

CORROSION PROTECTIVE POLYUREA COATINGS

BACKGROUND OF THE INVENTION

The present invention relates to corrosion protective coatings for the surfaces of metal structures. The corrosion protective coating of the present invention can be particularly useful with those metal structures exposed to severely corrosive environments.

The introduction of corrosion protective coatings onto metal surfaces is well known in the art. However, traditional alkyd, vinyl and phenolic low-cost coatings suffer from a variety of problems. The more serious of these problems include application restrictions, mixing errors and delays due to inclement field conditions. For example, traditional coatings can not typically be applied in humidities over 85 percent or when the surface to be treated is within 5° F of the dew point. Moreover, the coatings can not be applied the temperature falls below a particular point. For most of the popular plural component epoxy and inorganic coatings, the lower limit is 35-45° F.

While certain cold weather or surface tolerant specialty primers have been developed, their use is still subject to a variety of problems because not all of the components of these coating systems are weather or moisture tolerant.

One attempted solution to the foregoing problems has involved the use of moisture-curable urethanes. These coatings, which are more appropriately called "polyureas" were first developed by Bayer in Germany about twenty-five to thirty years ago. While these urethanes have proven effective in preventing corrosion, they remain extremely difficult to manufacture, particularly on a large scale basis.

Despite the manufacturing problems and the fact they have been known for years, much of the work in this area continues to be centered around only a few resins that are based on the Bayer technology, e.g., Desmodur E 21 of Mobay Chemical

Company. For example, U.S. Patent No. 4,279,962 uses the resin in a dual-layer protective coating for cathodically protected metal surfaces. The two-layer coating includes a base coating having highly divided zinc together with the Desmodur E 21 resin, and a cover coating comprising a mixture of tar with polyisocyanates, fillers, dryers, solvents and micaceous iron ore or hematite powder.

Only recently have alternative single component, moisture cure urethane coatings been developed. This technology is the subject of an article by W. Brinton entitled "Moisture-cured Urethane for Wet Environments" from the August 19, 1991 issue of American Paint and Coating Journal, which is incorporated by reference in its entirety.

This article discloses certain corrosion protective coating materials that include a primer coat of single-component, moisture-curable type polyurethane-urea resin containing zinc, and intermediate coat of single-component, moisture-curable type polyurethane-urea resin containing micaceous iron oxide and a top coat of single-component, moisture-curable type aliphatic polyurethane-urea resin optionally containing micaceous iron oxide.

These coatings are disclosed as having improved stability, interlayer adhesivity and hardening at low temperature/high humidity environments as compared to those corrosion protective coating materials traditionally considered usable in these environments.

Despite the effectiveness of these new coatings, further improvements in the combination of corrosion protective performance, workability and quality under high humidity conditions are still desired.

The present invention provides novel corrosion protective coatings capable of providing that combination of improved corrosion protection with workability, for use with the surfaces of metal structures.

SUMMARY OF THE INVENTION

The present invention relates to a corrosion protective coating comprising a plurality of resin layers on the surface of a metal structure. The layers can include a primer layer, an intermediate layer and a top layer where at least the primer layer comprises a moisture-curable polyurethane-urea resin.

The primer layer also preferably contains zinc powder and/or micaceous iron oxide in an amount of 70-95 percent by weight, after drying.

In one preferred embodiment, the corrosion protective coating includes a primer layer in conjunction with an intermediate layer and a top layer, and each of the layers includes a moisture-curable type polyurethane-urea resin and micaceous iron oxide.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1 and 2 illustrate corrosion protective coatings according to the present invention. These figures include metal structure surface, 1; primer layer, 2; intermediate layer, 3; and top layer, 4.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention relates to a corrosion protective coating in which at least one layer of the coating comprises a moisture-curable polyurethane-urea resin.

The single-component, moisture-curable polyurethane-urea resins that can be employed in the present invention include those single-component, isocyanate prepolymer resins recognized in the art.

Suitable prepolymer resins can be provided, for example, by reacting a polyether, polyester and acrylic resin with a polyisocyanate such as diphenylmethane diisocyanate, toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI) or isophorone diisocyanate (IPDI), to obtain a solution comprising an isocyanate terminated single-component, moisture-curable polyurethane prepolymer. In particular, prepolymer resins having improved stability can be provided from ortho-formate (OF)

and p-toluene sulphonylisocyanate (PTSI).

A layer can then be formed on the surface to be treated from a solution of the prepolymer. For example, the prepolymer solution can be applied onto a surface of a base plate, reacted with moisture in the atmosphere and on the plate, and dried to remove the solvent. The prepolymer reacts to produce urea bonds and forms a hardened coating layer of polyurethane-urea resin.

The coating comprises at least one layer, and preferably, at least two layers. Each of the layers can be formed, as described in the foregoing, by applying paint solution(s) to the desired surface. The coating solution(s) can be applied by techniques recognized in the art. Such techniques can include spraying, painting, dipping, and the like.

The metal structure can comprise any metal that is subject to corrosion, with steel being the most common. Moreover, the surface to be coated can be untreated or treated, e.g., painted or cleaned, by techniques recognized in the art prior to coating in accordance with the present invention.

The prepolymer-containing solution(s) employed in the coating layers can be the same or different depending on the environment the coated metal is to be employed.

In one preferred embodiment, the coating includes a primer layer, an (optional) intermediate layer and a top layer. The present invention will be further discussed in terms of this embodiment. However, the present invention should not in any way be limited to that embodiment.

Turning first to the primer layer, zinc powder and/or micaceous iron oxide are preferably included in the prepolymer solution in an amount such that they are presented in the primer layer, after drying, in an amount of 70-95 percent by weight, preferably 75-90 percent by weight.

If the total content of zinc powder and/or micaceous iron oxide in the primer layer is less than 70 percent by weight, the desired corrosion protection is difficult to

obtain. On the other hand, if present in excess of 95 percent by weight, applicability of the solution can be degraded.

In one embodiment capable of providing improved corrosion protection and applicability, zinc powder and micaceous iron oxide are added to the primer layer-forming solution in an amount such that the primer layer, after drying, contains zinc powder in an amount of 50 percent by weight or more, and micaceous iron oxide in an amount of 30 percent by weight or less.

It has been found that corrosion protection can be further improved where a zinc powder is added to the primer layer forming solution such that the zinc is present in the primer layer after drying in an amount of 85 percent by weight or more.

On the other hand, it has also been found that where a surface that is effectively cleaned, e.g., blast cleaned, prior to applying the coating, effective corrosion protection can be provided without the use of micaceous iron oxide.

If the metallic surface to be coated is a non-ferrous metal such as galvanized steel, stainless steel or aluminum, it is preferable to use a primer layer containing a polyurethane urea resin and micaceous iron oxide as essential ingredients, in view of long-term adhesion. In this case, it is not necessary to use zinc powder.

In the corrosion protective coating of the present invention, it is often preferable to provide an intermediate layer on the primer layer.

A solution for forming an intermediate layer preferably includes one or more of micaceous iron oxide, zinc powder and tar. Because of its ability to provide more effective corrosion protection, paint application and layer to layer adhesion, the inclusion of micaceous iron oxide, either alone or in combination with either zinc oxide or tar, is preferred.

However, the coloring of coating layers containing micaceous iron oxide, zinc powder and tar would be restricted to dark colors. Thus, in those environments where a bright color is required, the intermediate layer forming solution can be at least substantially free of micaceous iron oxide, zinc powder and tar.

By "at least substantially" it is meant that, if the intermediate layer contains such components, they are present in an amount of 1 percent by weight or less.

In the corrosion protective coating of the present invention, it is further preferable to include a top layer. The top layer is typically provided on the intermediate layer. However, if the metal structure is installed in an environment that is considered only moderately corrosive, such as a mountainous site, the top layer may be provided immediately onto the primer layer, omitting the intermediate layer.

As was the case with the primer and the intermediate layer, the top layer can be formed from a solution comprising at least one single-component, moisture-curable type polyurethane prepolymer having the isocyanate terminal thereon. Because the top layer should be resistant to weathering, the use of an alicyclic or aliphatic isocyanate polyurethane prepolymer is preferred.

However, it is the belief of the inventor that the intended corrosion protection is largely provided by the primer layer and/or intermediate layer. Accordingly the resin constituting the top layer can comprise resins other than the single-component, moisture-curable type polyurethane-urea resin. Thus, other suitable resin paints for the top layer include commercially available phthalic resin paints, chlorinated rubber resin paints, polyurethane resin paints, fluorocarbon resin paints, alkyd resin paints, silicone alkyd resin paints, tar epoxy resin paints, tar urethane resin paints, and acrylic silicone resin paint.

Because the top layer largely determines the appearance of the metal structure, the additives included therein should be chosen depending on the requirements for gloss or color or both.

For example, when the surface is required to be not glossy and/or of a subdued color, the combination of an intermediate layer containing micaceous iron oxide or micaceous iron oxide and zinc powder and a top layer containing micaceous iron oxide is preferred. In such cases, micaceous iron oxide is preferably added to the top layer forming solution so that it is contained in the top layer after drying. Furthermore, a

coating comprising micaceous iron oxide containing primer layer, micaceous iron oxide containing intermediate layer and micaceous iron oxide containing top layer can provide particularly superior corrosion protection.

On the other hand, where the desired surface is glossy and/or of a relatively bright color, the top layer is preferably at least substantially free of micaceous iron oxide.

Conventional primers containing zinc powder are "inorganic zinc rich paints" or "organic zinc rich paints". The inorganic zinc rich paints showing especially excellent corrosion performance require mist coat for overcoating, since they have a porous structure. However, a primer of a moisture-curable type polyurethane urea resin of the present invention containing zinc powder as an essential ingredient can be overcoated with a moisture-curable type polyurethane resin as an intermediate or top coat, or with other commercially available paints without a mist coat.

The top layer may be employed in combination with an intermediate layer containing micaceous iron oxide or micaceous iron oxide and zinc powder, or an intermediate layer at least substantially free of these substances.

In those environments, e.g., metal structures in a recreational ground, where colors of a glossy tone are desired, it is preferable that both the intermediate layer and the top layer are at least substantially free of micaceous iron oxide and zinc powder.

Where a metal structure is situated under in a severe corrosive environment, e.g., sea water, it is preferable to form an intermediate layer containing micaceous iron oxide and tar, then provide a top layer containing micaceous iron oxide and tar thereover. In this case, the top layer forming single-component, moisture-curable type polyurethane prepolymer may not necessarily be alicyclic or aliphatic but may employ the same as the single-component, moisture-curable type polyurethane prepolymer used in the intermediate layer.

In the corrosion protective coating of the present invention, the solution of the moisture-curable type polyurethane prepolymer forming the primer, intermediate and

top layers of the single-component, moisture-curable type polyurethane-urea resin may contain, other additives normally employed in paints, such as coloring pigments, titanium oxide, aluminum flakes, catalysts, fillers, ultraviolet-dispersants, antigelling agents and solvents.

The corrosion protective coating of the present invention can be employed in environments requiring heaving corrosion protection such as road and bridge structures, electric power, oil and other energy related plants and equipment, factory equipment of paper and food industries, ship and port equipment, recreation ground, swimming pool and other amusement facilities, and environment related plants and equipment. Moreover, it is suitably usable for repainting at sites subject to change of weather or metal surface condition.

The corrosion protective coating of the present invention can provide improved corrosion protection without impairing the good workability and applicability which are the features of the single-component, moisture-curable type polyurethane-urea resin. Moreover, the adhesive property of the coating for poorly prepared metal surfaces can be improved, while superior anti-corrosion property can be maintained over a long period of time.

By overcoating the intermediate and top layers comprised of a single-component, moisture-curable type polyurethane-urea resin on the primer layer provided by this invention, it is possible to maintain corrosion protection, gloss retention, anti-discoloration, anti-blistering over a long period of time. However, in another embodiment of the invention, weather resistance can be increased by overcoating commercially available intermediate and top coat adopted to the conventional anti-corrosion coating systems on the primer layer provided by the present invention.

Based on the foregoing, it becomes clear that the coatings according to the present invention are especially suited for severe corrosion circumstance such as bridge, harbor facilities, ships, and the likes.

The present invention will now be described in terms of certain examples.

These examples are solely illustrative in nature and should in no way limit the scope of the present invention.

EXAMPLES

In the following examples of the corrosion protective coating of the invention, the corrosion protective performance is measured by the corrosion protection test by salt fog test under ASTM B117 and is evaluated by the spraying time until generation of rust.

Examples 1-4

A steel plate having rust was generated by spraying an aqueous solution of 3% NaCl at a frequency of once a week and exposing to atmosphere for 3 months. The rust was then removed with a power tool to the surface cleaned level of ISO St3. The steel plate then had a polyurethane-urea resin paint shown in Table 1 applied for primer coat, intermediate coat and top coat under the conditions of humidity at 98% and temperature at 20°C, then the steel plate thus coated was dried under the conditions of humidity 98% and temperature 20°C for 1 week and taken as a test specimen.

Then, with an X-cut scribe given to the coated surface to reach to the grounding surface, the specimen was subjected to the combined cycle test with the testing conditions (4 steps, 6 hours) shown in Table 2 as one cycle for evaluation of the corrosion protective performance, and the results shown in Table 3 were obtained. In the test, those parts of the film which were within about 10mm from the periphery of the specimen and within 2mm on the respective sides of the scribe given to the film were taken to be outside of the evaluation.

The specimen was also subjected to the salt fog test under ASTM B117, with the results thereof shown in Table 3.

Examples 5 and 6

A steel plate having the surface prepared by sand blasting to a level of ISO 5a2.5 had a polyurethane-urea resin shown in Table 4 applied for primer coat, intermediate coat and top coat under the conditions of humidity 98% and temperature 20°C then dried at humidity 98% and temperature 20°C for 1 week.

Then, with an X-cut scribe given to the coated surface to reach to the grounding surface, the specimen was subjected to the combined cycle test with the test conditions (4 steps, 6 hours) shown in Table 2 as one cycle for evaluation of the corrosion protective performance, and the results shown in Table 5 were obtained. In the test, those parts of the film within about 10 mm from the periphery of the specimen and within 2 mm on the respective sides of the scribe given to the film were taken to be outside of the evaluation.

The specimen was also subjected to the salt fog test under ASTM B117, with the results thereof shown in Table 5.

Examples 7 and 8

A material to be coated had the surface preparation according to the method of Example 1 and had the respective primer coat, intermediate coat and top coat shown in Table 6 applied under the conditions of humidity 60% and temperature 20°C. It was then dried for 1 week under the conditions of humidity 60% and temperature 20°C and taken as a test specimen.

With an X-cut scribe given to the coated surface to reach to the grounding surface, the specimen was subjected to the combined cycle test with the test conditions (4 steps, 6 hours) shown in Table 2 taken as 1 cycle for evaluation of the corrosion protective performance, and the results shown in Table 6 were obtained. In the test, those parts of the film which were within about 10 mm from the periphery of the specimen and within 2 mm from the respective sides of the scribe given to the film were taken to be outside of the evaluation.

Example 9

A material to be coated had the surface preparation according to the method of Example 5 and had a primer coat paint used in Example 1 applied. Then, it was immediately submerged in water of 20°C and, after allowing to stand for 7 days, had a bonding strength of 13 kg/cm² measured according to the method specified in ASTM D4541.

References 1 and 2

A material to be coated was prepared according to the method of Example 1, and had the primer coat, intermediate coat and top coat shown in Table 1 applied under the conditions of humidity 60% and temperature 20°C, then it was dried for 1 week under the conditions of humidity 20% and temperature 20°C and taken as a test specimen.

With an X-cut scribe given to the film surface to reach to the grounding surface, the specimen was subjected to the combined cycle test under the conditions shown in Table 2 for evaluation of the corrosion protective performance, and the results shown in Table 7 were obtained.

This specimen was subjected to the salt fog test under ASTM B117, and there were obtained the results shown in Table 7.

Reference 3

A material to be coated had the surface preparation according to the method of Example 5 and had an organic zinc-rich paint (Zinke 8000HB; Product of Nippon Paint Co.) applied at a rate of 300 g/m³, then it was immediately submerged in water of 20°C and allowed to stand for 7 days and had a bond strength of 0 kg/cm² measured according to the method specified in ASTM D4541.

TABLE 1

Components	Composition of components in dry film			
	Ex. 1 (Ref. 1)	Ex. 2	Ex. 3	Ex. 4 (Ref. 2)
Primer coat				
Vehicle	15	15	15	15
Pigments				
Micaceous iron oxide	20	20	20	20
Zinc powder	60	60	60	60
Others	3	3	3	3
Additives	2	2	2	2
Dry film thickness (μm)	75	75	75	75
Intermediate coat				
Vehicle	42	3	46	51 ^{*1}
Pigments				
Micaceous iron oxide	40	25	-	35
Zinc powder	-	39	-	-
Others	16	4	51	12
Additives	2	2	3	2
Dry film thickness (μm)	75	75	75	150
Top coat				
Vehicle	54	83	98	51 ^{*1}
Pigments				
Micaceous iron oxide	38	-	-	35
Others	6	-	-	12
Additives	2	3	2	2
Dry film thickness (μm)	75	40	40	150

*1: Vehicle contains 23 percent by weight (to dry film weight of refined tar.

TABLE 2

Steps	Tests
1	Salt water spray test 5% aqueous solution of NaCl, $30\pm 2^{\circ}\text{C}$, 0.5h
2	Wetting test $30\pm 2^{\circ}\text{C}$, $95\pm 3\%$ RH, 1.5h
3	Hot air drying test $50\pm 2^{\circ}\text{C}$, 2.0h
4	Warm air drying test $30\pm 2^{\circ}\text{C}$, 2.0h

TABLE 3

Test items	Ex. 1	Ex. 2	Ex. 3	Ex. 4
Combined cycle test				
Cycles	360	360	360	360
X-cut scribe part	Within 1mm blisters at the scribe area	Within 1mm blisters at the scribe area	Within 1mm blisters at the scribe area	Within 1mm blisters at the scribe area
Normal part	No rust spots, no blistering	No rust spots, no blistering	No rust spots, no blistering	No rust spots, no blistering
Salt fog test				
2000h	No rust spots, no blistering	No rust spots, no blistering	No rust spots, no blistering	No rust spots, no blistering

TABLE 4

Components	Composition of components in dry film (wt%)	
	Ex. 5	Ex. 6
Primer coat		
Vehicle	8	8
Pigments		
Zinc powder	88	88
Others	3	3
Additives	1	1
Dry film thickness (μm)	75	75
Intermediate coat		
Vehicle	42	46
Pigments		
Micaceous iron oxide	40	-
Others	16	51
Additives	2	3
Dry film thickness (μm)	75	75
Top coat		
Vehicle	54	98
Pigments		
Micaceous iron oxide	38	-
Others	6	-
Additives	2	2
Dry film thickness (μm)	75	40

TABLE 5

Test items	Ex. 5	Ex. 6
Combined cycle test		
Cycles	480	480
X-cut scribe part	No rust spots, no blistering	No rust spots, no blistering
Normal part	No rust spots, no blistering	No rust spots, no blistering
Salt fog test		
4000h	No rust spots, no blistering	No rust spots, no blistering

TABLE 6

Components	Composition of components in dry film (wt%) and paints	
	Ex. 7	Ex. 8
Primer coat		
Vehicle	15	15
Pigments	20	20
Micaceous iron oxide	20	20
Zinc powder	60	60
Others	3	3
Additives	2	2
Dry film thickness (μm)	75	75
Intermediate coat		
Paints	Phthalic resin paint intermediate coat (Zuvoid SR intermediate coat)	Polyurethane resin paint intermediate coat (V Top H intermediate coat)
Dry film thickness (μm)	75	75
Top coat		
Paints	Phthalic resin coat (Zuvoid SR Top coat)	Polyurethane (V Top H Top coat)
Dry film thickness (μm)	25	25
Combined cycle test		
Cycles	120	120
X-cut scribe part	No rust spots, no blistering	No rust spots, no blistering
Normal part	No rust spots, no blistering	No rust spots, no blistering

TABLE 7

Test items	Ref. 1	Ref. 2
Combined cycle test		
Cycles	360	360
X-cut scribe part	Within 1mm blisters at the scribe area	No rust spots, no blistering
Normal part	No rust spots, no blistering	No rust spots, no blistering
Salt fog test		
2000h	No rust spots, no blistering	No rust spots, no blistering

Example 10

After completion of intermediate coat in Example 5, a commercially available polyurethane resin paint (V Top HB produced by Dai Nippon Toryo Co., Ltd.) was applied as a top coat to have a dry film thickness of 50 μm , and a salt fog test of 2000 hours was carried out according to ASTM B117. Neither the X-cut scribe part nor the normal part showed any rust or blister.

Example 11

After completion of primer coat in Example 5, a commercially available tar epoxy resin paint (SDC Coat produced by Dai Nippon Toryo Co., Ltd.) was applied to have a dry film thickness of 240 μm , and a salt fog test of 4000 hours was carried out according to ASTM B117. Neither the X-cut scribe part nor the normal part showed any rust or blister.

Example 12

A galvanized steel sheet with 550 g/m^2 of zinc deposited was ground on the surface by sand paper, coated with the top coat of Example 1, and dried at 20°C for 7 days. The specimen was kept in an atmosphere of $50 \pm 1^\circ\text{C}$ and 95% relative humidity for 90 days, and the bonding strength was measured according to ASTM D 4541, and found to be 40 kgf/cm^2 .

Although the present invention has been described in terms of various preferred embodiments thereof, it is apparent that various modifications, omissions, substitutions and other changes may be made without departing from the spirit thereof. Thus, the invention should be limited only by the scope of the following claims including equivalents thereof.



What is claimed is:

18

1. A corrosion protective coating for use with surface of a metal structure, comprising a moisture-curable type polyurethane urea resin and micaceous iron oxide as essential ingredients in a primer coating.
2. The corrosion protective coating of claim 1, wherein the primer layer is overcoated with one or more layers.
3. A corrosion protective coating for use with surface of a metal structure, comprising a moisture-curable type polyurethane urea resin and zinc powder as essential ingredients in a primer coating.
4. The corrosion protective coating of claim 3, wherein the primer coating is overcoated with one or more layers.
5. The corrosion protective coating of claim 3, wherein the zinc powder content in the primer layer is 85% or more.
6. The corrosion protective coating of anyone of claim 1 to 5, wherein the overcoatings are formed by materials selected from moisture-curable type polyurethane urea resins, polyurethane resins, epoxy resins, chlorinated rubber resins, alkyd resins, phthalic resins, fluorine resins, phenol resins, acrylic resins and acrylic silicone resins.
7. The corrosion protective coating of anyone of claim 1 to 6 wherein said coating comprises a primer layer, an intermediate layer and a top layer.
8. The corrosion protective coating of claim 1 or 3 wherein the primer layer contains zinc powder and micaceous iron oxide in an amount of 75-90 percent by weight.
9. The corrosion protective coating of claim 1 or 3 wherein the amount of zinc powder in the primer layer is 50 percent by weight or more and micaceous iron oxide is 30 percent by weight or less.
10. The corrosion protective coating of claim 7 wherein the intermediate layer further comprises zinc powder.
11. The corrosion protective coating of claim 7 or 10 wherein the



intermediate layer further comprises tar.

12. The corrosion protective coating of claim 7 wherein the top layer further comprises tar.

13. The corrosion protective coating of claim 7 or 13 wherein the top layer is substantially free of micaceous iron oxide.

14. A composite material comprising a metal structure having a corrosion protective coating in accordance with any one of claims 1-13 on a surface thereof.

15. The composite material of claim 14, wherein said metal surface is a galvanized steel surface.

16. A corrosion protective coating method, comprising keeping the metal surface wet when the corrosion protective coating of claim 1 or 3 is applied.

17. A corrosion protective coating method, comprising keeping the lower limit of the environmental temperature at -6°C or higher when the corrosion protective coating of claim 1 or 3 is applied.

18. A corrosion protective coating method, comprising the environmental humidity at 6 to 99% RH when the corrosion protective coating of claim 1 or 3 is applied.