Effect of curing agent content on properties of zinc-rich epoxy primer nano-coating

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Abstract. In this paper, properties of zinc-rich epoxy primer nano-coating affected by the curing agent content were researched, which is one of the heavy-duty anticorrosive coating system, including the viscosity, applying time, bonding strength, hardness and corrosion resistance. So as to optimize coating system, shorten process and increase benefits. Results indicated that the viscosity decreased, the applying time shortened, and the drying time curtailed with the dosage of curing agent increment. And the bonding strength and the micro hardness of the cured coating increased first and then decreased. Furthermore, the coating corrosion resistance could be reduced due to the excessive curing agent to some extent.

1. Introduction

With the enhancement of people's awareness of environmental protection, higher requirements are put forward for the safety of the disposal of some toxic substances. Using metal containers to store and then bury those materials is the general way [1, 2]. And in order to protect metal vessels from corrosion in buried media effectively, a heavy-duty anticorrosive coating system with excellent corrosion resistance has been developed, compositions are listed in Table 1 [3]. Among them, zinc-rich epoxy nano-paint is the primer, which consists of conductive zinc micro and nano-level powder posed as filler, modified epoxy resin served as binder, and polyamide and amine additives acted as curing agent. A continuous and compact coating is formed on the metal surface contacts with substrate closed. It is widely used for its dual protection of cathodic protection and shielding, because the potential of conductive zinc powder is lower than that of steel which lead zinc is corroded first[4].

Table 1. Compositions of heavy-duty anticorrosive coating system

| Composition                              | Thickness(μm) |
|------------------------------------------|---------------|
| Zinc rich epoxy primer nano-coating      | 80            |
| Sealing epoxy primer nano-coating        | 60            |
| Stainless steel flakes epoxy intermediate nano-coating | 120          |
| Sealing epoxy finish nano-coating        | 120           |
| Total thickness                          | 380           |

Previous practical construction experience showed that increasing the amount of curing agent could shorten the drying and curing time of coatings under the same ambient temperature and humidity.
According to the basic curing principle of organic coatings, cross-linking reaction between curing agent and resin to produce structurally stable cross-linked products [5, 6], therefore, the amount of curing agent could affect the curing process of coating and the properties of coating after film-forming [7, 8]. Based on the standard addition of curing agent for practical construction, influences of the content of curing agent on the viscosity, application time, hardness, adhesion, drying time and corrosion resistance of zinc-rich epoxy primer nano-coating were studied, which provided references for optimizing coating system, shorten construction period and raise project benefit.

2. Experiment

2.1. Materials and preparation of samples
Low carbon steel was selected as the substrate, and size were designed to be 100mm×60mm×6mm and 10mm×10mm×6mm, which were used as macroscopic and electrochemical samples, respectively. After cleaning by acetone and sandblasted to Sa2.5 level, zinc-rich epoxy primer with 120μm thickness was prepared on the surface of the samples by the coating machine with different curing agent contents of 1, 1.5, 2.5 and 3 times to the standard measure. Macroscopic specimens were coated on two working surfaces of 100mm×60mm for testing coating properties, and the electrochemical samples were coated on single 10mm×10mm working face with wires welded on the back and epoxy resin sealed off on the non-working face.

2.2. Measurements
Viscosity of coating was measured by coating-4 viscometer, bonding strength was measured by Hydraulic Adhesion Tester, and micro-hardness was generated by HVS-1000Z automatic turret digital display micro-hardness tester loaded as 0.098N. PARSTAT 2273 electrochemical workstation was adopted to electrochemical testing with three-electrode electrolytic cell. The reference electrode was saturated calomel electrode, the auxiliary electrode was carbon rod, and the test medium was 3.5% NaCl solution. The test temperature stabled at room temperature, the sinusoidal wave with amplitude of 5 mV was used and the test frequency ranged from 10 mHz to 100 kHz.

3. Results and discussions

3.1. Effect of curing agent content on the coating viscosity
According to the GB/T1723-93 "Coating Viscosity Measurement Method", Fig.1 showed the variation trend of coating viscosity with time under different curing agent content. It could be seen from the figure that at the initial time, only the 3 times curing agent content coating whose viscosity was lower than that of the standard curing agent content coating, which might be zinc powder affected the dispersion of the curing agent. The coating viscosity increased with time increasing throughout the testing period. At the end of the test, the coating viscosity of the standard curing agent amount coating was the lowest, while the three times curing agent coating reached the highest level. It is analyzed that dispersed curing agent reacted with the resin to form cross-linking products, the longer the time, the more cross-linking products and the higher the viscosity of the paint.
Fig.1. Variation trend of coating viscosity with different curing agent content in different time

3.2. Effect of curing agent on coating applicable time
Applicable period of coatings, also known as activation period and construction time limit, refers to the maximum time when the curing agent and additives are mixed in the coatings until the viscosity of the system rises to unusable. This index has an important influence on the performance of the final curing coating [9].

According to the GB/T1728-1979, coating drying time is divided into surface drying time, practical drying time and completely drying time. In the experiment, finger touch method was used to judge whether the coating reached surface dryness and practical dryness, and gauze with special diluent was used to wipe the surface of the test piece to determine whether the coating reached completely dryness. It was a relatively stable experimental environment with the temperature was 16.6-18.3℃ and the relative humidity was 35-40% RH. Recording time was shown in Table 2.

Table 2 showed that the coatings surface drying time did almost unchanged with the increase of curing agent content, which could be related to the thickness of the coatings. There was a significant effect on the coating practical and completely drying time, under the same environmental conditions, the increase of curing agent content could reduce the practical drying time by 15 hours and the completely drying time by 12 hours. However, with the increase of curing agent content, the curing speed of the paint film increased, and the application period of the paint was shortened obviously. When the curing agent content was 3 times, the stirred paint must be used up within 6 hours.

**Table.2.** Applicable time of coatings with different curing agent contents

| Curing agent content | Surface drying time/h | Practical drying time/h | Completely drying time/h | Applying time/h |
|----------------------|------------------------|------------------------|--------------------------|-----------------|
| Standard             | 6                      | 27                     | 36                       | 12              |
| 1.5 times            | 6                      | 27                     | 36                       | 12              |
| 2.0 times            | 6                      | 24                     | 33                       | 9               |
| 2.5 times            | 6                      | 24                     | 30                       | 9               |
| 3.0 times            | 6                      | 12                     | 24                       | 6               |

3.3. Effect of curing agent content on the coating bonding strength and hardness
Fig.2. provided the bonding strength and micro-hardness of coatings with different curing agent content. It was obvious that the adhesion and micro-hardness of coatings increased first and then
decreased with the increasing of curing agent content. It could be that resin cross-linking reaction became more sufficient with the dosage of curing agent increment, coating bonding strength increased and hardness increased for the flexible chains decreasing. However, with the content of curing agent increasing further, the active group in curing agent was much more than that in resin, and the excess curing agent could not participate in cross-linking reaction and dispersed in macromolecular chains, which caused discontinuous phases raised and blooming appeared and resulted in declining of the coating bonding strength [10]. In addition, the redundant active groups could reduce the cross-linking density and the amount of rigid groups of the resin. Therefore, the coating hardness kept decreasing with the curing agent dosage improved.

![Fig.2. Bonding strength and micro-hardness of coatings with different curing agent content](image)

**3.4. Effect of curing agent content on the coating corrosion resistance**

Electrochemical samples coated with different curing agent content coating were immersed in 3.5% NaCl solution to measure the impedance of the coating at different immersion time, and EIS spectrums were obtained to evaluate the corrosion resistance of the coating, the results were presented in Fig.3. According to the schema, impedance modulus of the different curing agent content coatings was all above 108Ω•cm2 at the initial immersion period, which indicated the coating retained good corrosion resistance [11]. Among them, the impedance modulus of the standard addition of curing agent coating was the lowest, possibly because the higher the content of curing agent, the more active groups initiated cross-linking curing and formed a compact layer in a short time to prevent the initial penetration of solution [7, 11, 12]. With the prolongation of immersion time, the coatings impedance modulus showed a downward trend indicated that the electrolyte solution had penetrated into the coating. The impedance modulus of the standard addition of curing agent coatings decreased slightly and a time constant appeared in the low frequency region, which demonstrated the permeation of electrolyte solution to the coatings reached saturation state [13]. The impedance modulus of coatings with 1.5 times, 2.5 times and 2.5 times of the standard amount of curing agent decreased by an order of magnitude, and that 3 times coatings decreased by two orders of magnitude, furthermore, time constant also appeared in the low frequency region of 1.5 times and 3 times coatings. It might be due to the dispersal of active groups introduced by excessive curing agents in coatings, which increased the number of discontinuous defects and electrolyte solution enriched at defects, caused the decrease of coating impedance modulus [14]. However, there was without corrosion occurred in the coatings captured from Fig.4 (d).
Fig.3. EIS spectrum of coatings with different curing agent content and immersion time: (a)0 day, (b)7 days, (c)15 days and (d)30 days

4. Conclusion
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In this study, it was found that the change of curing agent content had certain influences on the performance of zinc-rich epoxy primer nano-coating, as described follows:
(1) With the increase of curing agent content, the coating viscosity decreased, the application time shortened and the drying time declined.
(2) The bonding strength and micro-hardness of the coating increased first and then decreased after drying and curing.
(3)Within the scope of studying, excessive content of curing agent might lead to an increase in the number of defects in the coating, which could reduce the coating corrosion resistance to a certain extent.
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