Preparation and research of brush-coated solvent-free polyurethane anti-corrosion coatings

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Abstract. In order to solve the problem of short gel time and difficulty in brushing of solvent-free polyurethane coatings, the coatings choose polyether polyester polyol and polyisocyanate prepolymer as the main film-forming materials, adding spherical ceramic powder to improve the wear resistance of the coating, combination of molecular sieve physical dehydration and oxazolidine chemical dehydration, effectively solves the problem of water sensitivity of paint, a solvent-free polyurethane anticorrosive coating for brush application was prepared. The coating also has good adhesion, excellent wear resistance and corrosion resistance.

1. Introduction
Polyurethane coatings have strong corrosion resistance, good weather resistance, excellent performance, especially the emergence of cross-linked two-component polyurethane coatings, combined with environmentally friendly functions, making polyurethane coatings leapfrog. Polyurethane coatings are widely used in wood, construction, plastics, anti-corrosion, machinery and other fields, becoming one of the fastest growing coating varieties [1, 2].

With the gradual strengthening of environmental protection requirements in China, reducing the VOC content and emissions in coatings, the use of solvent-free and water-based environmentally friendly coatings instead of solvent coatings has become the development direction of anti-corrosive coatings. Solvent-free polyurethane coating is a solvent-free, non-flammable, 100% solids environmentally friendly coating with excellent oil resistance, acid and alkali resistance, low temperature curability, and ductility [3-5].

At present, the high viscosity of the solvent-free polyurethane coating makes it need to be heated and sprayed. The construction requires special high-pressure airless impact spraying equipment. The surface of the coating is easy to form pitting, orange peel, the appearance is poor, the wettability to the substrate is not good, the reaction is exothermic, the internal stress is large, and will have negative effect on adhesion. The fast curing speed of the coating also results in a short pot life of the coating, which is not conducive to small-area construction and repair work on site [6-8].

To this end, this study develop a solvent-free polyurethane anticorrosive coating that can be brushed by studying the polyol and curing system in the polyurethane coating film. The coating has excellent physical properties, mechanical properties and corrosion resistance, making it suitable for small-area construction and repair work.
2. Experimental part
Preparation of paint: step one, The molecular sieve activated powder, the antifoaming agent and the dispersing agent are added to a certain amount of the polyether polyester polyol, and dispersed at a high speed for 1 hour to obtain a dehydrating agent;

Step two, The ceramic powder, the talc powder, the titanium dioxide powder, the barium sulfate and the carbon black are heated in a 150 °C high-temperature cabinet for 12 hours to obtain a coating pigment filler;

Step three, the polyether polyester polyol, the water removing agent, the defoaming agent and the dispersing agent are mixed. The mixture is stirred at a high speed and room temperature. The coating pigment and filler are added under stirring, and the high-speed stirring is continued for 30 to 40 minutes to uniformly disperse the components. And then grind with a grinder for 0.5 to 1 hour to obtain a mixture.

Step four, a dehydrating agent and an antifoaming agent obtained in the step one are added to the mixture obtained in the step three, and dispersed at a high speed for 30 minutes to obtain a component A of the solventless polyurethane coating.

Step five, dispersing polymethylene polyphenyl isocyanate PM200 to form component B.

Step six, mixing the A component and the B component uniformly to obtain the Solvent-free polyurethane coating.

3. Results and discussion
3.1. Study on polyether polyols
Among the polyurethane raw materials, a hydroxyl group (resin) mainly composed of a polyol is an important component. As a soft segment structure of polyurethane coatings, polyols are also an important factor in determining the properties of polyurethanes. In polyurethane raw materials, there are two main categories: polyether polyols and polyester polyols [9].

Polyether polyols are cheaper than polyester polyols and have a wide range of raw materials. Polyester polyurethane has more polar groups such as ester groups and urethane groups, has strong cohesive strength and adhesion, and has high strength and wear resistance. Therefore, after the urethane bond is embedded in the molecular chain of the low molecular weight polyether polyol, the strength of the paint film can be greatly improved, and the paint film has a high hardness.

The polyether polyols based on ether bonds were used in this test, and four different types of polyether polyols were used for basic performance testing. The test results are shown in Table 1.

**Table 1. Basic properties of different types of polyether polyols**

| Polyether polyol type                      | surface drying time (min) | hard drying time (h) | Impact Strength (J) | Adhesion (MPa) | Anti-bending (1.5°) | Hardness (Shore D) |
|-------------------------------------------|---------------------------|---------------------|---------------------|----------------|---------------------|-------------------|
| Branched polyol                           | 120                       | 10                  | 16                  | 9.2            | No cracks           | 58                |
| Branched polyether/polyester primary hydroxyl polyol | 90                        | 6                   | 14                  | 13.2           | No cracks           | 71                |
| Castor oil modified polyol                | 60                        | 5                   | 16                  | 9.5            | No cracks           | 55                |
| Cashew nut shell modified polyol          | 40                        | 4                   | 10                  | 12.8           | No cracks           | 85                |

As can be seen from Table 1, the branched polyol has good impact resistance and chemical resistance, but the hardness of the coating is low and the Shore D is only 58. Through comparative analysis, the branched polyether/polyester primary hydroxyl polyol has good physical and mechanical properties and chemical resistance, and the basic properties meet the requirements.
3.2. Study on isocyanate curing agent

Two-component polyurethane coating polyisocyanate prepolymer as a polyurethane curing agent has many advantages such as high thermal stability, corrosion resistance, radiation resistance, fast curing and high hardness. There are very few free isocyanate monomers in the polyisocyanate prepolymer, which is beneficial to the chain extension and crosslinking reaction to be carried out quickly and thoroughly. It can reduce the occurrence of side reactions, improve the compatibility of the raw material system, and improve the physical properties of the coating [10].

The suitable curing agent is selected to make the coating have a long pot life, so that the solvent-free polyurethane coating can be brushed. This experiment selected four prepolymers from three manufacturers on the market to test the properties of coatings. Branched polyether/polyester primary hydroxyl polyol for polyol component. The test results are shown in Tables 2 and 3.

| type  | surface drying (min) | hard drying (h) | pot life (h) | Impact Strength (J) | Anti-bending (1.5°)  | Adhesion (MPa) | Hardness (ShoreD) |
|-------|----------------------|-----------------|--------------|---------------------|----------------------|----------------|------------------|
| PM1   | 90                   | 6               | 3            | 14                  | No cracks            | 13.2           | 71               |
| PM2   | 30                   | 5               | 1            | 12                  | No cracks            | 14.3           | 82               |
| PM3   | 100                  | 8               | 3.5          | 16                  | No cracks            | 12.8           | 59               |
| PM4   | 90                   | 6               | 3            | 15                  | No cracks            | 13.6           | 75               |

Table 2. Basic properties of different types of isocyanates

| type  | H₂SO₄ (10%, 30d) | NaOH (10%, 30d) | NaCl (30%, 30d) | Diesel resistance (2#, 30d) | Cathodic disbanding (65°C, -1.5V, 48h) |
|-------|------------------|-----------------|-----------------|-----------------------------|----------------------------------------|
| PM1   | Coating intact   | Coating intact  | Coating intact  | Coating intact              | 12mm                                   |
| PM2   | Coating intact   | Coating intact  | Coating intact  | Coating intact              | 14mm                                   |
| PM3   | Coating intact   | Coating intact  | Coating intact  | Coating intact              | 15mm                                   |
| PM4   | Coating intact   | Coating intact  | Coating intact  | Coating intact              | 10mm                                   |

Table 3. Chemical resistance of different types of isocyanates

As can be seen from Tables 2 and 3, PM2 isocyanate has good impact resistance and chemical resistance, but the coating has a short pot life. PM3 isocyanate has a longer surface dry time, lower hardness and a Shore D hardness of only 59. PM4 and PM1 isocyanate have good physical and mechanical properties and chemical resistance, and PM4 is better than PM1 in cathodic resistance. Therefore, PM4 polyisocyanate prepolymer was used as polyurethane coating isocyanate component confirmed by the above study.

3.3. Study on wear-resisting filler

Solvent-free polyurethane coatings require coatings with good abrasion resistance. The addition of wear-resistant fillers can improve the wear resistance of epoxy coatings, and ceramic powders are the most common in wear-resistant fillers. Mainly because ceramic powder itself has high hardness and good wear resistance.

Ceramic powder is used as a wear-resistant filler. Under the conditions of the film-forming resin, the coating is prepared according to the different proportions of the ceramic powder in the pigment filler. The performance comparison data of the coating is shown in Table 4.
| Ceramic powder proportion (%) | Wear resistance (CS17, 1kg, 1000r) mg | Anti-bending (1.5°) | Flexibility (mm) | Adhesion (Grade) | Impact Strength (J) | Hardness (ShoreD) |
|-------------------------------|---------------------------------------|--------------------|-----------------|-----------------|-------------------|-------------------|
| 5                             | 55.3                                  | No cracks          | 1               | 1               | 15                | 79                |
| 10                            | 52.4                                  | No cracks          | 1               | 1               | 16                | 81                |
| 15                            | 59.8                                  | No cracks          | 1               | 1               | 16                | 82                |
| 20                            | 48.2                                  | No cracks          | 1               | 1               | 17                | 84                |
| 25                            | 46.7                                  | cracks appear      | 1               | 1               | 15                | 85                |
| 30                            | 46.4                                  | cracks appear      | 2               | 1               | 14                | 85                |

With the increase of the amount of ceramic powder, the wear resistance of the coating is enhanced, the flexibility is decreased, the impact resistance is first increased and then decreased, the overall change of adhesion is not large, and the hardness gradually increases. Ceramic powder was used to add 20% of pigment and filler.

### 3.4. Study on coating additive system

In the polyurethane paint, the reaction between NCO and water produces CO₂, which is the main source of bubbles in the paint film. By adding a dehydrating agent, the water in the solvent can be effectively removed, bubbles and pinholes are eliminated [11].

The system uses physical dehydration combined with chemical water removal. The physical dewatering of polyurethane coatings mainly uses molecular sieves. The molecular sieves are aluminosilicates, which are mainly composed of silica-alumina and oxygen bridges to form an open skeleton structure. The chemical dehydrating agent has an effect on inhibiting the bubbles of the polyurethane paint, wherein the effect of the oxazolidine is most obvious, and the effect of moisture can be effectively suppressed, bubbles and pinholes are avoided. This is because when the oxazolidine encounters a trace amount of moisture in the formulation raw material or is exposed to moisture, the oxazolidine preferentially reacts with water, thereby preventing the isocyanate from reacting with moisture to generate carbon dioxide.

During the construction process, the isocyanate in the prepolymer will produce a certain amount of bubbles in the coating when it comes into contact with a trace amount of moisture in the air. Therefore, defoaming agents should be added to eliminate or inhibit. Therefore, when a defoaming agent is used, a suds suppressor is often used in combination to suppress the generation of bubbles. The polyurethane coating system uses an antifoaming agent produced by BYK Chemical Company of Germany, and its dosage is usually 0.3–0.5% of the coating content.

The dispersing agent has the functions of wetting, reducing viscosity, improving leveling, preventing floating color, sagging, sedimentation and so on. The coating selected a polyacrylate dispersant, which has good compatibility with the film-forming resin, and has a high molecular weight to effectively separate the pigment particles, and the dispersant is used in an amount of 0.4% of the total formulation.

### 3.5. Physical and chemical properties of coatings

The physical and chemical properties of the coatings were tested in accordance with relevant standards. The test results are shown in Table 5.
Table 5. Performance of coatings

| type                                      | actual measurement |
|-------------------------------------------|--------------------|
| Solid content (%)                         | 98.6               |
| surface drying time (25°C, min)           | 18                 |
| hard drying time (25°C, min)              | 80                 |
| pot life (h)                              | 3                  |
| shore hardness (Shore D)                  | 84                 |
| Anti-bending (1.5°)                       | Coating intact     |
| Impact strength (J)                       | 15                 |
| Adhesion (MPa)                            | 12.8               |
| Wear resistance (Cs17, 1kg, 1000r)mg      | 48.6               |
| Cathodic disbonding (65°C, 48h)mm         | 9.3                |
| H₂SO₄, NaOH and NaCl (10%, 30d)           | Coating intact     |
| Salt spray resistance (1500h)             | Coating intact     |

As can be seen from Table 4, the developed coating has a suitable pot life, making it suitable for small-area construction and repair work. Coatings have excellent physical and mechanical properties and corrosion resistance.

4. Conclusion

Through the study of polyether polyols and isocyanates, solvent-free polyurethane coatings have a suitable pot life and can be applied by brushing. The addition of spherical ceramic powder as a wear-resistant filler in the coating improves the wear resistance of the coating. The combination of physical dehydration and chemical dehydration effectively solves the problem of water sensitivity of the coating, eliminates bubbles and pinholes of the coating, and reduces loss of light and haze.

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