ABSTRACT

Title: An organic-inorganic hybrid coating composite and a process for preparing the same.

The present invention relates to the development of organic composite coating for galvanized steel material. The organic-inorganic hybrid coating is water based coating which consists of styrene acrylic resin, polyurethane resin, polyethylene wax, and colloidal silica and corrosion inhibitors and other additives. The corrosion inhibitors consisted of zinc oxide (ZnO) along with either or combination of inhibitors such as zinc phosphate, sodium phosphate, sodium phosphate dibasic dodecahydrate. This novel coating composition is the best suited for the surface treatment of the zinc coated steel known as galvanized material.
The present invention relates to enhance white rust resistance of the galvanized steel by the application of organic composite coating. In addition to corrosion resistance, this organic composite coating enhance the antifinger resistance and lubricity to the coated sheet.

WE CLAIM:

1. An organic-inorganic hybrid coating composition comprising:
   (a) 40 to 80 ml of styrene acrylic resin (b) 20 to 50 ml of polyurethane dispersion (c) 2 to 8 ml of polyethylene wax (d) 0.5 to 5 ml of colloidal silica (e) 0.01 to 2 gm of zinc oxide (f) 0.05 to 5 gm of either or combination zinc phosphate, sodium phosphate, sodium phosphate dibasic dodecahydrate.

2. The organic-inorganic hybrid coating as claimed in claim 1, wherein the styrene acrylic emulsion having basic properties consisted of 25-50 wt% solid, pH 7-9.0 particle size 0.05-0.5 μm, sp. Gr. 1.01-1.2, white milky appearance is used.

3. The organic-inorganic hybrid coating as claimed in claim 1, wherein polyurethane dispersion is a high molecular weight polymer having 25-40 wt% solid, pH 8.0-10, viscosity 50-500 cps can be used.

4. The organic-inorganic hybrid coating as claimed in claim 1, wherein colloidal silica used in this formulation contains 15 to 30% solid content, the average particle size is 4-15 nm and the pH of the solution is 9.5-10, its density is 1.1 to 1.25 g/cm^3.

5. The organic-inorganic hybrid coating as claimed in claim 1, wherein the commercial polyethylene wax emulsion used in this coating is a white translucent non-ionic or cationic emulsion having 15-40% solid content, pH 3.0-10 with typical particle size of 0.6 microns.

6. The organic-inorganic hybrid coating as claimed in claim 1, wherein zinc oxide of size 20 nm to 1000 nm size was dispersed in the water medium using dispersing agents by either or combination of mild stirring, ball mill, high speed homogenizer, ultrasonication etc.

7. The organic-inorganic hybrid coating as claimed in claim 1, wherein the said corrosion inhibitors comprises of zinc phosphate, sodium phosphate, sodium phosphate dibasic dodecahydrate or combination of thereof.

8. The organic-inorganic hybrid coating as claimed in claim 1, wherein said coating is applied on galvanized material either by dip, spray or roller method and subsequently dried on oven at the peak metal temperature of 60-120 degree centigrade.

Date this 5th day of May 2009

OF L.S.DAVAR & CO
APPLICANTS' AGENT

FIELD OF THE INVENTION:

This invention relates to an organic-inorganic hybrid coating composite.

The present invention also relates to a process for preparing organic-inorganic hybrid coating composition.

BACKGROUND OF THE INVENTION:

The out of the bath surface of zinc and zinc alloy coatings are highly susceptible to corrosion. Corrosion products formed on zinc coating are generally referred to as 'white rust'. Inorganic chromate passivation is usually applied directly after galvanizing in line to enhance the corrosion protection properties of zinc and zinc alloy steel. This technique is widely applied as an economical method of corrosion prevention.

In recent past a new technology was developed in the post treatment of galvanized sheets known as "Thin Organic Coating" (TOC) or "Organic Composite Coating". This coating formulation contains both organic and inorganic compounds in the formulation.

The prior art mention in United States Patent No. 3036934, 5482787 and 5294485 describe the TOC coating formulations which contains the chromium compound more particularly, the hexavalent chromium. However, hexavalent chromium is classified as hazardous substances (toxic, sensitizing and carcinogenic).

In the present work, the organic coating developed is environmental friendly. It does not contain any of the chromium compounds.

OBJECTS OF THE INVENTION:

An object of this invention is to propose an organic-inorganic hybrid coating composition;

Another object of this invention is to propose a process for the preparation of organic-inorganic hybrid coating composition;

Still another object of this invention is to propose an organic-inorganic hybrid coating on GI surface gives 1 to 9 μm dry film coating;

Further, object of this invention is to propose an organic-inorganic hybrid coating which improves the corrosion resistance performance of the product;

Still further object of this invention is to propose an organic-inorganic hybrid coating which imparts paint adhesion and anti-finger resistance.

BRIEF DESCRIPTION OF THE INVENTION:

According to this invention an organic-inorganic hybrid coating composition comprising:

(a) 40 to 80 ml of styrene acrylic resin (b) 20 to 50 ml of polyurethane dispersion (c) 2 to 8 ml of polyethylene wax (d) 0.5 to 5 ml of colloidal silica (e) 0.01 to 2 gm of zinc oxide (f) 0.05 to 5 gm of either or combination zinc phosphate, sodium phosphate, sodium phosphate dibasic dodecahydrate.

DETAILED DESCRIPTION OF THE INVENTION:

The objective of this invention is to develop an organic composite coating formulation that after application on GI surface gives 1 to 9 μm dry film coating thickness depends on the application method. This coating can be applied in continuous galvanizing line as a post treatment process to improve the corrosion resistance performance of the product.

Another objective of this invention is to make the organic composite coating formulation such that after application on galvanized material, it not only enhance the corrosion resistance but also give the lubrication, paint adhesion, anti-finger resistance.

The organic composite coating formulation comprises of styrene acrylic emulsion, polyurethane dispersion, polyethylene wax, colloidal silica, zinc oxide, corrosion inhibitors such as zinc oxide (ZnO) and along with either or the combination of zinc phosphate, sodium phosphate, sodium phosphate dibasic dodecahydrate etc. The additives such as dispersing agent, antifoaming agent, antifouling agents etc are used during the organic composite coating preparation. All the constituents are commercially available and are collected from different sources.

The organic composite coating formulations made from commercially available chemicals whose detail is given in Table 1 below.

Table 1: The name and basic properties of commercially available chemicals.

S.No	Product Name	Description	Make
1.	Visicryl-7650	Water based styrene acrylic resin emulsion, pH = 7.5-9.0, Specific gravity = 1.05, Particle size =0.05-0.15, Viscosity = 20-70, Solid Content = 50%, MFFT =18°C	Visen Organic Industries Ltd. (India)
2.	Worleecryl-7120	pH = 8.2-9.0, Density = 1.09, Viscosity = 200-800, 49% solid contents, MFFT = 15°C	Worlee-Chemie GMbH (Germany)
3.	Cytec-1035	Polyurethane dispersion pH = 9.0-9.5, Specific gravity =1.05, Surface tension = 49, MFFT=1°C, Glass transition temp. =25°C, Particle size=150nm, Viscosity = 50-100, Solid Content=35%, VOC=32 (grams/litre)	Cytec Industries Inc.
4.	Ludox-AM 30	Colloidal in nature, Corrosion resistant, 30 wt% in suspension, pH=10, Density=1.22 gm/ml at 25°C	Sigma Aldrich
5.	Lakewax-37	Polyethylene Wax	Enva chem. (India) Ltd & Lakeland Laboratories Limited (England)
6.	Zinc	Solid white powder, m.p.= 912°C, Solubility in water: <0.1% (20°C, pH =6-8 (100gm/l H_2O/20°C, Density = 1.1 gm/cm^3	Sigma Aldrich
7.	Zinc Oxide, Nanopowder	Particle size less than 100nm, White solid powder, m.p. = 1975°C	Sigma Aldrich
8.	Nuosperse FX-365	Wetting & Dispersing agent Nonionic Clear liquid, Solid content=90%, Density= 1116 kg/m^3, Viscosity=850 m Pa.S	Elemantis Specialties

The commercial available polymers were diluted before coating formulation and the diluted polymers was used for the further synthesis, as per the detail given below.

1. Both the acrylic polymers, Visicryl-7650 and Worleecryl-7120, contain about 50% of the solid content. This styrene acrylic emulsion was dissolved in water under high stirring condition to make 30% solid content and then filtered it with 300 μm filter cloth.
2. This commercial grade Polyurethane dispersion, Cytec-1035, contains 35% solid content. This polyurethane dispersion was dissolved in water under high stirring condition to make 25% solid content and then filtered it by 300 μm filter cloth.
3. The nano scale zinc oxide particle used in this work was below 100 nm in size. Zinc oxide is water insoluble pigment. The nano zinc oxide was taken and made slurry forms by adding deionized water with the help of Mortar and pestle and then added dispersing agent and put in the planetary mill for milling and grinding for 30 minutes for complete dispersion.

Synthesis and application of organic composite coating

The organic-inorganic hybrid coating formulation was made from the above modified constituents. The constituents were added as per the sequence mentioned below in Table 2 under mild stirring and then filtered it by 300 μm filter cloth. The Table 2 given below describes the coating formulation chemistry.

The above formulation was applied on galvanized sheet samples of size 150x100 mm by dip coating process followed by oven drying at 80 degree C for 30 minutes. In this process of coating application, 6-8 μm of the dry film formed on GI surface. The coating properties were evaluated by simulated corrosion test like salt spray, water immersion and cyclic corrosion tests, as given in Table 3.

Table 2: Formulations (ingredients concentration noted in parts by weight)

Example	1	2	3	4	5	6	7	8	9	10	11
Mix these first three ingredients- "PREMIX"											
Water	50	50	50	50	50	50	50	50	50	50	50
Nuosperse FX-365	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Nano ZnO	25	25	25	25	25	25	25	25	25	25	25
Total premix	75.05	75.05	75.05	75.05	75.05	75.05	75.05	75.05	75.05	75.05	75.05
Mix in the following in order											
Visicryl-7650	65	65	65	65	65	65	65	65	65	65	65
Cytec-1035	30	30	30	30	30	30	30	30	30	30	30
Nano ZnO/Nuosperse FX-365 "Premix"	-	0.05	0.1	0.3	0.2	0.2	0.2	0.2	0.2	02	02
Ludox-AM 30	2	2	2	3	4	4	4	4	4	4	4
Lakewax-37	2	2	2	3	4	4	4	4	4	4	4
Nuosperse FX-600	0.5	0.5	0.5	1	1	1	1.5	1.5	1.5	1.5	1.5
Zinc phosphate	-	-	0.1	-	-	0.2	-	-	1	-	-
Sodium phosphate	-	-	-	0.1	-	-	0.2	-	-	1	-
Sodium phosphate dibasic dodecahydrate	-	-	-	-	0.1	-	-	0.2	-	-	1
Total Formulation	99.5	99.5	99.7	102.4	104.3	104.4	104.9	104.9	105.7	105.7	105.7

Table 3- corrosion resistance performance Test procedure of 8 micron organic coated GI sheet sample.

Examples	1	2	3	4	5	6	7	8	9	10	11
Result	Appearance of 10% white rust in the coated sample surface (hours)										
Salt spray test	24	72	240	240	240	600	600	600	240	120	240
Cyclic corrosion test (hours)	480	1900	1900	1900	1900	1900	1900	1900	1900	1900	1900
Water immersion test (hours)	72	168	240	240	312	420	420	420	420	420	420

Corrosion performance evaluation

The edges of the sheet were covered by lacquer to prevent the galvanic corrosion from the edges during corrosion tests. The salt spray test, cyclic corrosion test and water immersion test were done as per standard ASTM B117, SAE J2334 and ASTM D823 respectively. The 10% white rust formation on the sample surface was considered as failure. It was observed in salt spray test that the example 1 and 2 showed salt spray test that the example 1 and 2 showed salt spray resistance of 24 and 72 hours respectively. The example 1 contains only the polymer resin where as the example 2 formulation contains polymer as well as the nano zinc oxide. The examples 3 to 11 contain corrosion inhibiting compound along with the resin and nano ZnO that enhance the organic coating performance.

The best performance was observed in example 5 to 8 in salt spray test. In cyclic corrosion test, the example 2 to 11 passed 1900 hours of test time. In water immersion test, the example 6 to 11 showed the similar performance and passed 420 hours in test medium.

Zinc oxide Dispersion technique:

Zinc oxide is water insoluble pigment, it was dispersed by various techniques. First of all nano zinc oxide was taken and made slurry forms by adding deionized water with the help of Mortar and pestle and then added dispersing agent and put in the planetary mill for milling and grinding for 30 minutes for complete dispersion. Now the calculated amount of dispersed nano zinc oxide was added in the polymer matrix while the solution was in stirring condition. The polymer solution was then kept for ultrasonication (ELMAS 30 H Elmasonic Cleaner bath) for 30 minutes for the breakdown of agglomeration of the nano particles. Further, the solution was agitated in high speed homogenizer during stirring and added about few drops of dispersing agent to get the complete breakdown of and dispersion of the particle in the polymer matrix.