Preparation and Research of Solvent-Free Epoxy Coating for Drinking Water Tank

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Abstract. By compounding E42 and E51 epoxy resin, blending modified polyamide curing agent and modified fatty amine curing agent, optimizing glycidyl ether reactive diluent system, using safe non-toxic pigment filler and grading wear resistance filling and optimization auxiliaries system, the developed coating sanitary index meets the requirements of “Sanitary Standard for Drinking Water”, and the wear resistance (cs17, 1000g/1000r, mg) is 64.4mg. The coatings passed 6J impact resistance test and is resistant to bending 1.5° without cracks. The coatings also have excellent resistance to medium corrosion and salt spray.

1. Introduction

The anti-corrosion coating technology is used to effectively protect the water pipeline and the inner wall of the container. It is an anti-corrosion method commonly used in urban drinking water pipelines, long-distance water distribution steel pipelines, reinforced concrete pipelines and drinking water vessels. It is widely used in drinking water pipelines and container engineering [1-4]. This method owns the advantage such as smooth surface, low roughness, small friction coefficient, less wall voids, significantly reduced microbial adhesion, good adhesion between coating and substrate.

As environmental requirements increase, the demand for low VOC coatings is growing. Solvent-free coating contain no organic solvents, are safe, harmless to the human body, and owns no environmental pollution. They avoid the problem of solvent-based coatings polluting the environment and wasting a lot of organic solvents. Moreover, the solvent-free coating don’t own solvent volatilization during the curing process, and the paint film is dense, which improves the dielectric corrosion resistance of the coating, and the film formation is thicker at one time, which reduces the times of construction, improves the construction efficiency, and reduces the construction cost [5].

This work has developed the solvent-free drinking water coating with good wear resistance, bending resistance, impact resistance, medium corrosion resistance and salt spray resistance. The sanitary indicators meet the requirements of GB/5749-2006 and corresponding international standards. The standard requirements [6], obtained the health permit issued by the Health Bureau concerning the sanitary safety products for drinking water [7], the measured performance meets the performance requirements of GB/5369-2008 "General technical conditions for marine drinking water tank coatings".
2. Experimental part

2.1. Main raw materials
Epoxy resin: E-51 and E-42 mixed, South Asia Epoxy Co., Ltd.; Curing agent: modified polyamide and modified fatty amine mixed, American Air Products Co., Ltd., Cardolite Chemical Co., Ltd.; Talc powder, quartz powder, Tianjin Yandong Mineral Products Co., Ltd.; Titanium dioxide, Nanjing Titanium White Chemical Co., Ltd.; dispersant, BYK Chemical Company; Defoamer, BYK Chemical Company; Anti-settling thixotropic agent, ARKEMA.

2.2. Preparation of coating
Firstly, the epoxy resin, the reactive diluent and the auxiliary agent are uniformly mixed. After 20 minutes of pre-dispersion process, the polyamide wax powder and the pigment filler are sequentially added in the process of stirring in the high-speed disperser, and the dispersion was set at 2300r/min. Then, the dispersion speed was adjusted at any time, and the temperature of the material was maintained in the range of 50 to 60 °C for 30 minutes to activate the polyamide wax thixotropic anti-settling agent. After that, it is ground by a sand mill to achieve a grinding fineness of less than 100 μm. Products are packaged after filtered.

The specific production process is shown in Figure 1.

2.3. Preparation of the sample
The prepared coating and the curing agent are uniformly mixed in proportion, and the test sample plate is prepared according to the relevant standard requirements of GB/5369-2008 "General technical conditions for marine drinking water tank coatings".

2.4. Coating performance test
The performance of the coating was tested in accordance with the corresponding standards such as GB/T 5210 and GB/T 19754.

3. Results and discussion

3.1. Effect of film-forming epoxy resin on coating properties
For protective materials involving drinking water hygienic safety products, first of all, to ensure their safety. Bisphenol A type epoxy resin is widely used because it has excellent adhesion and corrosion resistance, and it belongs to the epoxy resin coating protective material resin base specified in the Catalogue of Drinking Water Hygiene and Safety Products issued by the Ministry of Health of the People's Republic of China. The molecular structure diagram is shown in Figure 2.
Reactivity Flexibility Chemical resistance Reactivity Heat resistance

As the molecular weight of the bisphenol a type epoxy resin increases, the molecular chain increases, the viscosity and softening point of the resin increase, and the flexibility increases. E51 epoxy resin owns relatively short molecular chain, good resistance to medium corrosion, low viscosity and relatively brittleness; E42 epoxy resin owns relatively long molecular chain. E42 and E51 epoxy resin can be adjusted to adjust the viscosity, corrosion resistance and flexibility of the system. Using modified fatty amine as curing agent, the effect of different ratios of E-42 and E51 epoxy resin on the properties of coating was studied. The adhesion, bending resistance (1.5°), impact strength and other properties were tested. The results were shown in Table 1.

| Test number | E51:E42 | Adhesion (Grade) | Anti-bending (1.5°) | Impact strength 6J | Water resistance (80°C,7d) | Coating viscosity cp,6r,25°C |
|-------------|---------|------------------|---------------------|--------------------|-------------------------|--------------------------|
| 1           | E51     | 2                | 300-350um           | Fail               | Coating intact          | 18700                    |
| 2           | 10:1    | 1                | 350-400um           | Passing            | Coating intact          | 20800                    |
| 3           | 7.5:1   | 1                | 350-400um           | Passing            | Coating intact          | 22920                    |
| 4           | 5:1     | 1                | 350-400um           | Passing            | Coating intact          | 25425                    |
| 5           | 2.5:1   | 1                | 350-400um           | Passing            | Coating intact          | 28289                    |
| 6           | 1:1     | 1                | 400-450um           | Passing            | Coating intact          | 31896                    |

It can be seen from Table 1 that the E42 epoxy resin was added to the E51 epoxy resin system to improve the adhesion, bending resistance and impact resistance of the coating. As the amount of E42 epoxy resin increases, the viscosity of the system increases. A film-forming epoxy resin with a ratio of E51 to E42 of 7.5 to 10:1 was used to obtain a good balance between flexibility and viscosity.

3.2. Effect of reactive diluent system on coating properties

Reactive diluents are typically added to the solventless epoxy coating system to adjust the viscosity of the coating system. Three different safe, hygienic and non-toxic glycidyl ether reactive diluents were selected for research, which would not evaporate during the film formation process and reacted with the amine curing agent to form the film-forming material. The effect of the three reactive diluents on the coating properties is shown in Table 2, and the recommended amount is the added amount.
Table. 2 Effect of different reactive diluents on coating properties

| Reactive diluent number | Adhesion (Grade) | Anti-bending(1.5°) Dry film thickness at the beginning of crack initiation | Impact strength 6J | Coating viscosity cp,6r,25°C | Water resistance (80°C,7d) |
|-------------------------|------------------|---------------------------------------------------------------------|---------------------|-------------------------------|-----------------------------|
| No active dilution added | 1                | 350-400um                                                           | Passing             | 22345                         | Coating intact              |
| Reactive diluent A       | 1                | 250-300 um                                                          | Fail                | 16870                         | Coating intact              |
| Reactive diluent B       | 1                | 350-400um                                                           | Passing             | 17900                         | Coating intact              |
| Reactive diluent C       | 1                | 350-400um                                                           | Passing             | 15406                         | Coating intact              |

It can be seen from Table 2 that three different reactive diluents can effectively reduce the viscosity of the coating. Considering the bending resistance, impact strength and system viscosity of the system, Reactive diluent C is selected as the reactive diluent of the system.

The amount of reactive diluent also has a significant impact on the state of the coating and the properties of the coating. Table 3 shows the effect of the amount of active dilution C added on the properties of the coating.

Table. 3 Effect of the amount of reactive diluent added on the properties of the coating

| Active diluent dosage | Adhesion (Grade) | Anti-bending(1.5°) Dry film thickness at the beginning of crack initiation | Impact strength 6J | Water resistance (80°C,7d) | Coating viscosity cp,6r,25°C |
|-----------------------|------------------|---------------------------------------------------------------------|---------------------|-------------------------------|-----------------------------|
| 0                     | 1                | 350-400um                                                           | Passing             | Coating intact               | 22345                       |
| 2.5%                  | 1                | 350-400um                                                           | Passing             | Coating intact               | 20124                       |
| 5%                    | 1                | 350-400um                                                           | Passing             | Coating intact               | 18500                       |
| 7.5%                  | 1                | 350-400um                                                           | Passing             | Coating intact               | 17320                       |
| 10%                   | 1                | 350-400um                                                           | Passing             | Coating intact               | 15406                       |
| 12.5%                 | 2                | 300-350um                                                           | Fail                | Coating intact               | 13260                       |
| 15%                   | 3                | 250-300 um                                                          | Fail                | Coating intact               | 11438                       |

As can be seen from Table 3, as the amount of reactive diluent added increases, the viscosity of the coating system decreases significantly. When the amount of the reactive diluent exceeds 10wt%, the adhesion, impact resistance and bending resistance of the coating are remarkably deteriorated.

3.3. Effect of curing agent system on coating properties

The study was conducted using different types of curing agents that can be used in drinking water coating systems. The amount of curing agent used is the theoretical amount obtained from the active hydrogen equivalent data of each curing agent. The effect of the curing agent system on the coating properties is shown in Table 4.
| project/curing agent number | G1                          | G2                          | G3                          | G4                          | G5                          |
|----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
| Curing agent type          | Modified phenolic amine     | Modified polyamide          | Modified alicyclic amine    | Modified Cashew Shell Oil   | Modified aliphatic amine    |
| surface drying time, 25°C, h | 1                          | 4                          | 3.5                         | 1.5                         | 0.5                         |
| hard drying time, 25°C, h   | 6                          | 15                         | 14                          | 8                           | 4                           |
| Adhesion (Grade)            | 1                          | 1                          | 1                           | 1                           | 1                           |
| Anti-bending(1.5°)          | 300-350um                  | 600-650um                  | 550-600um                  | 350-400um                  | 350-400um                  |
| Dry film thickness at the beginning of crack initiation | 6J Impact strength | Passing                  | Passing                  | Passing                  | Passing                  |
| Wear resistance (cs17, 1000g/1000r,mg) | 113.2                     | 96.5                      | 111.6                      | 121.8                      | 90.3                      |
| Water resistance (80°C,30d) | slight softening              | Coating intact            | Coating intact            | Coating discoloration      | Coating intact            |
| 10%H2SO4 (90d)              | Coating intact              | Coating intact            | Coating blistering         | Coating discoloration      | Coating intact            |
| 10%NaOH (90d)               | Coating intact              | Coating intact            | Coating intact            | Coating discoloration      | Coating intact            |
| Salt water resistance(90d)  | Coating intact              | Coating intact            | Coating intact            | Coating intact            | Coating intact            |

As can be seen from Table 4, the modified polyamide-based curing agent G2 and the modified fatty amine curing agent G5 have good overall performance. The modified polyamide curing agent G2 has excellent flexural resistance and flexibility, and the application period and the curing time of the paint film are relatively long. The modified fatty amine curing agent G5 has excellent comprehensive performance, relatively short pot life, and fast curing time. In the solvent-free drinking water coating system, the on-site construction environment requires a suitable period of application and a moderate curing speed. The compound modified polyamide curing agent G2 and the modified fatty amine curing agent G5 can obtain a good balance between the pot life and the curing speed.

3.4. Effect of pigment and filler on coating properties

The pigments and fillers selected for the wading product protective coatings should meet the non-toxic, non-polluting water quality and meet the safety and hygiene requirements of drinking water coatings. According to the scope of the types of epoxy resin protective coatings and pigments in the Catalogue of Hygienic Coatings for Drinking Water Hygiene and Safety Products issued by the Ministry of Health in 2007, select titanium dioxide with good hiding power, high brightness, non-toxicity and chemical inertness as coating. For pigments, choose ceramic powder with high hardness and good wear resistance and talcum powder with excellent leveling, gloss retention and medium corrosion resistance as filler for coating. The grading of 400 mesh, 800 mesh and 1250 mesh wear-resistant filler ceramic powder effectively improves the wear resistance of the coating.
3.5. Effect of additive system on coating properties
The solvent-free epoxy coating system has a large viscosity. In order to avoid defects such as shrinkage holes, pinholes, and spiral patterns after curing, the additive system is very important.

Adding fatty acid modified polyester with 0.5% mass fraction of coating component as system dispersing agent to help disperse pigment and filler evenly, improve dispersion and grinding efficiency; add polyamide wax powder with 0.6% mass fraction of coating component as system thixotropic protection. The sinking agent obtains a good balance between viscosity and thixotropy of the system and improves the storage stability of the system; As a system defoaming defoaming agent, the non-silicone defoaming agent and the modified silicone defoaming agent are added in an amount of 0.6% of the mass fraction of the coating component, effectively eliminating defects such as fish eyes, shrinkage cavities and bubbles do not eliminate after curing; Adding polyacrylate as a leveling agent with a coating component mass fraction of 0.4%, effectively reducing the surface tension of the coating, reducing the coating film defects caused by the difference in surface tension gradient, and improving the system leveling property. The paint has a good production adaptability and construction adaptability, smooth surface without pinholes, no orange peel and other apparent defects.

3.6. Hygienic safety inspection of solvent-free drinking water coatings
Entrusted the China Center for Disease Control and Prevention Environmental and Health-related Product Safety to adopt the “Test Method for Drinking Water Standards” (GB/T5750-2006) to conduct hygienic and safe immersion tests on the prepared solvent-free drinking water coatings, the acute mice mouth toxicity test, mouse bone marrow cell micronucleus test and biological Ames test. The test results are in line with the "Sanitary Drinking Water Distribution Equipment and Protective Materials Health Safety Evaluation Specification" (2001) on the sanitary requirements of protective materials. The solvent-free epoxy drinking water coatings obtained the approval document for the sanitation permit for drinking water hygiene and safety products issued by the Health Bureau.

3.7. Comprehensive performance of solvent-free drinking water coatings
The prepared solvent-free drinking water coatings were tested for wear resistance, impact resistance and bending resistance. The results are shown in Table 5. The test results show that the prepared solvent-free drinking water coating meets the performance requirements of GB/5369-2008 "General technical conditions for marine drinking water tank coatings", and has excellent wear resistance, bending resistance and impact resistance. The health indicators meet GB/ 5749-2006 "Standards for the Hygienic Standard for Drinking Water". The solvent-free epoxy drinking water coatings obtained the approval document for the sanitation permit for drinking water hygiene and safety products issued by the Health Bureau.
### Table 5 Coating performance test results

| Project                          | Inspection Result | Testing Standard                                      |
|---------------------------------|-------------------|-------------------------------------------------------|
| Solid content                   | 98.5%             | SY/T 0457-2010 Appendix A                             |
| Finess                          | 80                | GB/T 1724-1979                                        |
| Glossiness                      | 83                | GB/T 19754-2007                                       |
| Density, g/cm³                  | 1.50              | GB/T 6750-2007                                        |
| Primary film thickness, μm      | 500~600           | Actual measurement                                    |
| Surface drying time (25°C)      | 2h                | GB/T 1728-1979                                        |
| Hard drying time (25°C)         | 8h                | GB/T 6750-2007                                        |
| Anti-bending                    | Coating intact    | SY/T 0442-2010 Appendix E                             |
| (1.5°, 25°C, 500μm dry film)    |                   |                                                       |
| Flexibility                     | 1mm               | GB/T 1731-1993                                        |
| Impact strength, J              | 6J                | SY/T 0442-2010 Appendix F                             |
| Adhesion, MPa                   | 19.4              | GB/T 5210-2006                                        |
| Wear resistance                 | 64.4              | GB/T 1768-2006                                        |
| (1000g/1000r,C17), mg           |                   |                                                       |
| Chemical resistance             |                   |                                                       |
| NaCl, 90d                       | Coating intact    | GB/T 9274-1988                                        |
| NaOH, 90d                       | Coating intact    | GB/T 1733-1993                                        |
| H₂SO₄, 90d                      | Coating intact    | GB/T 1771-1993                                        |
| Water resistance, 720h          | No blistering, no rust, no peeling | GB/T 1733-1993 |
| Boiling resistance              | Coating intact    | GB/T 1733-1993                                        |
| (tap water, 80°C, 7d)           |                   |                                                       |
| Salt spray resistance, 600h     | No blistering, no rust, no peeling | GB/T 1771-1993 |
| Sanitary safety of drinking water | Obtain test report and health permit | GB/T 5750-2006 |

### 4. Conclusion

1. The E51 epoxy resin system is compounded with E42 epoxy resin, which can effectively improve the bending resistance of the coating.

2. The reactive diluent can effectively reduce the viscosity of the coating system, but when the amount exceeds 10% of the epoxy resin, the adhesion, impact resistance and bending resistance of the coating are significantly deteriorated.

3. The blending modified polyamide curing agent and the modified fatty amine curing agent are used to obtain a good balance between the pot life and the curing time, and the system has excellent resistance to medium corrosion.

4. The grading of 400 mesh, 800 mesh and 1250 mesh wear-resistant filler ceramic powder effectively improves the wear resistance of the coating.

5. The solvent-free epoxy drinking water coating is safe and non-toxic, and the health indicators meet the requirements of GB/5749-2006 “Sanitary Standard for Drinking Water”. The performance meets the requirements of GB/5369-2008 "General technical conditions for marine drinking water tank coatings", wear resistance (cs17, 1000g/1000r, mg) is 64.4mg, through 6J impact resistance test, 500μm paint film is resistant to bending 1.5° No cracks.
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