Study on Application of Polyurea in Anticorrosion of Inner Wall of Mine Bottom Pipeline

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Abstract. Aiming at the serious corrosion problem of the inner wall of the existing mine bottom exhaust and small pipe diameter pipe (Φ108, Φ159), a new polyurea-epoxy hybrid heavy-duty anticorrosive coating which can be applied to the inner wall anticorrosion of the pipe was developed, and the small pipe diameter was also The problem of difficulty in painting the inner wall of the pipeline is to apply the coating equipment of the inner wall of the pipeline to the coating of the anti-corrosion coating on the inner wall of the pipeline, and carry out industrial experiments and apply it to the mine. At this stage, the inner wall is sprayed with a new type of polyurea-epoxy hybrid heavy-duty anti-corrosion. The pipeline of the paint is in good condition on the spot, and there is no corrosion or falling off of the inner wall.

Introduction

Various types of small-diameter metal pipes, such as water supply and drainage pipes, positive pressure air pipes, spray pipes and gas drainage pipes, used in coal mines, because the mine water conveyed has certain acidity and alkalinity, and is mixed with coal, sand and the like. The impact of the object on the inner wall of the pipeline, the current wear resistance and anti-corrosion performance of the inner wall of the pipeline is limited. Once the anti-corrosion coating is broken, the inner wall of the pipeline and the transporting mine water have a long-term effect, causing corrosion of the inner wall of the pipeline [1], which is urgently needed to solve the mine water transportation problem. In addition, after the long-term use of the small diameter pipe in the underground, the inner wall is rusted and scaled, which causes the water quality to deteriorate, and the water flow becomes small or even blocked, which seriously affects the normal production and life.

Aiming at the serious corrosion of mine pipeline equipment, a lot of research and exploration on pipeline anti-corrosion measures have been carried out at home and abroad [2,3,4]. At present, domestic water-based metal anti-corrosion coatings [5,6] have been published, and the anti-corrosion effect is remarkable, but there is still a certain gap compared with foreign countries. Rust-proof anti-corrosion coating [7] can effectively solve the problem of re-embroidery and improve the adhesion of coating and metal matrix, but such coatings often cannot completely replace the rust-removing methods such as sand blasting and pickling. Certain restrictions. At present, there are chemical methods, vibration methods, electromagnetic methods, bushing methods, mechanical methods, cyclone methods, etc. for the inner wall cleaning and anti-corrosion technology [8], but for pipeline turning, variable diameter, vertical and small diameter pipes, It is limited in practical applications.

Aiming at the problems of downhole water delivery, severe corrosion of small diameter pipe and difficulty in painting the inner wall of the pipe, the new polyurea-epoxy hybrid heavy-duty anti-corrosion coating and the combination with the rotary cup spraying technology have been studied to enhance the corrosion resistance of the pipe. The utility model effectively solves the problem of...
difficulty in spraying the inner wall. This work describes in detail the development of the new polyurea-epoxy hybrid heavy-duty anti-corrosion coating and the rotary cup spraying process, and is actually applied to the mine site, and the anti-corrosion effect is remarkable, and the anti-corrosion of the mine underground pipeline has great significance.

 Spray polyurea elastomer anticorrosion technology

 The spray polyurea elastomer technology is derived from the rapid reaction molding of polyurea elastomer in 1970. It is a low (no) pollution coating technology for high solids coatings, waterborne coatings, radiation curing coatings, powder coatings, etc. in the past ten years abroad. After that, a new solvent-free and pollution-free green construction technology developed and developed to meet environmental protection needs. Its inherited reaction injection molding (RIM) technology impacts the mixing principle and breaks through the limitations of RIM. It uses its instant curing and high-speed reaction characteristics to form a new coating, which is widely used in anti-corrosion, wear-resistant, marine and shore-based facilities. , high-speed rail, floor and other aspects [9]. The process belongs to a rapid reaction spraying system. The raw material system contains no solvent, fast curing speed and simple process. It can conveniently spray a coating of ten millimeters thick on the facade and curved surface without sag. Spray polyurea technology has completely broken through the limitations of traditional environmentally friendly coating technology. Therefore, once this technology was introduced, it was rapidly developed.

 Synthesis and construction process design of a new polyurea-epoxy hybrid heavy-duty anticorrosive coating

 This paper is mainly for the new drainage pipeline (Φ273mm), Φ159 and Φ108mm old drainage pipelines of the 18 pumping station of Jining No.3 Coal Mine. The inner surface of the pipeline is caused by factors such as uneven coating thickness and poor coating ability to avoid manual painting. The shortcomings of poor corrosion resistance, combined with the construction conditions of high humidity and poor surface cleanliness of coal mine site, combined with the existing research foundation, optimize the design of existing polyurea anticorrosive coating formulations, and develop new polyurea elastomer coatings. The material is coated on the inner wall by a rotating cup spraying device coated on the inner wall of the pipe.

 Development of a new polyurea-epoxy hybrid heavy-duty anticorrosive coating

 The research methods of this coating are as follows:

 (1) The heavy-duty anticorrosive coating with appropriate micro-phase separation structure is synthesized by blending and copolymerization method; the amino-based polyether with high regularity is used to improve the micro-phase separation performance, and liquid rubber is added to improve the resilience. The molecular structure of polyurea is a high molecular polymer containing a plurality of groups, that is, a soft segment and a hard segment are simultaneously contained, and the soft segment contains a crystal region and an amorphous region, and the hard segment also contains a crystal region and an amorphous region. Area. The prepolymer is synthesized by blending and copolymerization, and the hard segment phase is highly improved, which can significantly increase the degree of separation of the two phases in the structure. The use of an amine-based polyether having a highly regular amino-based polyether structure can improve the regularity of the hard segment, thereby improving the microphase separation performance, increasing the hydrogen bond energy, and significantly improving the physical properties of the elastomer.

 (2) By introducing functional fillers, such as ultra-high molecular weight polyethylene micropowder, polytetrafluoroethylene micropowder, molybdenum disulfide, etc., the friction coefficient is reduced and the tear strength is improved. For the surface treatment of functional fillers, the surface of the filler is treated with surface oxidation modification, silane coupling agent, titanate coupling agent, etc., and the surface is attached with a reactive group to improve its adhesion to the polyurethane resin. Connectivity. If the direct addition method introduces the functional filler into the
polyurethane elastomer, there is a property of migrating from the inside to the surface of the material, so that the modification effect is lost in a short period of time. A silane coupling agent, a titanate coupling agent, or the like, having a reactive group capable of chemically bonding with an inorganic material and a reactive group chemically bonded to the organic material, and modifying the functional filler. It can improve the adhesion of the filler to the polyurethane resin, as shown in Fig.1 and Fig.2.

![Fig.1 Unsurfaced filler](image1) ![Fig.2 Filler after silane coupling agent treatment](image2)

(3) A chain extender for synthesizing fluorine-containing elements, which is modified by a chemical method to improve the durability of the low friction coefficient. Fluorine-containing compounds have advantages unmatched by other materials, and are therefore often used for the modification of polymer compounds, which can significantly improve their various properties. The fluorine-containing compound and the amine chain extender are mixed in a certain ratio, and reacted at 50 to 100 °C for two hours to obtain a fluorine-containing amine chain extender. The modification of the polyurethane by this chemical method significantly reduces the friction coefficient and the modification effect is lasting.

![Fig. 3 Schematic diagram of molecular structure of fluorine-containing amine chain extender](image3)

(4) Improving the adhesion of polyurethane to various substrates, especially wet adhesion, by means of epoxy resin modification.

Epoxy resin has the characteristics of high strength, small shrinkage, good chemical resistance and high adhesion, but the product has poor deformability and brittleness. Modification of polyurethane with epoxy resin can combine the advantages of both materials to form a new material with excellent performance. An amine-based polyether or an amine chain extender or the like is added to the epoxy according to the designed ratio, and reacted at 65 to 100 °C for two hours to form a terminal amine-based epoxy adduct (Fig. 4). The terminal amine-based epoxy adduct reacts with the isocyanate to form an epoxy-modified polyurethane. Due to the good combination of the excellent adhesion of the epoxy resin, the adhesion of the high polyurethane to various substrates is especially wet adhesion.

![Fig.4 Reaction mechanism of polyamine epoxy adducts](image4)
The new polyurea-epoxy hybrid heavy-duty anticorrosive coating comprises A and R two components (A: R = 1:1), wherein the A component is composed of a semi-prepolymer synthesized from a polyisocyanate and a polyether polyol; The components include a chain extender, a hydroxyl terminated polyether, and a wear resistant filler. The method for synthesizing the component A is to add a precisely metered polyisocyanate to a reactor protected with nitrogen, stir it at a constant speed, heat to 60-80 °C, and slowly add a metered polyether polyol to the reactor, at 70- At 90 °C, the reaction was 2-3 h, sample analysis, the free isocyanate content in the semi-prepolymer was determined to be between 15-20%, and the output was cooled; the R component was prepared by adding a filler to the R component. (Including wear-resistant filler and pigment filler), the filler is first mixed with the terminal hydroxyl polyether in part of the R component, and then dispersed into a color paste by a grinding device such as a sand mill. Finally, according to the formula, the milled color paste, the remaining part of the hydroxyl terminated polyether, the chain extender and its auxiliary agent are added into the paint pot, and the high shear stirring equipment is used for high-speed stirring for 30 min, and the production process flow diagram is as follows:

Fig.5 Flow chart of the production process of the new polyurea-epoxy hybrid heavy-duty anti-corrosion coating

**Rotary cup spraying process**

For the anti-corrosion of the inner wall of the pipe with a small diameter, it is difficult for the worker to carry out the internal construction of the pipeline, and the thickness and surface flatness of the ordinary construction are difficult to control. Spraying construction in the pipeline, especially in the interior of some pipelines with smaller inner diameters, becomes a difficult point in the inner wall of the pipeline.

The construction of the anti-corrosion coating on the inner wall of the pipeline adopts the rotary cup spraying construction process. The rotary cup spray coating process is shown in Figure 1. The air compressor, generator, transfer pump and metering pump are used to transport the paint from the material tank to the metering requirements. The conveying pipe is then conveyed to the nozzle through the hose reel and the umbilical conveying pipe, and the drawn A and B components are thoroughly mixed by the in-line mixer at the nozzle, and the coating is sent to the high speed. On the rotating cup, a huge acceleration is obtained to move to the edge of the cup, and it is broken into tiny droplets under the action of centrifugal force, and sprayed on the inner surface of the pipe to form a
uniform, smooth, smooth and full-bodied coating film. As the nozzle gradually rotates back, the paint is continuously sprayed onto the inner wall of the pipe.

The rotary cup spraying method is flexible, the coating thickness is adjustable, the spraying speed is adjustable, and the coating amount is saved. It can meet the requirements of various performance spraying construction processes and is suitable for spraying the inner wall of pipelines.

![Rotating cup spraying](image)

**Fig. 6 Rotating cup spraying**

**Polyurea elastomer practical application**

Test the main performance index of polyurea elastomer, its Shore hardness value $A \leq 75^\circ$, tensile strength $\geq 25$ MPa, tear strength $\geq 55$ kN/m, rebound elasticity $\geq 70\%$, NBS wear $\geq 360\%$, Acron Wear $\leq 0.05$ cm$^3$, polyurea elastomer wear-resistant and resistance-resisting performance is excellent, and the existing inner wall spray polyurea pipeline is now used for 3 months, on-site inspection, found that its inner wall is in good condition, no falling off and so on. As shown in Fig. 7.

![Comparison of actual use of polyurea elastomer spray](image)

**Fig. 7 Comparison of actual use of polyurea elastomer spray**

**Conclusions**

In view of the problem of poor anti-corrosion performance of mine bottom pipeline, a new polyurea-epoxy hybrid heavy-duty anti-corrosion coating and matching rotor cup spraying construction technology were developed according to the special environment of the mine bottom to improve the uneven thickness and anti-corrosion effect of the coating coating on the inner wall of small-diameter pipeline. The poor status quo, the following conclusions are obtained:

1. The poly-aspartate main chain toughening technology is applied to the anti-corrosion of underground coal mine equipment, and the polyurea-epoxy anti-corrosion coating adds a long-chain...
flexible group to the main chain of polyaspartic acid ester to improve the elongation. The index effectively improves the performance of polyurea-epoxy hybrid heavy-duty coatings.

(2) Adding anti-corrosive pigment to pure polyurea-epoxy anti-corrosion coating to inhibit chemical and electrochemical reactions, and also inhibit the physical reaction of the closed pigment to achieve synergistic anti-corrosion effect of organic or inorganic.

(3) Rotary cup spraying technology has flexible construction mode, adjustable construction thickness, adjustable spraying speed, and saves coating dosage. It can meet the requirements of spraying performance of various performances and is suitable for the construction scope of pipeline inner wall spraying.

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References


