

Preparation of light color antistatic and anticorrosive waterborne epoxy coating for oil tanks

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Abstract Utilizing waterborne epoxy resin as a main film-forming material, a kind of light color antistatic and anticorrosive waterborne epoxy coating with volume resistivity of $10^6 \Omega\text{m}$ was prepared by adding light color conductive pigments and anticorrosive pigments. The coating has excellent corrosion protective and outstanding decorating properties, which is applicable for the inner coating of oil tank. The effects of the type and the amount of conductive pigments, the film thickness, the curing temperature, and the curing time on the volume resistivity of the film were discussed. The properties of the several kinds of waterborne epoxy resin were compared and the determining of anticorrosive pigments was discussed.

Keywords Light color, Antistatic, Anticorrosive, Conductive pigment, Waterborne epoxy resin, Oil tank

Introduction

Fires and explosions have been mainly attributed to electrostatic discharges (ESD) in explosives industry and some hazardous industrial situations.¹ The accidents of static electricity in petrochemical industry frequently occur in the world. During the years between 1960 and 1975, there were 116 accidents of fires and explosions by electrostatic discharges in the American petrochemical industry.² Data from Sino-

Petrochemical Corporation in the 1980s shows that more than 20 serious accidents by ESD occurred in the last 10 years in China, and eight of them were explosion accidents, which were induced by static electricity in oil tanks.³ Obviously, oil tanks are the main areas that gather static electricity and may induce explosion accident in petrochemical industry.

Recognizing the ESD hazard that exists in petrochemical industry and other explosives industry, countries all over the world have started to establish and execute the electrostatic protection control standards.⁴ After having accumulated much experience for several years since 1970s, the America Military Department constituted DOD-STD-1686 “ESD Control Program for Protection of Electrical and Electronic Parts, Assemblies, and Equipment” in 1980. In order to put this ESD Control Program into practice, America Military Department constituted DOD-HDBK-263, at the same time, which is a controlling plan notebook of establishing, implementing, and monitoring electrostatic discharge. The current authentic edition is MIL-HDBK-263B.⁵ While the establishment and promulgation of ESD standards in China^{4,6} started in the middle of the 1980s, more than ten kinds of national standards and industry standards were established referring to the relational standards from abroad. The concept of “Electrostatic Hazardous Areas” was defined for the first time in 1995 and classified protective technical grades and measures were put forward. But the amount and quantity of Chinese ESD standards cannot meet the rapid development of electrostatic protective engineering in China, and need to be supplemented.

In order to ensure the safe operation of oil tanks, the inner wall of oil tanks should be coated with antistatic and anticorrosive coatings, which can prevent the corrosion of the oil tanks, restrain the generation of static charges, and accelerate releasing charges in the inner wall of oil tanks. The characteristics of materials

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which can protect ESD are dependent upon factors such as resistivity, decay time, and triboelectric properties. The similarities and differences between Chinese standards and overseas standards about antistatic and anticorrosive coatings are shown in Table 1.

According to China National Standard GB13348-1992, “Liquid Petroleum Product Static Safety Rules,” the volume resistivity of the antistatic and anticorrosive coatings for oil tanks should be lower than $10^8 \Omega \text{ m}$ and the surface resistivity should be lower than $10^9 \Omega$. As for oil tanks that are usually grounded on different parts of the outside of the tank body or directly built on the ground, the antistatic coating needs to bleed the charge through the coating to the underlying metal and the volume resistivity is the controlling factor for the antistatic property.

The electrical conductivity of the coatings increases greatly by using antistatic agents, conductive pigments (including metal or nonmetallic oxides, graphite, carbon black, and so on), and intrinsically conductive polymers in organic polymer coatings. Different types of composite antistatic coatings have been prepared.⁷⁻⁹ Antistatic and anticorrosive coatings of carbon system have already been widely used in China;¹⁰ however, the bad adhesion and oil resistance, black color, the carbon pigments easily escape from the film and pollute the oil, and the organic solvent evaporation results in many problems to their application in oil tanks. The inherent conductive polymers such as polyaniline, polypyrrole, and polythiophene used as conductive pigments in antistatic and anticorrosive coatings⁹ have been manufactured in the Western countries, but their application was limited because of the complex preparation processes and high cost. So in the present antistatic coating market, composite antistatic coatings with conductive pigments held the largest position.

The antistatic property of composite antistatic coatings depends on the connection of conductive pigments. Percolation theory^{11,12} can describe the connectivity properties of large numbers of objects which individually have some spatial extent, and for which their spatial relationships are relevant and statistically prescribed. Percolation theory comes in three basic varieties: bond, site, and continuum. A

continuum percolation problem had received attention in the 1970s in a network of sintered glass and metallic particles. Such networks have analogues in the xerox industry. If the detailed structure is known, the percolation theory can predict the electrical conductivity of the system.

The volume concentration or volume fraction of dispersed pigmentary solid phase in the polymeric binder of organic coating is normally defined as the pigment volume concentration (PVC), which has great effect on the protective performance and physical properties of coatings.^{13,14} As the concentration of pigment particles in a polymeric matrix increases, those particles start touching others and forming multiplsets, rather than staying as singlets. This onset of clustering occurs at very low concentration, typically less than 5% PVC, when the shape of particles is nodular. As the concentration increases further, eventually those aggregates reach a sufficient size that at least one of them spans the thickness dimension of the film, then the coatings will have conductivity property. This is called the initial of percolation (or percolation threshold), which usually occurs at PVC about 15–25%. When the PVC value eventually reaches the point of phase inversion between pigment particles and resin matrix, that value is the point of critical PVC (CPVC). CPVC usually occurs at PVC about 50–60%. Beyond CPVC, the porosity of the films increases abruptly and exponentially. Below CPVC, the porosity is relatively low and increases very slowly with the increasing of PVC.

The shape of pigments also has effect on the PVC of each transition. If the pigments are platy, such as mica or lamellar zinc, the PVC of each transition will be substantially lower. According to the studies^{15,16} the dependence of coating properties on the lamellar zinc concentration exhibits a completely other course than that obtained by using the spherical zinc. The transition of some performances such as hardness, impact resistance, and resistance with cupping occurred at lower lamellar zinc concentrations, where a rapid reduction takes place. People commonly use platy pigments when they want antistatic behavior at low PVC without the loss of film integrity that occurs below CPVC.

Table 1: Similarities and differences between Chinese standards and overseas standards about antistatic and anticorrosive coating

Country	Standard	Coating resistivity	Testing method
USA	MIL-HDBK-263B	$10^5 < \rho_s < 10^{12} \Omega$	ASTM D 257
China	GB13348-1992	$10^2 < \rho_v < 10^9 \Omega \text{ m}$ $\rho_s < 10^9 \Omega$	GB/T 16906-1997 ^a
China	GB 6950-2001 ^b	$\rho_v < 10^8 \Omega \text{ m}$	ASTM D 257
China	GB 15599-1995	$10^5 < \rho_s < 10^9 \Omega$ $\rho_s < 10^9 \Omega$	GB/T 16906-1997

^a GB/T 16906-1997 is referred to ASTM D 2624-94a

^b GB 6950-2001 is referred to API.RP.2003 (The standard named “Protection against Ignitions Arising out of Static, Lightning, and Stray Currents”, established by American Petroleum Institution)

But it should be pointed out that antistatic behavior is quite different from conductive behavior of conductive materials. According to MIL-HDBK-263B,⁵ ESD protective materials can be divided into conductive and dissipative materials, based upon ranges of material resistivity. By the definition, a conductive material has a volume resistivity of less than $10^4 \Omega\text{cm}$ or a surface resistivity of less than $10^5 \Omega$, and a static dissipative material has a volume resistivity of 10^4 – $10^{11} \Omega\text{cm}$ or a surface resistivity of 10^5 – $10^{12} \Omega$.

It can be concluded that antistatic behavior is usually associated with the systems which are above their percolation thresholds, but far less than the CPVC. Such antistatic coatings would still retain their physical properties, while readily dissipating static charges. In this article, light color conductive pigments such as conductive mica and conductive titanium dioxide, which have excellent resistance to chemical medium and anticorrosive performance, were used in waterborne epoxy resin system. A light color antistatic and anticorrosive waterborne epoxy coating was prepared and the antistatic and anticorrosive properties of the coating were discussed. The environmental friendly antistatic and anticorrosive coating has excellent antistatic behavior, while retaining an outstanding anticorrosive and decorating performance, and can satisfy the requirements for using in the inner wall of oil tanks.

Experimental

Materials

Conductive mica A, B, C, and D were prepared by coating a layer of conductive metal oxide including In_2O_3 and SnO_2 on mica natural mineral from China. Conductive titanium dioxide E were commercial products of China prepared by coating a layer of conductive metal oxide including In_2O_3 and SnO_2 on titanium dioxide. And the powder resistivities of the five kinds of conductive pigments are shown in Table 2, which were provided by the supplier.

Composite Ferrotitanium anticorrosive pigment WD-D 500 was obtained from Wanda Science and Technology Co. Ltd (China, Wuxi), prepared by introduction several kinds of nano-powders into polyphosphates of ferrum and titanium. Ferric Oxides were provided by Bayer Corporation (Germany). Titanium

dioxides were provided by Shangdong Dongjia Corporation (China).

Four kinds of commercial waterborne epoxy resin, a, b, c, d, and their curing agents (China), were used as film-forming material for comparison. Their composition descriptions are shown in Table 3.

Formulation of waterborne epoxy antistatic anticorrosive coating

The formulations of waterborne epoxy antistatic anticorrosive coating, primer, and topcoat are different, which are shown in Table 4. Ferric oxide was chosen for primer, while titanium dioxide was applied in topcoat to get the light color and good covering ability. The conductive pigment in primer and topcoat is the same, the pigment volume concentration is 25% below the CPVC of this pigment system, and the conductive pigment volume percent changes from 0% to 50%.

Characterization

Particle size distribution and other particle properties of five kinds of conductive powder were characterized by LS13320 Laser Particle Diameter Analyzer (Beckman Coulter Company, U.S.A). Their morphology was characterized by Leica USD28500 optics microscope (Germany) and XL30 Scanning electron microscopy (SEM) (Philips Corporation, Holland). The fractured surfaces of coatings with different pigment volume concentrations were also characterized by XL30 SEM.

Preparation of coatings

According to the coating formulation, anticorrosive pigments and waterborne coating additives (such as dispersing agent, wetting agent, and so on) were added into water. The mixture was mixed at high-speed stirring for 30 min, ensuring the size of the particles was lower than 50 microns. Then the conductive pigments were added and stirred mildly for 20 min, and a kind of conductive slurry was obtained. The conductive slurry and waterborne epoxy resin were mixed together homogeneously. Other additives such as antifoaming agent, leveling agent, corrosion inhibitor, thickener, and rheology modifier were added into

Table 2: Comparison of five kinds of conductive pigments

Conductive pigments	A	B	C	D	E
Type	Conductive mica	Conductive mica	Conductive mica	Conductive mica	Conductive titanium dioxide
Powder resistivity (Ωcm)	36	43	40	48	96

Table 3: Comparison of the commercial waterborne epoxy resin

Item	Composition description	Epoxy equivalent (g/mol)	Amine value (mg of KOH)
Epoxy resin a	Low-molecular weight bisphenol a epoxy emulsion	210	–
Curing agent a	Modified amine	–	135
Epoxy resin b	Low-molecular weight bisphenol a epoxy emulsion	420	–
Curing agent b	Alicyclic amine	–	270
Epoxy resin c	High-molecular weight solid epoxy aqueous dispersions	480	–
Curing agent c	Modified amine	–	270
Epoxy resin d	High-molecular weight solid epoxy aqueous dispersions	520	–
Curing agent d	Aliphatic amine	–	335

Note: The order of molecular weight of waterborne epoxy resins is $d > c > b > a$, which were provided by the suppliers.

Table 4: Formulation of waterborne epoxy antistatic anticorrosive coating

Coating cord	Coating type	Waterborne epoxy resin/its curing agent	Conductive pigment	Anticorrosive pigments	Pigment volume concentration (%)
P-x-Y-z	Primer	x	Y	Composite ferrotitanium pigment and ferric oxide	25
T-x-Y-z	Topcoat	x	Y	Composite ferrotitanium pigment and titanium dioxide	25

Note: (1) x = a, b, c, and d denote the type of waterborne epoxy resins and their curing agents respectively, which have been described in Table 3; (2) Y = A, B, C, D, and E denote five kinds of conductive pigments respectively in Table 2; (3) z = 1, 2, 3, ... n (n = positive integer) is responding to the changing of conductive pigments volume concentration, when the conductive pigments volume concentration increase once, the value of z will augment one. The detail relationship of z and the corresponding conductive pigments volume concentration are shown in Table 5.

the mixture, keeping stirring mildly for 10 min, then component A of waterborne epoxy antistatic anticorrosive coating was obtained. The component A and its curing agent (component B) were mixed together homogeneously in the practice.

Testing of coatings

The volume resistivities of coatings were tested according to ASTM D 257 by using PC27-7H Ohmmeter (Guangzhou Yijie Architectural Materials Company, China). Carbon steel with a nominal thickness of 0.8 mm was used as the substrate in the corrosion tests. Corrosion tests were performed in water, acid (5 wt% H_2SO_4), alkali (5 wt% NaOH), NaCl (5 wt%), and 90 # gasoline by the placement of samples in 3-in. diameter porcelain dishes in the aforementioned media. Samples with dimension of 120 x 50 mm² were machined for the corrosion resistance. Tin plates with dimension of 120 x 50 x 0.28 mm³ were used as substrates for the bending test (ASTM D 3281-04), adhesion test (ASTM D 3359-93), and impacting resistance test (GB/T 1732-93, China). All the

substrates were prepared according to ASTM D 1653. The coating and its curing agent are mixed together according to the ratio proportion and applied to the substrate after curing for 30 min. All tests were performed after 7 days to ensure that the coatings were completely dry.

Results and discussion

Antistatic mechanism of the coating

The antistatic mechanism¹⁷ of coating is based on the contacting of conductive pigment particles with each other, and thus forming a consecutive chain in the coating system. The electrostatic charges can transfer freely on the chain and consequently the film becomes static dissipative. Before the curing of antistatic coating, the conductive pigments are independent and cannot have contact with each other in the resin. However, after the resin has been cured and dried thoroughly, the resin and conductive pigments are mixed together, and the conductive pigments contacted with each other, forming an electrostatic conductive

network to make the film electrostatic conductive and static dissipative. The antistatic property of coating is influenced by many factors, such as the type, shape, amount and dispersion of conductive pigments, the type of resin, and the properties of additives.

When the volume concentration of conductive pigments is lower than the critical pigment volume concentration for forming the electrostatic conductive network, that is called percolation threshold; the pigments are separated, thus the film does not have antistatic property. However, when the volume concentration of conductive pigments exceeds the percolation threshold, the pigment particles contact with each other and the electrostatic conductive chains are formed. The antistatic mechanism of the film is shown in the SEM figure (Fig. 1). Electrostatic conductive chain is not formed in the film (Fig. 1A) with conductive pigment volume concentration of 4.4% under the percolation threshold, while it is formed in the film (Fig. 1B) with conductive pigment volume concentration of 13.3% above the percolation threshold.

Influence of the conductive pigments on the antistatic properties of coatings

Effects of the type and content of conductive pigments on antistatic property

Conductive pigment is the important component of antistatic coating. In this experiment, different types, shapes, and content of conductive pigments were chosen for preparing the antistatic and anticorrosive coatings. The influence of the type and content of conductive pigments on antistatic property of the films is listed in Table 5.

When the volume concentration of conductive pigments is lower than percolation threshold, the volume resistivity of the films approaches the volume resistivity of pure polymer, and there is little variation of volume resistivity with the increasing of the conductive pigments concentration. However, when the conductive pigments concentration reaches to percolation threshold, the volume resistivity of the

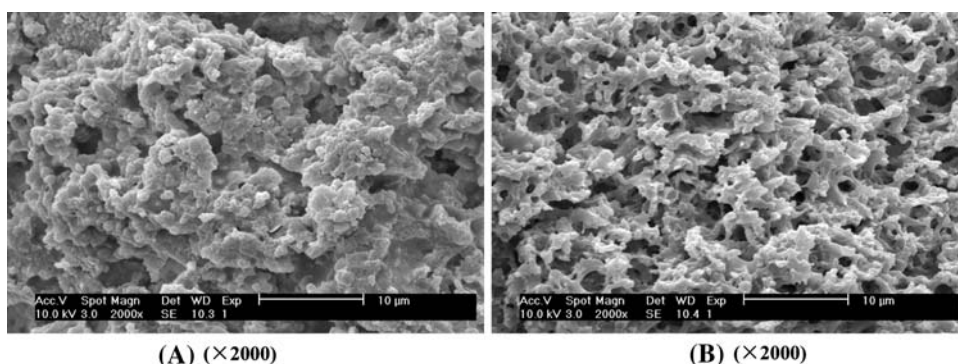


Fig. 1: SEM figures of antistatic mechanism of film: (A) Unformed electrostatic conductive chain; (B) Formed electrostatic conductive chain

Table 5: Effects of the type and concentration of conductive pigments on resistivity of the film

Coating cord	Conductive pigment volume concentration (%)	Conductive pigment weight concentration (%)	Volume resistivity (Ω m)				
			A	B	C	D	E
P-a-Y-1	0	0	$\geq 10^{11}$	$\geq 10^{11}$	$\geq 10^{11}$	$\geq 10^{11}$	$\geq 10^{11}$
P-a-Y-2	2.2	5	$\geq 10^{11}$	$\geq 10^{11}$	$\geq 10^{11}$	$\geq 10^{11}$	$\geq 10^{11}$
P-a-Y-3	4.4	10	$\geq 10^{11}$	$\geq 10^{11}$	$\geq 10^{11}$	$\geq 10^{11}$	$\geq 10^{11}$
P-a-Y-4	6.6	15	$\geq 10^{11}$	$\geq 10^{11}$	$\geq 10^{11}$	$\geq 10^{11}$	$\geq 10^{11}$
P-a-Y-5	7.9	18	10^8	10^8	10^9	$\geq 10^{11}$	$\geq 10^{11}$
P-a-Y-6	8.8	20	10^8	10^8	10^8	$\geq 10^{11}$	$\geq 10^{11}$
P-a-Y-7	10.1	25	10^8-10^7	10^7	10^8	10^9	$\geq 10^{11}$
P-a-Y-8	12.3	28	10^7-10^6	10^7-10^6	10^8-10^7	10^8	$\geq 10^{11}$
P-a-Y-9	13.3	30	10^6-10^5	10^6	10^7-10^6	10^8-10^7	$\geq 10^{11}$
P-a-Y-10	15.4	35	10^5-10^4	10^6-10^5	10^6-10^5	10^7	$\geq 10^{11}$
P-a-Y-11	17.6	40	10^4	10^4	10^5	10^6	10^9
P-a-Y-12	22.7	50	10^4	10^4	10^5	10^6	10^8

film decreases sharply. Similarly, further increasing of conductive pigments content will not have obvious effect on the conductive property of the films.

The antistatic property of the film prepared by conductive pigments is determined by their density, their particle diameter distribution, and their resistivities. From the results of Table 5, the percolation thresholds of the five conductive pigments are listed as follows, respectively (the conductive pigment volume percent of total solids): A, 7.9%; B, 7.9%; C, 7.9%; D, 10.1%; E, 17.6%. From the data given in Table 2, it can be seen that the differences of volume resistivities of conductive pigments are not distinct, and the volume resistivities of A, B, and C are lower than others. And the percolation threshold of A, B, and C is lower than D and E.

The percolation threshold of conductive titanium dioxide E is much more than that of conductive mica when getting the same antistatic property. The first reason is that the density of conductive titanium dioxide is larger than conductive mica so the amount to forming conductive chain is much larger; secondly, the conductive mica, which has flake shape and bigger surface area, is easier to form electrostatic conductive chain.

Influence of particle shape, diameter, and diameter distribution of conductive pigments on antistatic property

The shape, particle diameter, and diameter distribution of conductive pigments have great influence on the antistatic property of coatings. The SEM micrographs of the conductive pigments are shown in Fig. 2 and the particles diameter distribution graph of the conductive

pigments are shown in Fig. 3, respectively. The shape and particle diameter size and coating properties of the five kinds of conductive pigments are listed in Table 6.

From Table 6 and Fig. 2, it can be seen that conductive pigment E has a nodular shape, which has only three contacting midpoints with smaller aspect ratio. So it is harder to form contacting chain in the film. As shown in Fig. 3, there are four sharp peaks in the diameter distribution curve of conductive pigment E with the highest polydispersity index, indicating the bad particle size distribution in the film. The antistatic property of its film is the poorest, which has been confirmed in Table 5.

From Fig. 2, it can be seen that conductive mica A, B, C, and D have flake shape with more contact points. They are easy to contact with each other to form

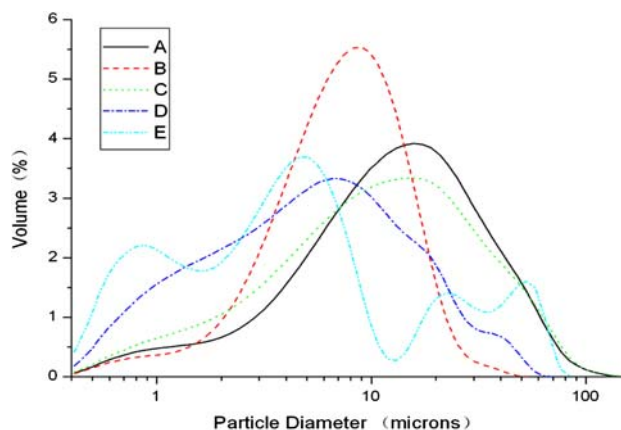


Fig. 3: Particle diameter distribution curves of conductive pigments

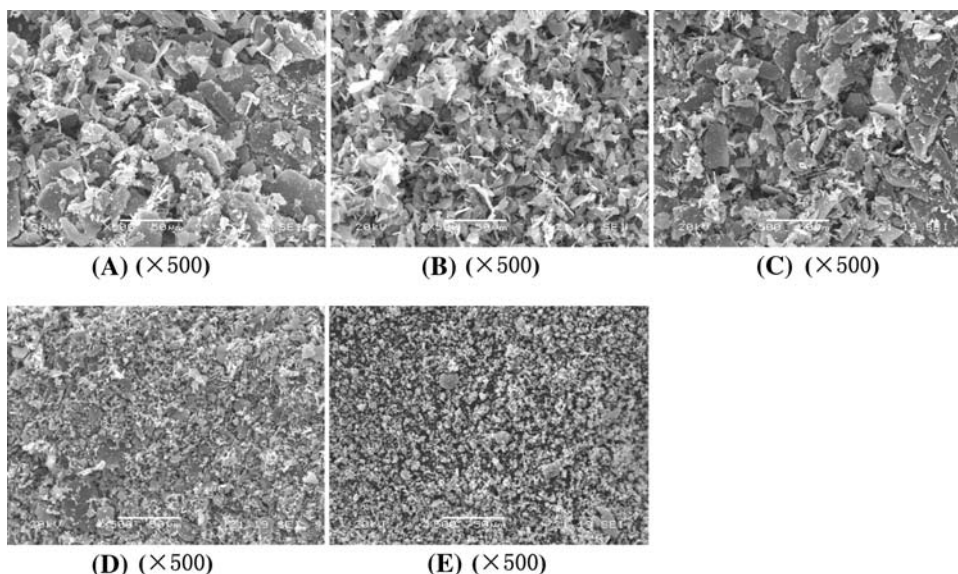


Fig. 2: SEM micrograph of five kinds of conductive pigments

Table 6: Shape and diameter of the five kinds of conductive pigments

Item	A	B	C	D	E
Particle shape	flake	flake	flake	flake	nodular
Aspect ratio ^a	2.07	2.53	1.89	2.58	1.65
Median diameter (microns) ^b	12.40	7.01	10.57	5.03	3.83
Mean diameter/volume average diameter(microns) ^b	16.96	8.10	15.93	7.92	9.84
Polydispersity index ^b	1.368	1.155	1.507	1.575	2.572
Number of modes in distribution curve ^b	3	2	4	4	4
Mean of each mode (microns) ^b	0.84, 15.65, 40.12	0.80, 8.94	1.20, 7.80, 15.65, 39.98	0.80, 6.76, 18.28, 42.50	0.87, 4.65, 22.73, 52.63
Conductive pigment weight solids at transition (%)	18	18	18	25	40
Conductive pigment volume concentration at transition (%)	7.9	7.9	7.9	10.1	17.6
Percolation threshold for pigment system (%)	7.9	7.9	7.9	10.1	17.6
PVC for pigment system (%) ^c	25	25	25	25	25
Critical PVC for pigment system (%) ^d	35	35	35	35	35

Note: ^a Aspect ratio (ratio of longest length/thickness) were tested by USD28500 optics microscope

^b Median diameter, mean diameter (volume average diameter), polydispersity index (was characterized by ratio of mean diameter to median diameter), number of modes in distribution curve and mean of each mode were all obtained from the analyzing results of LS13320 Laser Particle Diameter Analyzer

^c The PVCs for pigment system are calculated by the amount and density of each component in the coating

^d The Critical PVCs for pigment system are calculated by the formula in reference (18)

electrostatic conductive chain and have better dispersion performance in the waterborne epoxy coating. The mean diameters of A and C are near, and the mean diameters of B and D are much smaller. From Table 6 and Fig. 3, we can see that the number of peaks and the polydispersity index of B are the smallest and that of A are the second, and the diameter distributions of C and D are wider than A and B. According to the results of Table 5, the conductive pigment B has the best conductive performance and pigment A is the second one; however, the price of B is very high. Considering the ratio of performance to price, A was chosen as the conductive pigment in this experiment.

Effect of film thickness on the volume resistivity of the film

Effect of film thickness on the volume resistivity of the film is shown in Fig. 4.

It can be seen from Fig. 4 that the antistatic performance of the film improved as the film thickness increased. It is reasonable that the sediment pigments in the coating will be increased as the film thickness increases, and form much more completely electrostatic conductive chain, so the volume resistivity will be decreased as the film thickness increases. But for further increase of the film thickness, there is no

obvious variation of the volume resistivity, because the conductive chain formed is integrated and compact, so the thickness has no effect on the volume resistivity. As the thickness of the coating is just under the percolation threshold, the volume resistivity of the film can actually decline with the increase of the film thickness, because thicker film can offer additional chances for a random chain to actually span the thickness of the film by allowing greater degrees of torturous pathways to connect. Essentially, increasing film thickness has the effect on reducing the percolation threshold of the coating.

Effect of curing temperature on the volume resistivity of film

From Fig. 5, it can be seen that when the temperature is low, the curing activity of waterborne epoxy coating is very low and the film is not formed completely. The conductive particles in the film cannot contact with each other and so the volume resistivity is high. With the increasing of temperature from 10°C to 30°C, the curing activity of waterborne epoxy coating increased, the reaction between waterborne epoxy resin and its curing agent became sufficient. The curing of film makes the volume of film become shrunken and the distance between conductive particles in the film become nearer and they can contact much more

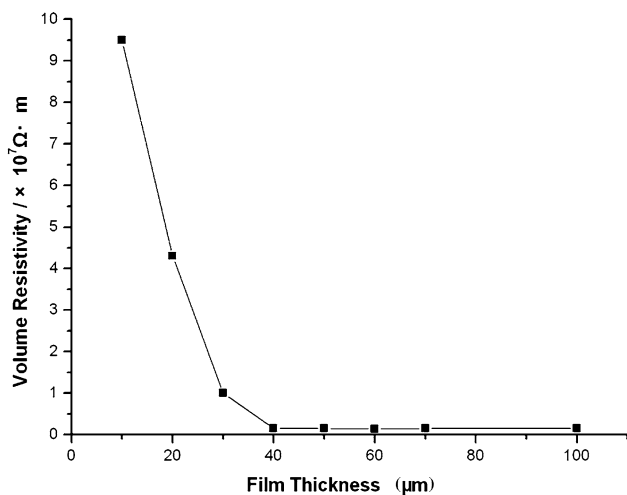


Fig. 4: Effect of film thickness on the volume resistivity of the film

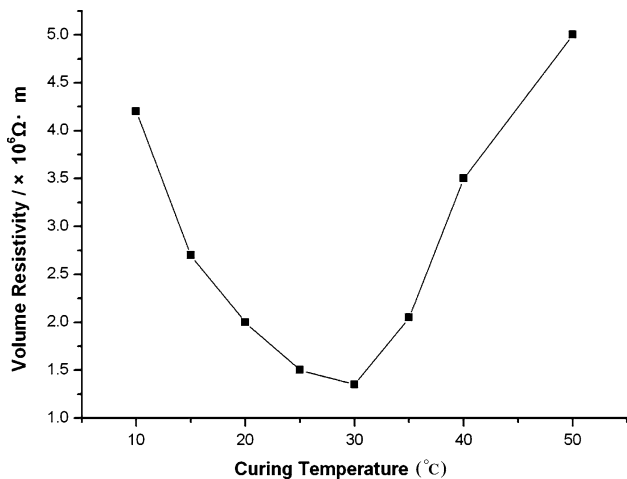


Fig. 5: Effect of curing temperature on the volume resistivity of film

sufficiently and so the volume resistivity decreases. As the curing temperature increases further above 30°C, the volatilizing of water from the film happens more quickly and a lot of pinholes will be formed in the film even though the curing activity of waterborne epoxy coating increased too. The pinholes make the film become porous and the conductive chain become incomplete. So the volume resistivity of film starts to increase. At 30°C both the volatilizing speed of water and the curing activity of waterborne epoxy coating are suitable, the conductive chain forming in the film is completed, and so the volume resistivity is the lowest.

Effect of curing time on the volume resistivity of film

The curing time has effect on the coating performance. After having been cured and crosslinked completely at

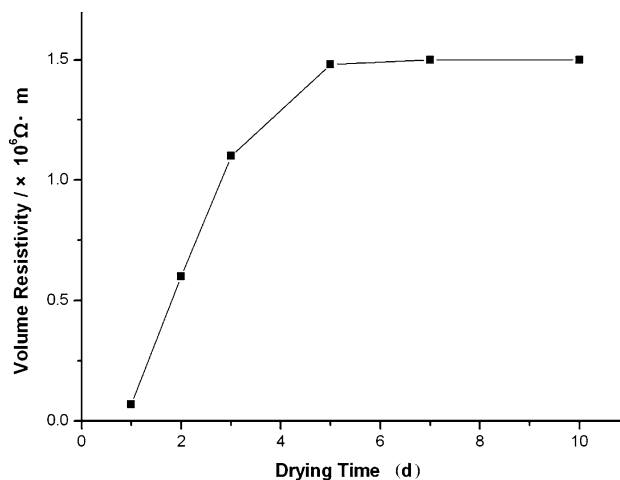


Fig. 6: Effect of curing time on the volume resistivity of film at 25°C

25°C, the antistatic anticorrosive coating shows good physical and chemical performance and steady antistatic performance. From Fig. 6, it can be seen that the volume resistivity increases continually with the increasing of curing time and the volume resistivity value becomes a constant after curing for 5 days at 25°C.

Influence of film-forming material

In the antistatic anticorrosive coating, the matrix resin should have excellent anticorrosive and antistatic performance, good film-forming performance, adhesion, durability, and other traditional performances. Besides, the matrix resin should have good affinity and wetting performance for conductive pigments and additives. The epoxy resin was chosen as the matrix resin, because it has good toughness, adhesion, resistance to acid, alkali, and various kinds of organic solvent, and it shows good conductive performance after adding conductive pigments.

In waterborne systems, the selection of curing agent has great influence on the performances of the coating. The popular commercial waterborne curing agents for epoxy resin are amine (including aliphatic amine and alicyclic amine), modified amine and polyamide, which have been mentioned previously. The volatility of modified amine curing agent^{10,19} has been decreased greatly and its resistance to oil and corrosion has been improved, the weakness of poisonous amine curing agent has overcome by changing its molecule structure. The resin curing by polyamide¹⁹ has excellent adhesion and good compatibility, but has a weakness of bad impacting resistance and too quick curing speed, which restrict its application in oil tanks. There are also other curing agents for epoxy resin, such as poly amido-amine, thiols, isocyanates, and so on. Poly amido-amine is a new type curing agent with the dendritic

structure,²⁰ and has high density of amino groups, which is expected to be a new effective curing agent for resin systems. But this curing agent has only been prepared in laboratory in China and not been put into production, almost purchased from abroad. Thiols and isocyanates also can be used for curing waterborne epoxy resin, but are not popular in the Chinese market. Thiols curing agents²¹ can be used for the quick curing of water epoxy resin at around 25°C, which are applied in adhesives more than coatings (most are purchased abroad). Isocyanates curing agents are usually applied in waterborne low-temperature curable cathodal electrophoretic epoxy coatings.²² Considering the price, performance, and the applying condition of the coating in practice, a modified amine curing agent was chosen in this experiment.

There are four kinds of waterborne epoxy resins and their curing agents are listed in Table 3. Their performances are compared and the results are shown in Table 7 by using conductive mica A as conductive pigments with the volume concentration of 13.3%.

According to Table 3, epoxy resin c and d with higher molecular weight have long molecular chain and large number of hydroxide groups and methyl groups, which provide good adhesion and flexibility, but the hydrophilic property of hydroxide groups and the low degree of crosslinking leads to bad resistance chemistries. On the contrary, epoxy resin a and b has low molecular weight with high density of epoxy groups and the performances of coatings were reversed. The alicyclic groups in curing agent b make the cured epoxy resin b have high rigidity, but with bad bending ability and impacting resistance. From Table 7, it can be seen that the epoxy resin system a cured by modified amine has the best combined properties, which is suitable to be the matrix resin in this coating system.

Influence of anticorrosive pigments

The coating¹⁸ can protect metal substrates from corrosion via the electrochemical mechanism, inhibiting corrosive reactions by sharing an anticorrosive

pigment in the passivation of the metal, forming stable and strongly adhesive layers on the substrate, or via the barrier mechanism, inhibiting the access of corrosive environmental agents to the metal surface, which mainly depend on the pigmentation and to the chemical structure and the barrier properties of the binders. And these two mechanisms do not act separately.

Pigments in coatings could play many different functions, such as supplying color or enhancing their chemical or physical strength. And anticorrosive pigments increase the resistance of metal surfaces to corrosion. The inhibitor action of anticorrosive pigments takes place in different ways;²³ for example, some inhibitor pigments act by improving the barrier properties of the coating, and these kinds of pigments have a physical activity, in which they separate the metallic substrate from the corrosive medium such as water, oxygen, and electrolyte. Other pigments show a chemical activity and can be classified in four groups according to their mechanism of action. Firstly, some pigments decrease the rate of anodic reaction by binding the metal ions produced by corrosion reactions, and as a consequence, coordination compounds are formed at anodic zones. Secondly, some pigments decrease the activity of both anodic and cathodal processes by liberating passivating ions. A third kind of pigment reacts with the resin, and generates a compounds which decreases metal corrosion. The last kind of pigment acts by increasing the concentration of OH⁻ ions in water diffusing through the porous paint. In steel, the increase of pH decreases the activity of metallic corrosion processes.

The light color conductive mica or titanium dioxide (TiO₂) pigments can not only enhance the conductive property, but also the chemical resistance and durability of the antistatic coating for the excellent conductive and chemical stability of indium and tin oxide coatings on them. In this experiment, we chose three kinds of pigments for use in antistatic and anticorrosive coating system except the conductive pigments.

Composite ferrotitanium²⁴ is based on several kinds of phosphates, prepared by compositing with silicon-based, titanium-based, iron oxides-based, yttria and

Table 7: Performance comparison of four kinds of epoxy resin

Item	Coating cord			
	P-a-A-9 ^a	P-b-A-9 ^a	P-c-A-9 ^a	P-d-A-9 ^a
Waterborne epoxy resin system	a	b	c	d
Impact resistance (Kg cm)	50	40	50	50
Bending ability (1/4 in.)	Pass	Fail	Pass	Pass
Adhesion (grade) ^b	1	2	1	2
Volume resistivity (Ω m)	10 ⁶	10 ⁶	10 ⁶	10 ⁷
Salt solution resistance (5% NaCl, 70d)	ok	ok	A lot of blisters	A lot of blisters

Note: ^a When z equals to 9, the conductive pigment volume concentration of coating with the cord of P-x-Y-z (x = a, b, c, d; Y = A) is 13.3% and the conductive pigment weight concentration is 30%, corresponding to Table 5

^b The adhesion of coating is characterized by grades. The numbers of grade change from 0 to 5. As the number increase, the adhesion ability of coating becomes poorer

other nanometer powders. One of its anticorrosive mechanism is based on that the phosphates react with iron molecule on the steel surface to generate iron phosphate complexes, which adhere to the surface of steel firmly, then a passivating film is formed which could prevent the electrochemistry corrosion in the steel surface. And the nanometer materials in it make the film smooth, compact, and the barrier performance inhibit the eroding of H₂O, Cl⁻, and O₂ to steel substrate. The anticorrosive function of composite ferrotitanium is based on both electrochemical mechanism and barrier mechanism. In this experiment, the composite ferrotitanium, which combined with ferric oxide, was used in the primer and the composite ferrotitanium, which combined with titanium dioxide, was used in the topcoat.

Ferric oxide can improve the compactness of film, decrease its penetrability, and prevent the penetration of water and oxygen, which was used in primers below the CPVC, because when the coating PVC is above CPVC, many pores would be introduced into the film and the corrosion resistance would decline precipitously.

In this experiment, TiO₂ pigments have good covering power and color ability, which makes it easy to obtain light color and used to be applied in surface coating, satisfying the requirements of using light color antistatic coating in the inner wall of the oil tank, in order to test the inner film conveniently. The surface of TiO₂ pigments have been deposited by solid coatings of SiO₂ for durability and chemical resistance and the porous coatings of Al₂O₃ on top of the silica for dispersability and whiteness. The durability and chemical resistance of antistatic coating have been enhanced.

Characterization of the combined properties of coating

The antistatic and anticorrosive coating should have excellent combined properties including not only antistatic ability but also anticorrosive performance. The protective coating applied in practice usually is the composite coating system including two coats of primer and two coats of topcoat. The combined properties of primer, topcoat, and the composite coating system with the thickness of 200 microns are listed in Tables 8 and 9.

It can be seen from Tables 8 and 9 that the single coating of primer and topcoat possess excellent physical properties (such as adhesion, bending ability, impact resistance) and antistatic performance. And the composite coating system has excellent anticorrosive property with good antistatic performance, which can be applied in practice to protect the oil tanks.

Conclusions

The influence of type and the amount of conductive pigments, the film thickness, the curing temperature,

Table 8: Properties of waterborne epoxy antistatic anticorrosive primer and topcoat

Item	Coating cord	
	P-a-A-9	T-a-A-9
Coating type	Primer	Topcoat
PVC (%)	25	25
Conductive pigment volume concentration (%)	13.3	13.3
Color	Red	Light gray
Adhesion (Grade)	1	1
Bending ability (1/4 in.)	Pass	Pass
Impact resistance (Kg cm)	50	50
Volume resistivity (Ωm)	10 ⁶	10 ⁷

Table 9: Properties of composite coating

Item	Composite coating
Acid resistance (5% H ₂ SO ₄ water solution)	22d ok
Salt solution resistance (5% NaCl water solution)	70d ok
Alkali resistance (5% NaOH water solution)	70d ok
Solvent resistance (90# gasoline)	70d ok
Water resistance	70d ok

and time on the volume resistivity of film were discussed. After curing for more than 5 days at 30°C, the film got the optimal antistatic performance with the lowest volume resistivity. As the volume concentration of conductive pigment B reaches 13.3%, the volume resistivity of the film decreases to 10⁶ Ωm in primer and 10⁷ Ωm in topcoat. The behaviors of several kinds of waterborne epoxy resin were compared and the curing mechanism was analyzed. Using waterborne epoxy resin as the main film-forming material, light color waterborne antistatic anticorrosive coating with volume resistivity of 10⁶ Ωm and excellent corrosion protective and ornamental behavior was prepared by adding light color conductive pigments and anticorrosive pigments, which can be applied to protect the oil tanks.

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