat. Therefore, when those skilled in the art are faced with the overall coating scheme formed by the powder coating and the zinc-rich primer of the container, it is difficult to find that the composition of the zinc-rich primer affects the corrosion spread resistance of the powder coating, and only thinks that the powder coating itself has problems.

The applicant of the present disclosure creatively found that after research and analysis, the applicant found that the serious corrosion spread of current shipping containers is due to

the use of zinc-rich primer. When corrosion occurs, a large amount of zinc powder in the zinc-rich primer changes to form zinc salts, and the generation of zinc salts leads to the volume expansion of the primer. However, the single powder coating formed on the box body is extremely dense and cannot accommodate the volume-expanded zinc salts, which leads to the separation of the powder coating from the box body and the phenomenon of "blistering" of the powder coating in pieces. And as the zinc powder continues to corrode, the "blistering" will continue to extend.

Zinc powder reacts with chloride ions in chlorides to form zinc salt zinc chloride, that is, zinc ions are formed.

Zinc ions continue to react in the environment of oxygen, water and carbon dioxide to generate basic zinc carbonate. Basic zinc carbonate is a powdery substance insoluble in water and alcohol.

The specific reaction formulas are as follows:

$Zn + 2Cl^- \rightarrow ZnCl_2$,

$Zn^{2+}+O_2+H_2O+CO_2 \rightarrow ZnCO_3 \cdot Zn(OH)_2$.

At the same time, the applicant found that compared with the zinc-free system, the surface coating of the zinc-rich primer has a risk of quality degradation when combined with the subsequent powder coating. Therefore, the present disclosure provides A1 layer and/or B1 layer without zinc to eliminate the generation of zinc salts, thereby reducing the corrosion spread phenomenon.

The present disclosure provides a zinc-free primer applied to containers. The zinc-free primer is the material forming the A1 layer and the B1 layer.

Specifically, by mass percentage, the zinc-free primer comprises 25-30% of modified epoxy resin, 10-15% of anti-rust pigment, 3-5% of cyclohexanone, 8-10% of xylene, 3-6% of n-butanol, 8-20% of curing agent, and 0.5-10% of the non-metallic conductive material, the remainder being color filler.

The materials forming the A1 layer and the B1 layer each comprise, by mass percentage: 25-30% of modified epoxy resin, 10-15% of anti-rust pigment, 3-5% of cyclohexanone, 8-10% of xylene, 3-6% of n-butanol, 8-20% of curing agent, and 0.5-10% of the non-metallic conductive material, the remainder being color filler.

The modified epoxy resin can be isocyanate modified epoxy resin, silicone acrylic modified epoxy resin, dimer acid modified epoxy resin, acrylic modified epoxy resin, low polymerization degree modified epoxy resin, ZJ-101 epoxy modified acrylic resin produced by Suzhou Shengjia Resin Co., Ltd., and the like.

The curing agent comprises at least one of polyamide 650, modified polyamide, isocyanate trimer and triethylenetetramine.

The anti-rust pigment comprises at least one of aluminum tripolyphosphate, zinc phosphate, zinc oxide, aluminum phosphate, zinc molybdate and aluminum oxide.

The color fillers of the A1 layer and the B1 layer comprise but are not limited to at least one of titanium dioxide, iron red, iron yellow, ultramarine blue, phthalocyanine blue, phthalocyanine green, medium chrome yellow, DPP red, permanent red, permanent violet, barium sulfate, silica fume, wollastonite, mica powder, glass powder, quartz powder, carbon black and titanium dioxide.

The non-metallic conductive material comprises at least one of graphite, graphene or conductive mica.

The epoxy powder of the A2 layer and the B2 layer each comprises, by mass percentage: 25-50% of polyester resin, 22-45% of epoxy resin, 1-10% of phenolic curing agent, 0.1-2.4% of accelerator, 0.5-2% of leveling agent, 0.1-2% of degassing agent, 5-30% of composite filler and 0.2-2% of toughening agent, the remainder being color filler.

The acid value of the polyester resin of the A2 layer and the B2 layer is 34-76 mg KOH/g, and the viscosity is 3000-6000 mPa·s.

The epoxy value of the epoxy resin of the A2 layer and the B2 layer is 0.090-0.165 eq/100g, and the softening point is 87-105 °C.

The phenolic curing agent can be 969H06 type phenolic curing agent produced by Daqing Qing Lu Long green Technology Co., Ltd. or other existing phenolic curing agents.

The accelerator of the A2 layer and the B2 layer comprises at least one of imidazoline, colorless cobalt, methyldiethanolamine, aminophenol, and 2,4,6-tris(dimethylaminomethyl)phenol.

The leveling agent of the A2 layer and the B2 layer comprises at least one of polyacrylic acid, acrylic polymer, polyether polyester modified organosiloxane, acrylic acid, fluorine

modified acrylic acid, phosphate modified acrylic acid, acrylic resin, urea-formaldehyde resin and melamine formaldehyde resin.

The degassing agent of the A2 layer and the B2 layer comprises at least one of benzoin and stearic acid.

The composite filler of the A2 layer and the B2 layer comprises at least one of aluminum oxide, boron nitride, zinc oxide, mica powder and silicon dioxide.

The toughening agent of the A2 layer and the B2 layer comprises at least one of nano-silicon dioxide, methyl methacrylate-butadiene-styrene binary copolymer, dimethyl phthalate, diethyl phthalate, dibutyl phthalate, diethyl phosphate and tributyl phosphate.

The color fillers of the A2 layer and the B2 layer comprise but are not limited to at least one of titanium dioxide, iron red, iron yellow, ultramarine blue, phthalocyanine blue, phthalocyanine green, medium chrome yellow, DPP red, permanent red, permanent violet, barium sulfate, silica fume, wollastonite, mica powder, glass powder, quartz powder, carbon black and titanium dioxide.

The epoxy powder of the A3 layer comprises, by mass percentage: t30-60% of polyester resin, 20-36% of epoxy resin, 0.5-1% of leveling agent, 0.1-1% of defoamer, 0.2-2% of antioxidant and 0.5-3% of toughening agent, the remainder being color filler.

The acid value of the polyester resin of the A3 layer is 34-76 mg KOH/g, and the viscosity is 3000-6000 mPa·s.

The epoxy value of the epoxy resin of the A3 layer is 0.090-0.165 eq/100g, and the softening point is 87-105 °C.

The leveling agent of the A3 layer comprises at least one of polyacrylic acid, acrylic polymer, polyether polyester modified organosiloxane, acrylic acid, fluorine modified acrylic acid, phosphate modified acrylic acid, acrylic resin, urea-formaldehyde resin and melamine formaldehyde resin.

The defoamer of the A3 layer comprises at least one of TEGO Foamex 825, TEGO Foamex 810, BYK-028, BYK-024, TEGO-902W, defoamer NXZ, BYK-022 defoamer from BYK-Chemie GmbH, polydimethylsiloxane defoamer, AKN-3324, benzoin, BYK-066N and BYK085.

The antioxidant of the A3 layer comprises at least one of B215 composite antioxidant,

n-octadecyl β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, 2,6-di-tert-butyl-4-methylphenol, bis(3,5-di-tert-butyl-4-hydroxyphenyl)sulfide and BASF antioxidant 1010.

The toughening agent of the A3 layer comprises at least one of nano-silicon dioxide, methyl methacrylate-butadiene-styrene ternary copolymer, dimethyl phthalate, diethyl phthalate, dibutyl phthalate, diethyl phosphate and dibutyl phosphate.

The color fillers of the A3 layer comprise but are not limited to at least one of titanium dioxide, iron red, iron yellow, ultramarine blue, phthalocyanine blue, phthalocyanine green, medium chrome yellow, DPP red, permanent red, permanent violet, barium sulfate, silica fume, wollastonite, mica powder, glass powder, quartz powder, carbon black and titanium dioxide.

The polyester powder of the B3 layer comprises, by mass percentage: 30-45% of high weather-resistant polyester resin, 22-35% of ultra-weather-resistant polyester resin, 0-3.5% of triglycidyl isocyanurate, 0-2.5% of hydroxyalkylamide, 14-24% of blocked polyisocyanate, 0.5-1.5% of leveling agent, 0.1-3% of accelerator, 0.1-1% of defoamer, 0.5-3.2% of toughening agent, 0.2-2% of antioxidant and 2-25% of composite filler, the remainder being color filler.

The acid value of the high weather-resistant polyester is 29-34 mg KOH/g, and the viscosity is 4500-6000 mPa·s.

The hydroxyl value of the ultra-weather-resistant polyester is 100-120 mg KOH/g, and the viscosity is 3200-4200 mPa·s.

Triglycidyl isocyanurate is abbreviated as TGIC.

Hydroxyalkylamide is abbreviated as HAA.

The blocked polyisocyanate can be any one or more of EVONIK's grades B1400, BF1540 and BF1320.

The leveling agent of the B3 layer comprises at least one of polyacrylic acid, acrylic polymer, polyether polyester modified organosiloxane, acrylic acid, fluorine modified acrylic acid, phosphate modified acrylic acid, acrylic resin, urea-formaldehyde resin and melamine formaldehyde resin.

The accelerator of the B3 layer comprises at least one of imidazoline, colorless cobalt,

methyldiethanolamine, aminophenol, and 2,4,6-tris(dimethylaminomethyl)phenol.

The defoamer of the B3 layer comprises at least one of TEGO Foamex 825, TEGO Foamex 810, BYK-028, BYK-024, TEGO-902W, defoamer NXZ, BYK-022 defoamer from BYK-Chemie GmbH, polydimethylsiloxane defoamer, AKN-3324, benzoin, BYK-066N and BYK085.

The toughening agent of the B3 layer comprises at least one of nano-silicon dioxide, methyl methacrylate-butadiene-styrene ternary copolymer, dimethyl phthalate, diethyl phthalate, dibutyl phthalate, diethyl phosphate and dibutyl phosphate.

The antioxidant of the B3 layer comprises at least one of B215 composite antioxidant, n-octadecyl β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, 2,6-di-tert-butyl-4-methylphenol, bis(3,5-di-tert-butyl-4-hydroxyphenyl)sulfide and BASF antioxidant 110.

The composite filler of the B3 layer comprises at least one of aluminum oxide, boron nitride, zinc oxide, mica powder and silicon dioxide.

The color filler of the B3 layer is inorganic pigment and filler, comprising but not limited to at least one of titanium dioxide, iron red, iron yellow, ultramarine blue, phthalocyanine blue, phthalocyanine green, medium chrome yellow, DPP red, permanent red, permanent violet, barium sulfate, silica fume, wollastonite, mica powder, glass powder, quartz powder, carbon black and titanium dioxide.

In the entire protective coating, the epoxy group of the A1 layer can react with the polyester carboxyl group in the A2 layer to realize the connection between A1 and A2 layers through chemical bonding, and the carboxyl group of the polyester resin in the A2 layer can react with the epoxy group in the A3 layer to realize the connection between A2 and A3 layers through chemical bonding.

The epoxy group in the B1 layer can react with the polyester carboxyl group in the B2 layer to realize the connection between B1 and B2 layers through chemical bonding, and the carboxyl group of the polyester resin in the B2 layer can react with the curing agent of the B3 layer to realize the connection between B2 and B3 layers through chemical bonding.

Therefore, the interlayer bonding force of the entire protective coating is strong. In the adhesion pull-off test, the breaking strength reaches more than 10MPa, and the entire

protective coating partially falls off from the substrate without interlayer blistering.

After the A1 layer and the B1 layer are formed on the substrate, they protect the substrate through physical isolation and can meet the requirement of temporary protection for the substrate. The interior of the container product is corrosion-resistant through the A2 layer and A3 layer, and the exterior of the container is corrosion-resistant through the B2 layer and B3 layer.

The A1 layer is formed by coating before the metal plate forms the container. the A2 layer and the A3 layer are formed by spraying after forming the container body.

And/or, the B1 layer is formed by coating before the metal plate forms the container. The B2 and B3 layers are formed by spraying after forming the container body.

The thickness of the A1 layer is less than the thickness of the A2 layer and the A3 layer.

Preferably, the thickness of the A1 layer is 8-12 microns. When the thickness is less than 8 microns, the corrosion spread performance is poor. When the thickness is greater than 12 microns, the cost increases. The thickness of the A2 layer is 37-43 microns, and the thickness of the A3 layer is 38-43 microns. When the thickness of the A2 layer is less than 37 microns, the corrosion resistance is poor. When the thickness of the A2 layer is greater than 43 microns, the cost increases. When the thickness of the A3 layer is less than 38 microns, the corrosion resistance is poor. When the thickness of the A3 layer is greater than 43 microns, the cost increases.

And/or, the thickness of the B1 layer is less than the thickness of the B2 and B3 layers.

Preferably, the thickness of the B1 layer is 8-12 microns, the thickness of the B2 layer is 37-43 microns, and the thickness of the B3 layer is 44-46 microns.

The solid content ratio of the high-solid oil paint in the A1 layer is not less than 60%, and the content of the non-metallic conductive material ranges from 0.5% to 10% by weight of the high-solid oil paint.

And/or, the solid content ratio of the high-solid oil paint in the B1 layer is not less than 60%, and the content of the non-metallic conductive material ranges from 0.5% to 10% by weight of the high-solid oil paint.

The non-metallic conductive material in the A1 and B1 layers is graphite, and the content of graphite is approximately 2%.

The solid content ratio of the high-solid oil paint in the A1 and B1 layers is 70%, and the content of the non-metallic conductive material is 5% by weight of the high-solid oil paint.

The present disclosure also provides a construction method of a protective coating for engineering equipment, comprising the following steps:

S1. Performing laser derusting and/or abrasive blasting on the metal plate.

S2. Performing hot coating application: applying the A1 layer and the B1 layer after heating the coating material or the plate.

Specifically, when the thickness of the metal plate is greater than 4mm, heat the metal plate to ≥85 °C.

When the thickness of the metal plate is less than 4mm, it is usually heated to 85 °C.

The temperature for heating the coating is 40 °C.

S3. Drying or air-drying, wherein the air-drying adopts hot air.

S4. Processing the metal sheet, followed by welding, to form the container body..

S5. Performing abrasive blasting on the welded seams of the entire box.

S6. Spraying the A2 layer and B2 layer; spraying the A3 layer and B3 layer.

S7. Curing and cooling.

The present disclosure also provides a shipping container, comprising the above-mentioned protective coating; or adopting the above-mentioned construction process.

The above protective coatings are introduced through various examples below.

Example 1

Step 1: Perform derusting on the metal sheet, followed by fine abrasive blasting treatment to achieve a surface roughness between 15–35 micrometers. The derusting process employs laser derusting, which avoids pollution compared to conventional methods.

Step 2: Roller coating: Apply a first layer of high-solid solvent-based paint to the metal sheet with a thickness of 10 micrometers. The high-solid solvent-based paint has a solid content ratio of not less than 60%, mixed with 2% graphite to ensure uniformity. Hot roller coating may be used, with a temperature maintained at or above 40 °C.

Step 3: Air-dry the coated metal sheet.

Step 4: Process the dried metal sheet to form the container body.

Step 5: Remove the oxide layer from welded seams of the entire container.

Step 6: Two-layer powder spraying: First apply the primer powder, followed by the topcoat powder. The inner base powder of the box is 40 microns, which is epoxy powder; the outer base powder of the box is 40 microns, which is epoxy powder; the outer top powder of the box is 45 microns, which is polyester powder; the inner top powder of the box is 40 microns, which is epoxy powder.

Step 7: Cure and cool.

The metal plate of the container of the present disclosure can be cold-rolled steel plate or hot-rolled steel plate. The protective coating system includes three layers. The first layer, the base coat, is about 10 microns thick. The base coat thickness reduces the high-solid oil paint; compared with the existing base coat of 35 microns, it greatly reduces the usage of oil-based paint and can significantly reduce VOC emissions.

Optionally, the solid content ratio of the high-solid oil paint of the present disclosure is not less than 60%. The present disclosure adopts a solid content ratio of not less than 60%, which can greatly reduce VOC emissions compared with the existing solid content ratio of about 40%.

The zinc content of the present disclosure is zero: non-metallic conductive material is used to replace the original zinc. On the one hand, the conductivity of non-metallic is used, and on the other hand, the non-metallic conductive material itself has less pollution. The non-metallic conductive material can be graphite, and the like. For example, graphite is used to replace the original zinc material. On the one hand, the conductivity can be guaranteed, and on the other hand, the corrosion resistance can be improved. Optionally, the proportion of the non-metallic conductive material of the present disclosure is between 0.5% and 10%, and the surface resistance of the base coat is 102 ohms to 109 ohms. In this example, the solid content ratio is 70%, and the proportion of the non-metallic conductive material is 5%.

The second layer, about 40 microns thick, is epoxy powder. Materials that meet FDA requirements are used. Since the thickness of the first layer is significantly smaller than that of the existing first layer, in order to ensure the quality after coating, the present disclosure appropriately increases the thickness of the second layer to 40 microns.

The third layer, the outer thickness of the box is about 45 microns, which is polyester powder; the inner thickness of the box is about 40 microns, which is epoxy powder; it meets

FDA requirements: the present disclosure appropriately increases the spraying thickness of the outer box, thereby further ensuring the corrosion resistance effect after coating.

The powder coating of the present disclosure not only has excellent environmental performance, but also has comprehensive advantages in process stability and coating quality compared with traditional coating processes.

Example 2

Example 2 has the same steps as Example 1, except that the thickness of the first layer coating is 10 microns, the thickness of the second layer is 43 microns, and the thickness of the third layer is 43 microns for the inner box and 46 microns for the outer box.

Example 3

Example 3 has the same steps as Example 1, except that the thickness of the first layer coating is 12 microns, the thickness of the second layer is 41 microns, and the thickness of the third layer is 41 microns for the inner box and 44 microns for the outer box.

Example 4

The protective coating in this example is an A1 layer of 8 microns, an A2 layer of 37 microns and an A3 layer of 38 microns.

The material of the A1 layer includes, by mass percentage: 25% of of isocyanate modified epoxy resin, 15% of aluminum tripolyphosphate as an anti-rust pigment, 5% of cyclohexanone, 10% of xylene, 6% of n-butanol, 8% of modified polyamide as a curing agent, 10% of graphite as a non-metallic conductive material, and 21% of titanium dioxide as a color filler.

The epoxy powder of the A2 layer includes, by mass percentage: 50% of polyester resin (acid value: 34 mg KOH/g, viscosity: 3000 mPa•s), 26% of epoxy resin (epoxy value: 0.165 eq/100g, softening point: 87 °C), 2% of phenolic curing agent (969H06 type phenolic curing agent produced by Daqing Qing Lu Long green Technology Co., Ltd.), 0.1% of methyldiethanolamine as an accelerator, 0.5% of polyacrylic acid as a leveling agent, 0.1% of benzoin as a degassing agent, 5% of silicon dioxide as a composite filler, 0.2% of nano-silicon dioxide as a toughening agent, and 16.1% of iron red as a color filler.

The epoxy powder of the A3 layer includes, by mass percentage: 60% of polyester resin (acid value: 34 mg KOH/g, viscosity: 3000 mPa•s), 20% of epoxy resin (epoxy value: 0.165

eq/100g, softening point: 87 °C), 1% of polyacrylic acid as a leveling agent, 0.1% of TEGO Foamex 825 as a defoamer, 0.2% of antioxidant B215 as a composite antioxidant, 0.5% of nano-silicon dioxide as a toughening agent, and 18.2% of phthalocyanine blue as a color filler.

Example 5

The protective coating in this example is an A1 layer of 12 microns, an A2 layer of 43 microns and an A3 layer of 43 microns.

The material of the A1 layer includes, by mass percentage: 30% of organic acrylic modified epoxy resin, 10% of zinc phosphate as an anti-rust pigment, 3% of cyclohexanone, 8% of xylene, 3% of n-butanol, 20% of polyamide 650 as a curing agent, 0.5% of graphene as a non-metallic conductive material, and 25.5% of iron red as color filler.

The epoxy powder of the A2 layer includes, by mass percentage: 25% of polyester resin (acid value: 34 mg KOH/g, viscosity: 6000 mPa•s), 45% of epoxy resin (epoxy value: 0.160 eq/100g, softening point: 95 °C), 10% of phenolic curing agent (969H06 type phenolic curing agent produced by Daqing Qing Lu Long green Technology Co., Ltd.), 2.4% of aminophenol as an accelerator, 2% of acrylic polymer as a leveling agent, 2% of degassing agent stearic acid, 5% of composite filler boron nitride, 2% of toughening agent methyl methacrylate-butadiene-styrene ternary copolymer, and 6.6% of phthalocyanine blue as a color filler.

The epoxy powder of the A3 layer includes, by mass percentage: 30% of polyester resin (acid value: 76 mg KOH/g, viscosity: 6000 mPa•s), 36% of epoxy resin (epoxy value: 0.090 eq/100g, softening point: 105 °C), 1% of acrylic polymer as a leveling agent, 1% of defoamer BYK-028, 2% of n-octadecyl β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate as an antioxidant, 3% of dimethyl phthalate as a toughening agent, and 27% of ultramarine blue as a color filler.

Example 6

The protective coating in this example is an A1 layer of 10 microns, an A2 layer of 40 microns and an A3 layer of 40 microns.

The material of the A1 layer includes, by mass percentage: 28% of dimer acid modified epoxy resin, 12% of zinc oxide as an anti-rust pigment, 4% of cyclohexanone, 9% of xylene,

5% of n-butanol, 15% of isocyanate trimer as a curing agent, 5% of conductive mica as a non-metallic conductive material, and 22% of permanent violet as a color filler.

The epoxy powder of the A2 layer includes, by mass percentage: 30% of polyester resin (acid value: 54 mg KOH/g, viscosity: 4500 mPa•s), 40% of epoxy resin (epoxy value: 0.12 eq/100g, softening point: 105 °C), 5% of phenolic curing agent (969H06 type phenolic curing agent produced by Daqing Qing Lu Long green Technology Co., Ltd.), 1% of 2,4,6-tris(dimethylaminomethyl)phenol as an accelerator, 1% of fluorine modified acrylic acid as a leveling agent, 0.5% of benzoin as a degassing agent, 0.5% of stearic acid as a degassing agent, 15% of aluminum oxide as a composite filler, 1% of diethyl phthalate as a toughening agent, and 6% of phthalocyanine blue as a color filler.

The epoxy powder of the A3 layer includes, by mass percentage: 45% of polyester resin (acid value: 54 mg KOH/g, viscosity: 4500 mPa•s), 30% of epoxy resin (epoxy value: 0.110 eq/100g, softening point: 100 °C), 0.5% of phosphate modified acrylic acid as a leveling agent, 0.5% of defoamer BYK-024, 1% of 2,6-di-tert-butyl-4-methylphenol as an antioxidant, 2% of dibutyl phthalate as a toughening agent, and 21% of mica powder and ultramarine blue as a color filler.

Example 7

The difference between this example and Example 6 is the thickness of each layer. The A1 layer is 11 microns, the A2 layer is 41 microns, and the A3 layer is 41 microns.

Example 8

The protective coating in this example is an A1 layer of 9 microns, an A2 layer of 38 microns and an A3 layer of 39 microns.

The material of the A1 layer includes, by mass percentage: 28% of acrylic modified epoxy resin, 10% of anti-rust pigment zinc molybdate, 3% of cyclohexanone, 8% of xylene, 3% of n-butanol, 20% of triethylenetetramine as a curing agent, 2.5% of graphene as a non-metallic conductive material, and 25.5% of iron yellow as a color filler.

The epoxy powder of the A2 layer includes, by mass percentage: 25% of polyester resin (acid value: 76 mg KOH/g, viscosity: 6000 mPa•s), 45% of epoxy resin (epoxy value: 0.090 eq/100g, softening point: 105 °C), 3% of phenolic curing agent (969H06 type phenolic curing agent produced by Daqing Qing Lu Long green Technology Co., Ltd.), 2.4% of imidazoline

as an accelerator, 2% of acrylic polymer as a leveling agent, 2% of stearic acid as a degassing agent, 5% of silicon dioxide as a composite filler, 2% of methyl methacrylate-butadiene-styrene ternary copolymer as a toughening agent, and 13.6% of phthalocyanine green as a color filler.

The epoxy powder of the A3 layer includes, by mass percentage: 45% of polyester resin (acid value: 54 mg KOH/g, viscosity: 4500 mPa•s), 30% of epoxy resin (epoxy value: 0.110 eq/100g, softening point: 100 °C), 0.5% of phosphate modified acrylic acid as a leveling agent, 0.5% of defoamer BYK-022, 1% of 2,6-di-tert-butyl-4-methylphenol as an antioxidant, 2% of tributyl phosphate as a toughening agent, and 21% of mica powder and ultramarine blue as a color filler.

Example 9

The protective coating in this example is an A1 layer of 11 microns, an A2 layer of 41 microns and an A3 layer of 41 microns.

The material of the A1 layer includes, by mass percentage: 25% of low polymerization degree modified epoxy resin, 15% of aluminum oxide as an anti-rust pigment, 5% of cyclohexanone, 10% of xylene, 6% of n-butanol, 4% of isocyanate trimer as a curing agent, 4% of polyamide 650 as a curing agent, 10% of graphene as a non-metallic conductive material, and 21% of silica fume as a color filler.

The epoxy powder of the A2 layer includes, by mass percentage: 25% of polyester resin (acid value: 76 mg KOH/g, viscosity: 3000 mPa•s), 22% of epoxy resin (epoxy value: 0.165 eq/100g, softening point: 87 °C), 1% of phenolic curing agent (969H06 type phenolic curing agent produced by Daqing Qing Lu Long green Technology Co., Ltd.), 0.1% of colorless cobalt as an accelerator, 0.5% of polyacrylic acid as a leveling agent, 0.1% of benzoin as a degassing agent, 30% of boron nitride as a composite filler, 0.2% of nano-silicon dioxide as a toughening agent, and 21.1% of iron red as a color filler.

The epoxy powder of the A3 layer includes, by mass percentage: 39% of polyester resin (acid value: 60 mg KOH/g, viscosity: 5000 mPa•s), 35% of epoxy resin (epoxy value: 0.120 eq/100g, softening point: 100 °C), 0.5% of phosphate modified acrylic acid as a leveling agent, 0.5% of defoamer TEGO-902W, 1% of 2,6-di-tert-butyl-4-methylphenol as an antioxidant, 2% of dibutyl phthalate as a toughening agent, and 23% of mica powder and

ultramarine blue as a color filler.

Example 10

The protective coating in this example is a B1 layer of 8 microns, a B2 layer of 37 microns and a B3 layer of 44 microns.

The material of the B1 layer includes, by mass percentage: 25% of isocyanate modified epoxy resin, 15% of aluminum tripolyphosphate as a anti-rust pigment, 5% of cyclohexanone, 10% of xylene, 6% of n-butanol, 8% of modified polyamide as a curing agent, 10% of graphite as a non-metallic conductive material, and 21% of titanium dioxide as a color filler.

The epoxy powder of the B2 layer includes, by mass percentage: 50% of polyester resin (acid value: 34 mg KOH/g, viscosity: 3000 mPa•s), 26% of epoxy resin (epoxy value: 0.165 eq/100g, softening point: 87 °C), 2% of phenolic curing agent (969H06 type phenolic curing agent produced by Daqing Qing Lu Long green Technology Co., Ltd.), 0.1% of methyldiethanolamine as an accelerator, 0.5% of polyacrylic acid as a leveling agent, 0.1% of benzoin as a degassing agent, 5% of silicon dioxide as a composite filler, 0.2% of nano-silicon dioxide as a toughening agent, and 16.1% of iron red as a color filler.

The polyester powder of the B3 layer includes 30% of high weather-resistant polyester resin (acid value: 32 mg KOH/g, viscosity: 5000 mPa•s), 35% of ultra-weather-resistant polyester resin (hydroxyl value: 100 mg KOH/g, viscosity: 3200 mPa•s), 2.3% of curing agent TGIC, 24% of curing agent B1400, 0.5% of polyether polyester modified organosiloxane as a leveling agent, 0.1% of methyldiethanolamine as an accelerator, 0.1% of defoamer BYK-022 from BYK-Chemie GmbH, 0.5% of dimethyl phthalate as a toughening agent, 0.2% of 2,6-di-tert-butyl-4-methylphenol as an antioxidant, 5% of boron nitride as a composite filler, and 2.3% of phthalocyanine blue as a color filler.

Example 11

The protective coating in this example is a B1 layer of 12 microns, a B2 layer of 43 microns and a B3 layer of 45 microns.

The material of the B1 layer includes, by mass percentage: 30% of silicone acrylic modified epoxy resin, 10% of zinc phosphate as an anti-rust pigment, 3% of cyclohexanone, 8% of xylene, 3% of n-butanol, 20% of polyamide 650 as a curing agent, 0.5% of graphene as a non-metallic conductive material, and 25.5% of iron red as a color filler.

The epoxy powder of the B2 layer includes, by mass percentage: 25% of polyester resin (acid value: 34 mg KOH/g, viscosity: 6000 mPa•s), 45% of epoxy resin (epoxy value: 0.160 eq/100g, softening point: 95 °C), 10% of phenolic curing agent (969H06 type phenolic curing agent produced by Daqing Qing Lu Long green Technology Co., Ltd.), 2.4% of aminophenol as an accelerator, 2% of acrylic polymer as a leveling agent, 2% of stearic acid as a degassing agent, 5% of boron nitride as a composite filler, 2% of methyl methacrylate-butadiene-styrene ternary copolymer as a toughening agent, and 6.6% of phthalocyanine blue as a color filler.

The polyester powder of the B3 layer includes 30% of high weather-resistant polyester resin (acid value: 32 mg KOH/g, viscosity: 5000 mPa•s), 35% of ultra-weather-resistant polyester resin (hydroxyl value: 110 mg KOH/g, viscosity: 3800 mPa•s), 2.3% of curing agent TGIC, 24% of curing agent B1540, 0.5% of polyether polyester modified organosiloxane as a leveling agent, 0.1% of methyldiethanolamine as an accelerator, 0.1% of defoamer BYK-022 from BYK-Chemie GmbH, 0.5% of dimethyl phthalate as a toughening agent, 0.2% of 2,6-di-tert-butyl-4-methylphenol as an antioxidant, 3% of silicon dioxide as a composite filler, and 4.3% of phthalocyanine blue as a color filler.

Example 12

The protective coating in this example is a B1 layer of 12 microns, a B2 layer of 43 microns and a B3 layer of 46 microns.

The material of the B1 layer includes, by mass percentage: 30% of silicone acrylic modified epoxy resin, 10% of anti-rust pigment aluminum tripolyphosphate, 3% of cyclohexanone, 8% of xylene, 3% of n-butanol, 20% of polyamide 650 as a curing agent, 0.5% of graphene as a non-metallic conductive material, and 25.5% of iron red as a color filler.

The epoxy powder of the B2 layer includes, by mass percentage: 25% of polyester resin (acid value: 76 mg KOH/g, viscosity: 6000 mPa•s), 45% of epoxy resin (epoxy value: 0.090 eq/100g, softening point: 105 °C), 3% of phenolic curing agent (969H06 type phenolic curing agent produced by Daqing Qing Lu Long green Technology Co., Ltd.), 2.4% of imidazoline as an accelerator, 2% of acrylic polymer as a leveling agent, 2% of stearic acid as a degassing agent, 5% of silicon dioxide as a composite filler, 2% of methyl methacrylate-butadiene-styrene ternary copolymer as a toughening agent, and 13.6% of

phthalocyanine green as a color filler.

The polyester powder of the B3 layer includes 45% of high weather-resistant polyester resin (acid value: 29 mg KOH/g, viscosity: 4500 mPa•s), 22% of ultra-weather-resistant polyester resin (hydroxyl value: 120 mg KOH/g, viscosity: 4200 mPa•s), 2.7% of curing agent TGIC, 0.5% of curing agent HAA, 14% of curing agent B1320, 1.5% of polyether polyester modified organosiloxane as a leveling agent, 0.1% of methyldiethanolamine as an accelerator, 0.1% of defoamer TEGO-902W, 0.5% of tributyl phosphate as a toughening agent, 0.2% of antioxidant 1010 from BASF, 11% of boron nitride as a composite filler, and 2.9% of phthalocyanine blue as a color filler.

Example 13

The protective coating in this example is a B1 layer of 10 microns, a B2 layer of 40 microns and a B3 layer of 45 microns.

The material of the B1 layer includes, by mass percentage: 28% of dimer acid modified epoxy resin, 12% of zinc oxide as an anti-rust pigment, 4% of cyclohexanone, 9% of xylene, 5% of n-butanol, 15% of isocyanate trimer as a curing agent, 5% of conductive mica as a non-metallic conductive material, and 22% of permanent violet as a color filler.

The epoxy powder of the B2 layer includes, by mass percentage: 30% of polyester resin (acid value: 70 mg KOH/g, viscosity: 4500 mPa•s), 40% of epoxy resin (epoxy value: 0.120 eq/100g, softening point: 102 °C), 3% of phenolic curing agent (969H06 type phenolic curing agent produced by Daqing Qing Lu Long green Technology Co., Ltd.), 1% of 2,4,6-tris(dimethylaminomethyl)phenol as an accelerator, 1% of fluorine modified acrylic acid as a leveling agent, 0.5% of benzoin as a degassing agent, 0.5% of stearic acid as a degassing agent, 15% of aluminum oxide as a composite filler, 1% of diethyl phthalate as a toughening agent, and 6% of phthalocyanine blue as a color filler.

The polyester powder of the B3 layer includes 38% of high weather-resistant polyester resin (acid value: 34 mg KOH/g, viscosity: 6000 mPa•s), 25% of ultra-weather-resistant polyester resin (hydroxyl value: 111 mg KOH/g, viscosity: 3600 mPa•s), 2.5% of curing agent HAA, 15% of curing agent B1400, 0.5% of polyether polyester modified organosiloxane as a leveling agent, 3% of accelerator, 1% of polydimethylsiloxane as a defoamer, 3.2% of triethyl phosphate as a toughening agent, 2% of

bis(3,5-di-tert-butyl-4-hydroxyphenyl)sulfide as an antioxidant, 6% of mica powder as a composite filler, and 4.3% of phthalocyanine blue as a color filler.

Example 14

The difference between this example and Example 13 is the thickness of each layer. The B1 layer is 11 microns, the B2 layer is 41 microns, and the B3 layer is 41 microns.

Example 15

The protective coating in this example is a B1 layer of 8 microns, a B2 layer of 37 microns and a B3 layer of 44 microns.

The material of the B1 layer includes, by mass percentage: 25% of low polymerization degree modified epoxy resin, 15% of aluminum oxide as an anti-rust pigment, 5% of cyclohexanone, 10% of xylene, 6% of n-butanol, 4% of isocyanate trimer as a curing agent, 4% of polyamide 650 as a curing agent, 10% of graphene as a non-metallic conductive material, and 21% of silica fume as a color filler.

The epoxy powder of the B2 layer includes, by mass percentage: 25% of polyester resin (acid value: 38 mg KOH/g, viscosity: 3000 mPa•s), 22% of epoxy resin (epoxy value: 0.165 eq/100g, softening point: 87 °C), 1% of phenolic curing agent (969H06 type phenolic curing agent produced by Daqing Qing Lu Long green Technology Co., Ltd.), 0.1% of methyldiethanolamine as an accelerator, 0.5% of polyacrylic acid as a leveling agent, 0.1% of benzoin as a degassing agent, 30% of boron nitride as a composite filler, 0.2% of nano-silicon dioxide as a toughening agent, and 21.1% of iron red as a color filler.

The polyester powder of the B3 layer includes 30% of high weather-resistant polyester resin (acid value: 32 mg KOH/g, viscosity: 5000 mPa•s), 22% of ultra-weather-resistant polyester resin (hydroxyl value: 100 mg KOH/g, viscosity: 3200 mPa•s), 3.5% of curing agent TGIC, 14% of curing agent B1400, 0.5% of polyether polyester modified organosiloxane as a leveling agent, 0.1% of methyldiethanolamine as an accelerator, 0.1% of defoamer BYK-022 from BYK-Chemie GmbH, 0.5% of dimethyl phthalate as a toughening agent, 0.2% of 2,6-di-tert-butyl-4-methylphenol as an antioxidant, 25% of boron nitrideas a composite filler, and 4.1% of phthalocyanine blue as a color filler.

Comparative Example 1

First, degrease the surface of the metal plate, clean, dry, perform shot blasting, and pre-coat with 35 microns of zinc-rich primer. After the pre-treatment is completed, enter cold working (punching, shearing and pressing forming), perform steel structure assembly and welding, and after shot blasting cleaning of the welded seams, perform the entire container coating operation; spray 35 microns of intermediate paint as the second layer, and spray 40 microns of topcoat as the third layer.

Comparative Example 2

The protective coating is a B1 layer of 10 microns, a B2 layer of 40 microns and a B3 layer of 40 microns.

The B1 layer is oil-based epoxy zinc-rich primer (DWB ZINC 30) from Jiangsu Dowill Coatings Co., Ltd.

The epoxy powder of the B2 layer includes, by mass percentage: 30% of polyester resin (acid value: 70 mg KOH/g, viscosity: 4500 mPa•s), 40% of epoxy resin (epoxy value: 0.120 eq/100g, softening point: 102 °C), 3% of phenolic curing agent (969H06 type phenolic curing agent produced by Daqing Qing Lu Long green Technology Co., Ltd.), 1% of 2,4,6-tris(dimethylaminomethyl)phenol as an accelerator, 1% of fluorine modified acrylic acid as a leveling agent, 0.5% of benzoin as a degassing agent, 0.5% of d stearic acid as a egassing agent, 15% of aluminum oxide as a composite filler, 1% of diethyl phthalate as a toughening agent, and 6% of phthalocyanine blue as a color filler.

The polyester powder of the B3 layer includes 45% of high weather-resistant polyester resin (acid value: 29 mg KOH/g, viscosity: 4500 mPa•s), 22% of ultra-weather-resistant polyester resin (hydroxyl value: 120 mg KOH/g, viscosity: 4200 mPa•s), 3.5% of curing agent TGIC, 14% of curing agent B1400, 1.5% of polyether polyester modified organosiloxane as a leveling agent, 0.1% of methyldiethanolamine as an accelerator, 0.1% of defoamer TEGO-902W, 0.5% of tributyl phosphate as a toughening agent, 0.2% of antioxidant 1010 from BASF, 11% of boron nitride as a composite filler, and 2.6% of phthalocyanine blue as a color filler.

Comparative Example 3

The protective coating is an A1 layer of 10 microns, an A2 layer of 40 microns and an A3 layer of 40 microns.

The A1 layer is oil-based epoxy zinc-rich primer (DWB ZINC 30) from Jiangsu Dowill Coatings Co., Ltd.

The epoxy powder of the A2 layer includes, by mass percentage: 30% of polyester resin (acid value: 70 mg KOH/g, viscosity: 4500 mPa•s), 40% of epoxy resin (epoxy value: 0.120 eq/100g, softening point: 102 °C), 3% of phenolic curing agent, 1% of 2,4,6-tris(dimethylaminomethyl)phenol as an accelerator, 1% of fluorine modified acrylic acid as a leveling agent, 0.5% of benzoin as a degassing agent, 0.5% of stearic acid as a degassing agent, 15% of aluminum oxide as a composite filler, 1% of diethyl phthalate as a toughening agent, and 6% of phthalocyanine blue as a color filler.

The epoxy powder of the A3 layer includes, by mass percentage: 45% of polyester resin (acid value: 54 mg KOH/g, viscosity: 4500 mPa•s), 30% of epoxy resin (epoxy value: 0.110 eq/100g, softening point: 100 °C), 0.5% of phosphate modified acrylic acid as a leveling agent, 0.5% of defoamer BYK-024, 1% of 2,6-di-tert-butyl-4-methylphenol as an antioxidant, 2% of dibutyl phthalate as a toughening agent, and 21% of mica powder and ultramarine blue as a color filler.

Comparative Example 4

First, degrease the surface of the metal plate, clean, dry, perform shot blasting, and pre-coat with 10 microns of zinc-rich primer. After the pre-treatment is completed, enter cold working (punching, shearing and pressing forming), perform steel structure assembly and welding, and after shot blasting cleaning of the welded seams, perform the entire container coating operation; spray 20 microns of intermediate water-based epoxy zinc-rich paint as the second layer, and spray 50 microns of topcoat as the third layer.

The zinc-rich primer is DWep ZINC 500 from Jiangsu Dowill Coatings Co., Ltd.

The intermediate water-based epoxy zinc-rich paint is DWB AC PRIMER from Jiangsu Dowill Coatings Co., Ltd.

The topcoat is DWB AC INTERIOR from Jiangsu Dowill Coatings Co., Ltd.

Comparative Example 5

First, degrease the surface of the metal plate, clean, dry, perform shot blasting, and pre-coat with 10 microns of zinc-rich primer. After the pre-treatment is completed, enter cold working (punching, shearing and pressing forming), perform steel structure assembly and

welding, and after shot blasting cleaning of the welded seams, perform the entire container coating operation; spray 20 microns of intermediate water-based epoxy zinc-rich paint as the second layer, spray 50 microns of intermediate paint as the third layer, and spray 40 microns of polyurethane topcoat as the fourth layer.

The zinc-rich primer is DWep ZINC 500 from Jiangsu Dowill Coatings Co., Ltd. The intermediate water-based epoxy zinc-rich paint is DWB AC PRIMER from Jiangsu Dowill Coatings Co., Ltd.

The intermediate paint is DWB AC PRIMER from Jiangsu Dowill Coatings Co., Ltd.

The polyurethane topcoat is DWpu FINISH 20 from Jiangsu Dowill Coatings Co., Ltd.

Test Method and Results:

The test pieces produced by the construction processes of the examples and comparative examples were tested for corrosion spread resistance: the specific test method is:

Using cold-rolled steel plates of the same material, same thickness and same size, test pieces 1, 2, 3 and 4 were made by the construction processes of Example 1, Example 2, Example 3 and Comparative Example respectively.

Using cold-rolled steel plates of the same material, same thickness and same size, test pieces were made by the construction process of the present disclosure under the same conditions using the protective coatings of Examples 4-15 and Comparative Examples 2-5 respectively.

Make the same T-shaped lines on test pieces 1, 2, 3 and 4. The specific way to make the T-shaped lines is:

Draw T-shaped lines on the test piece with a blade to the bottom, and the lengths of the T-shaped lines are 50mm and 76mm respectively.

Make the same T-shaped lines on the test pieces of Examples 4-15 and Comparative Examples 2-5. The specific way to make the T-shaped lines is:

Draw T-shaped lines on the test piece with a blade to the bottom, and the lengths of the T-shaped lines are 50mm and 76mm respectively.

Put test pieces 1, 2, 3 and 4 into the same salt spray test chamber at the same time, and take them out after 1000 hours. Among them, in the test chamber: the concentration of the settled salt solution: 5% sodium chloride solution by mass fraction, the temperature of the test

chamber: (35 ± 2) °C, the pH value of the settled salt solution: 6.5 ~ 7.2 (25 °C).

Put the test pieces of Examples 4-15 and Comparative Examples 2-5 into the same salt spray test chamber at the same time, and take them out after 1000 hours. Among them, in the test chamber: the concentration of the settled salt solution: 5% sodium chloride solution by mass fraction, the temperature of the test chamber: (35 ± 2) °C, the pH value of the settled salt solution: 6.5 ~ 7.2 (25 °C).

The results are shown in FIGS. 1-4. After measurement, the test results of corrosion spread resistance are shown in Table 1, where the corrosion width is the average width.

Table 1

Examples and Comparative Examples	Corrosion Width
Example 1	1.64mm
Example 2	1.70mm
Example 3	1.60mm
Example 4	1.75mm
Example 5	1.59mm
Example 6	1.62mm
Example 7	1.60mm
Example 8	1.69mm
Example 9	1.72mm
Example 10	2.36mm
Example 11	1.62mm
Example 12	1.59mm
Example 13	1.55mm
Example 14	1.64mm
Example 15	1.68mm

Comparative Example 1	2.92mm
Comparative Example 2	2.52mm
Comparative Example 3	2.64mm
Comparative Example 4	3.10mm
Comparative Example 5	2.98mm

From the test results, it can be seen that the corrosion spread resistance of the present disclosure is significantly superior to that of the prior art. Among them, the corrosion width of Sample 4 is more than 1.8 times that of Sample 3. Moreover, from the overall corrosion effect of the samples, the corrosion of Sample 4 is significantly more severe than that of the present disclosure. That is, the thickness of the present disclosure is significantly lower than the spraying thickness in the prior art, and its corrosion resistance is significantly superior to that of the prior art. In particular, its corrosion spread resistance is significantly better than that of the prior art.

The corrosion widths of Examples 4-15 are obviously smaller than those of Comparative Examples 2-5. Therefore, the corrosion resistance of Examples 4-15 is obviously superior to that of the prior art.

Combining FIGS. 5-7 and FIG. 11, it can be clearly observed that the corrosion of Comparative Example 2 is more severe. Combining FIGS. 8-10 and FIG. 12, it can be clearly observed that the corrosion of Comparative Example 3 is more severe. Therefore, the use of the zinc-free primer in the present disclosure can avoid the accelerated corrosion spread caused by zinc and ensure the corrosion resistance of the entire protective coating.

Corrosion spread resistance is a very important parameter for shipping containers. Due to transportation at sea, the natural conditions are harsh. Containers often rub and collide with each other due to sea waves, which are very likely to cause partial wear of the containers. Therefore, there are extremely high requirements for corrosion spread resistance. The present disclosure not only uses fewer materials but also has significantly better corrosion spread resistance than existing products. In addition, the construction process of the present

invention avoids sewage discharge, reduces VOC emissions, and has a good environmental protection effect.

Although the embodiments of the present disclosure have been shown and described above, it can be understood that the above embodiments are exemplary and should not be construed as limiting the present disclosure. Those of ordinary skill in the art can make changes, modifications, substitutions and variations to the above embodiments within the scope of the present disclosure. Therefore, any changes or modifications made in accordance with the claims and specification of the present disclosure shall fall within the scope covered by the patent of the present disclosure.

WHAT IS CLAIMED IS:

1. A powder protective coating for a shipping container, wherein the container comprises an inner surface of the container and an outer surface of the container;

at least part of the container is processed from a metal plate;

wherein:

the metal plate forming the inner surface of the container is provided with at least a three-layer coating structure of A1 layer, A2 layer and A3 layer: the material of the A1 layer comprises a high-solid oil paint and a non-metallic conductive material; the A1 layer does not contain metallic zinc; the material of the A2 layer is epoxy powder; the material of the A3 layer is epoxy powder;

and/or, the metal plate forming the outer surface of the container is provided with at least a three-layer coating structure of B1 layer, B2 layer and B3 layer: the material of the B1 layer comprises a high-solid oil paint and a non-metallic conductive material; the B1 layer does not contain metallic zinc; the material of the B2 layer is epoxy powder; the material of the B3 layer is polyester powder.

2. The protective coating according to claim 1, wherein the A1 layer is formed by roller coating before the metal plate forms the container; the A2 layer and the A3 layer are formed by spraying after forming the container body;

and/or, the B1 layer is formed by roller coating before the metal plate forms the container; the B2 and B3 layers are formed by spraying after forming the container body.

3.The protective coating according to claim 1, wherein a thickness of the A1 layer is less than a thickness of the A2 layer and the A3 layer;

and/or, a thickness of the B1 layer is less than a thickness of the B2 and B3 layers.

4.The protective coating according to claim 1, wherein a solid content ratio of the high-solid oil paint in the A1 layer is not less than 60%, and a content of the non-metallic conductive material ranges from 0.5% to 10% by weight of the high-solid oil paint;

and/or, a solid content ratio of the high-solid oil paint in the B1 layer is not less than 60%, and a content of the non-metallic conductive material ranges from 0.5% to 10% by weight of the high-solid oil paint.

5. The protective coating according to claim 1, wherein a thickness of the A1 layer is

8-12 microns, a thickness of the A2 layer is 37-43 microns, and a the thickness of the A3 layer is 38-43 microns;

and/or, a thickness of the B1 layer is 8-12 microns, a thickness of the B2 layer is 37-43 microns, and a thickness of the B3 layer is 44-46 microns.

6. The protective coating according to claim 1, wherein the non-metallic conductive material in the A1 and B1 layers is graphite, and a content of graphite is approximately 2%; and/or

wherein a solid content ratio of the high-solid oil paint in the A1 and B1 layers is 70%, and a content of the non-metallic conductive material is 5% by weight of the high-solid oil paint.

7.The protective coating according to claim 1, wherein the materials forming the A1 layer and the B1 layer each comprise, by mass percentage: 25-30% of modified epoxy resin, 10-15% of anti-rust pigment, 3-5% of cyclohexanone, 8-10% of xylene, 3-6% of n-butanol, 8-20% of curing agent, and 0.5-10% of the non-metallic conductive material, the remainder being color filler; and/or

wherein the epoxy powder of A2 and B2 each comprises, by mass percentage: 25-50% of polyester resin, 22-45% of epoxy resin, 1-10% of phenolic curing agent, 0.1-2.4% of accelerator, 0.5-2% of leveling agent, 0.1-2% of degassing agent, 5-30% of composite filler and 0.2-2% of toughening agent, the remainder being color filler; and/or

wherein the epoxy powder of A3 comprises, by mass percentage: 30-60% of polyester resin, 20-36% of epoxy resin, 0.5-1% of leveling agent, 0.1-1% of defoamer, 0.2-2% of antioxidant and 0.5-3% of toughening agent, the remainder being color filler; and/or

wherein the polyester powder of B3 comprises, by mass percentage: 30-45% of high weather-resistant polyester resin, 22-35% of ultra-weather-resistant polyester resin, 0-3.5% of triglycidyl isocyanurate, 0-2.5% of hydroxyalkylamide, 14-24% of blocked polyisocyanate, 0.5-1.5% of leveling agent, 0.1-3% of accelerator, 0.1-1% of defoamer, 0.5-3.2% of toughening agent, 0.2-2% of antioxidant and 2-25% of composite filler, the remainder being color filler.

8. The protective coating according to claim 7, wherein the non-metallic conductive material comprises at least one of graphite, graphene and conductive mica.

9.The protective coating according to claim 7, wherein an acid value of the polyester resin is 34-76 mg KOH/g, and a viscosity is 3000-6000 mPa·s; and/or,

an epoxy value of the epoxy resin is 0.090-0.165 eq/100g, and a softening point is 87-105 °C; and/or

wherein an acid value of the polyester resin is 34-76 mg KOH/g, and a viscosity is 3000-6000 mPa·s; and/or,

an epoxy value of the epoxy resin is 0.090-0.165 eq/100g, and a softening point is 87-105 °C.

10.The protective coating according to claim 7, wherein an acid value of the high weather-resistant polyester is 29-34 mg KOH/g, and a viscosity is 4500-6000 mPa·s;

an hydroxyl value of the ultra-weather-resistant polyester is 100-120 mg KOH/g, and a viscosity is 3200-4200 mPa·s.

11. A construction process of the protective coating for the shipping container according to any one of claims 1-10, comprising the following steps:

performing derusting and/or abrasive blasting treatment on the metal sheet;

performing hot coating application: applying the A1 layer and the B1 layer after heating the coating material or the sheet;

drying or air-drying, wherein the air-drying utilizes hot air;

processing the metal sheet, followed by welding, to form the container body;

performing abrasive blasting treatment on welded seams of the container body;

spraying the A2 layer and B2 layer; spraying the A3 layer and B3 layer;

curing and cooling.

12. The construction process according to claim 10, wherein when air-drying with hot air, a temperature of a thick plate with a thickness of more than 4mm after hot air heating is not lower than 85 °C.

13. A shipping container, comprising the protective coating according to any one of claims 1-10; or adopting the construction process according to any one of claims 11-12.

14. A zinc-free primer applied to a shipping container, comprising, by mass percentage: 25-30% of modified epoxy resin, 10-15% of anti-rust pigment, 3-5% of cyclohexanone, 8-10% of xylene, 3-6% of n-butanol, 8-20% of curing agent, and 0.5-10% of the non-metallic

conductive material, the remainder being color filler.

15. The zinc-free primer according to claim 14, wherein the non-metallic conductive material comprises at least one of graphite, graphene and conductive mica.