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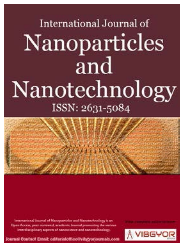

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Surface Modified TiO_2/PTFE Fluorocarbon Anti-Pollution Flashover Coating

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Abstract

A new type of surface modified TiO_2/PTFE fluorocarbon anti-pollution flashover coating material was prepared by using rutile nano TiO_2 modified by fluorosilane coupling agent and PTFE as composite filler, and then combined with fluorocarbon resin FEVE. The self-cleaning, UV aging resistance, physical and chemical properties and electrical insulation of the coating material were studied. The results showed that the optimum addition amount of modified rutile nano TiO_2 was 4%. At this time, the adhesion of the coating can reached grade 0, the maximum static contact angle was 121°, and the volume resistivity was basically unchanged. The fluorine-carbon anti-pollution flashover coating was prepared by compounding the modified TiO_2 with PTFE, which has good photocatalytic self-cleaning performance and anti-ultraviolet aging performance, the volume resistivity is 2.7 × 1010 Ω•m, the breakdown field strength is 23.7 kV/mm, the leakage tracking resistance TMA is 2.5, the electrical insulation performance is better. Therefore, it has excellent anti-pollution flashover performance.

Keywords

Coupling agent modification, Nano TiO_2, Fluorocarbon resin, Anti-pollution flashover, Self-cleaning

Introduction

With the rapid development of society and economy, the continuous construction of transmission lines such as west-east power transmission and north-south power transmission, the application of high-voltage and ultra-high voltage transmission equipment is becoming more and more popular. However, the surface of power electrical equipment and devices running outdoors is susceptible to accumulate pollution under electric field or natural conditions. In the humid environment such as rain, fog, dew and snow, the moisture in the air constantly wets the pollutants. Under the action of high voltage, the conductance and leakage current on the surface of insulation equipment increase sharply, and the conductive pollutants accumulated on the surface of insulators undergo destructive arc discharge, thus causing pollution flashover accidents [1,2]. Once a large-scale pollution flashover outage accident is caused, it will bring great losses to the national economy [3].

The commonly used anti-pollution flashover method is to spray anti-pollution flashover coatings on the surface of power electrical equipment [4]. Among them, room temperature vulcanized silicone rubber (RTV) and composite room temperature vulcanized silicone rubber (PRTV) are

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widely used. However, both of them have short service life, soft coating texture and easy fouling on the surface. Under the action of wind blowing, wiper and sunlight, the methyl C-H bond energy of the side chain is low and easy to be destroyed. The excessive consumption of the methyl group weakens its original shielding effect on the Si-O main chain, resulting in the loss of hydrophobicity, which is not suitable for large-scale popularization and application [5-7]. A large number of studies have shown that taking measures to reduce the surface pollution of insulators can effectively prevent the occurrence of pollution flashover accidents. The development of self-cleaning anti-pollution flashover coatings has become a new development trend [8,9].

The new fluorine-containing coupling agent has strong stability due to the small radius of fluorine atom, the length of C-F bond and the high bond energy. It has good compatibility with RTV silicone rubber and can significantly improve the mechanical properties of the coating. It can be applied to RTV silicone rubber coatings, and the coating also shows better adhesion, hydrophobicity and self-cleaning properties [10]. In addition, PRTV can be modified by nano-silica (SiO_2). In a certain content range, the surface of the coating forms nano-scale and micron-scale protrusions and disperses evenly, so that the surface forms a micron-nano composite lotus leaf structure with concave pores, which greatly improves the water contact angle of the coating [11]. However, the surface energy of fluorine-containing substances is low, and the cost of preparing the lotus leaf structure is high and difficult, which is not convenient for promotion.

The intermolecular force of fluorocarbon resin is very weak, which directly leads to the extremely low surface energy of fluorocarbon coating, and the coating is difficult to be soaked by water and organic matter. Therefore, fluorocarbon coating material has strong water resistance, stain resistance and corrosion resistance. In addition, due to the small polarizability of fluorine atoms, it is highly insulating on fluorocarbon resin. Therefore, fluorocarbon coating has high chemical inertness and thermal stability [12]. Nano-rutile TiO_2 is a commonly used nano-modifier for functional composite coatings. It has a strong absorption effect on UV below 400 nm, which can protect the polymer chain of the film-forming material from being degraded by ultraviolet light. Absorbing photons in solar energy to promote charge generation, interacting with adsorbed substances, a series of redox reactions occur [13,14].

In this paper, aiming at the key problems of nano-oxides in anti-pollution flashover coatings, such as short service life due to long illumination time, easy loss of hydrophobicity of room temperature vulcanized silicone rubber, and poor mechanical properties of conventional organic fluorocarbon coatings, fluorocarbon resin (FEVE) is used. The film has low surface energy, small adhesion ability, hydrophobic and oleophobic properties [15], as well as the high photocatalytic activity and wear resistance of nano-titanium dioxide (TiO_2) [16]. FEVE is used as a film-forming material, and rutile nano TiO_2 modified by fluorosilane coupling agent and polytetrafluoroethylene (PTFE) are used as composite fillers. A novel nano TiO_2/PTFE fluorocarbon anti-pollution flashover coating with self-cleaning effect was prepared.

Experiment

Materials and instruments used

Raw materials and reagents used in this paper are: FEVE fluorocarbon resin (GK570), Shenzhen Xiqi Technology Co., Ltd.; rutile nano TiO_2, Shanghai Huijing Sub-Nanoseale New Material Co., Ltd.; PTFE wax powder, Jiangsu Tianwen New Material Technology Co., Ltd.; gas phase SiO_2, Shanghai Kaiyin Chemical Co., Ltd.; fluorosilane coupling agent (G502), Nanjing Nengde New Material Technology Co., Ltd.; anhydrous ethanol, Anji Hengxing Chemical Co., Ltd..

The test instruments used in this paper are: Contact angle measuring instrument (JC-2000DS), Shanghai Solon Information Technology Co., Ltd.; surface/volume resistivity meter (WSYW-090), Guangzhou Runhu Instrument Co., Ltd.; gloss meter (UV-2550), Keynes (China) Co., Ltd.; salt spray test machine (DH-90), Zhejiang Niudun Testing Equipment Co., Ltd..

Sample preparation

Preparation of modified rutile nano TiO_2: According to the ratio of fluorosilane coupling agent: Anhydrous ethanol: Distilled water: Rutile nano TiO_2 mass ratio of 1: 8.5: 3.5: 4, the appropriate amount of TiO_2 was first weighed with a balance, and then anhydrous ethanol, deionized water and

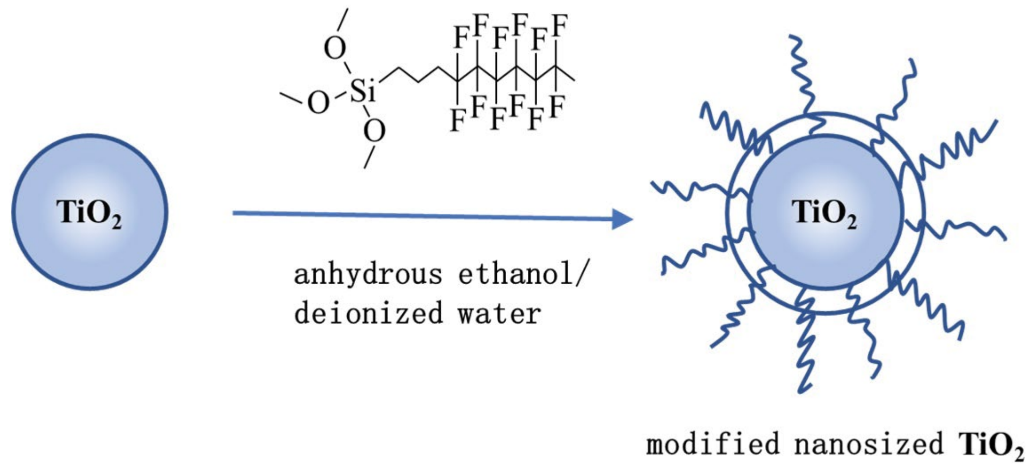

Figure 1: Description of fluorosilane modified nano TiO_2.

G502 were added in turn and mixed evenly. The water bath was heated to 80 °C, and the ultrasonic time was more than 2h. After centrifugation at 5500 r/s for 30 min, the prepared TiO_2 nanoparticles were purified by washing with deionized water and absolute ethanol several times. After vacuum drying at 60 ~ 120 °C for 3 h, the modified rutile nano TiO_2 was obtained by grinding the product into powder. The synthesis reaction diagram is shown in Figure 1.

Preparation of nano TiO_2/PTFE fluorocarbon anti-pollution flashover coating material: The modified rutile nano TiO_2 was dispersed in a mixed solvent, and PTFE was added, stirred evenly, and then milled for 40~60 min at a speed of 40 r/s to obtain nano TiO_2/PTFE composite filler. The nano TiO_2/PTFE fluorocarbon coating material was obtained by uniformly mixing with FEVE dissolved in the mixed solvent, adding dispersant, catalyst dibutyltin dilaurate, silicone defoamer and other additives, and then grinding at a speed of 20~50 r/s for 130~170 min. The coating material was sprayed on the surface of the insulator ceramic substrate by compressed air spraying. The coating thickness was 0.5~0.7 mm, and the coating sample was prepared after curing at room temperature for 24 h.

Results and Discussion

Effect of modified rutile nano TiO_2 addition on properties of fluorocarbon anti-pollution flashover coatings

The modified rutile nano TiO_2 is prepared into a fluorocarbon anti-pollution flashover coating according to the addition amount of 0, 1%, 2%, 4%, 6% and 8%. The test is carried out according to the standard test method of static water contact angle, adhesion and volume resistivity. The results are shown in Figure 2 and Figure 3. It can be seen from Figure 2 that with the increase of the amount of modified rutile nano TiO_2, the static water contact angle increases gradually and then decreases slightly, and reaches the maximum value of 121° when the addition amount is 4%. At the same time, the adhesion of the coating is gradually improved. When the addition amount is 2%, the adhesion reaches 0 level, and the adhesion remains unchanged with the continuous increase of the addition amount. It can be seen from Figure 3 that the volume resistivity of the coating surface decreases slightly, but it still maintains at the order of 10^{10} Ω·m. Therefore, under comprehensive consideration, 4% is determined as the best addition amount of modified rutile nano TiO_2. The addition of G502 can couple with the hydroxyl groups on the surface of nano TiO_2, and bind to the surface of nano TiO_2 in the form of chemical bonds, forming a stable chemical bond with PTFE polymer matrix, forming a micro-nano binary rough structure, so as to enhance the hydrophobicity of the coating.

Analysis of the self-cleaning property of the coating

Taking rutile nano TiO_2-FEVE coating and rutile nano TiO_2/PTFE-FEVE coating as reference, compare with modified rutile nano TiO_2/PTFE-FEVE coating, as shown in Table 1 and Figure 4. Before UV irradiation, the static water contact angle of TiO_2-FEVE coating surface is 103°, the static water contact angle of TiO_2/PTFE-FEVE coating surface

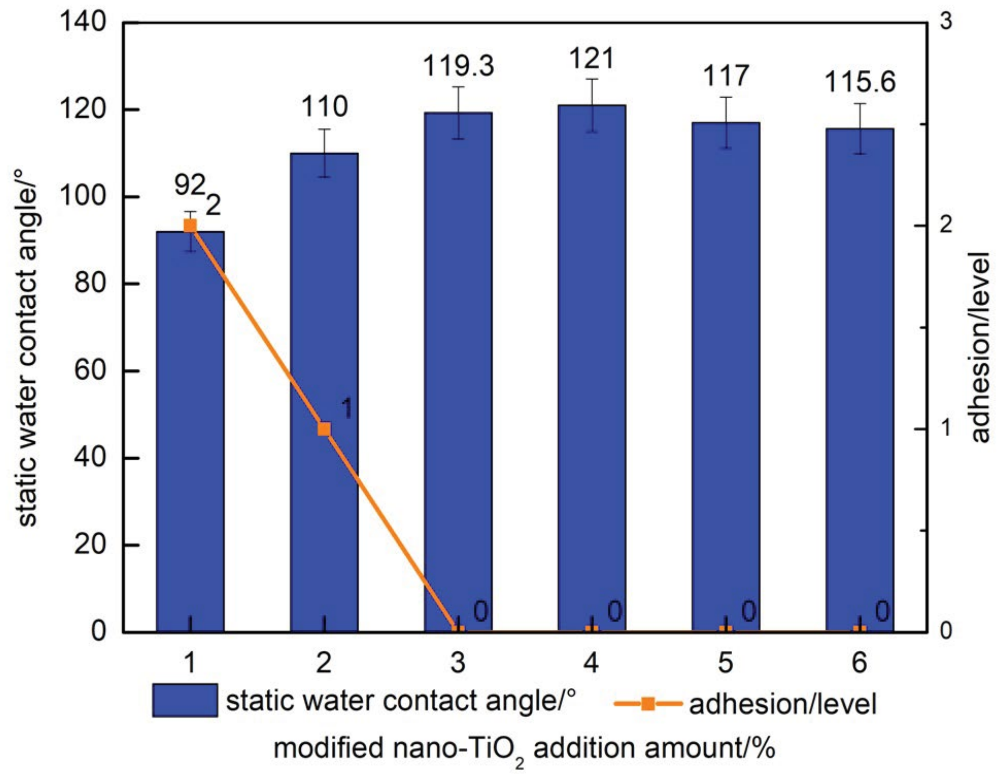

Figure 2: Effect of modified nano TiO_2 addition on static water contact angle and adhesion.

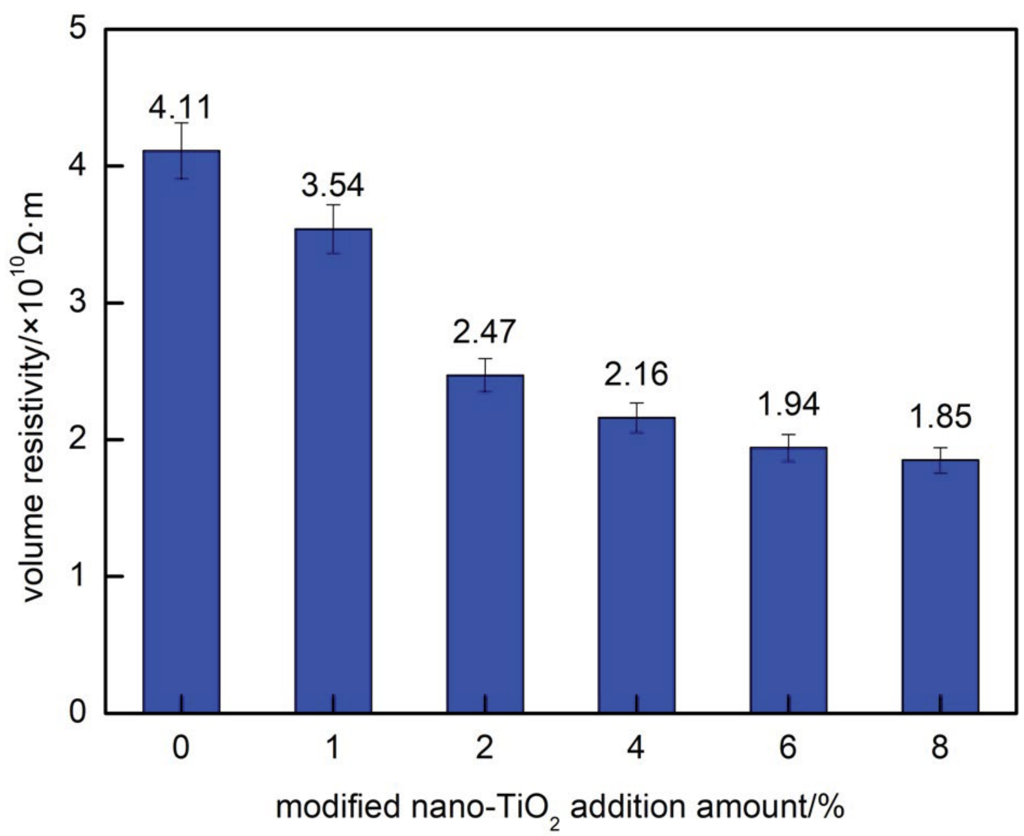

Figure 3: Effect of modified rutile nano TiO_2 addition on volume resistivity.

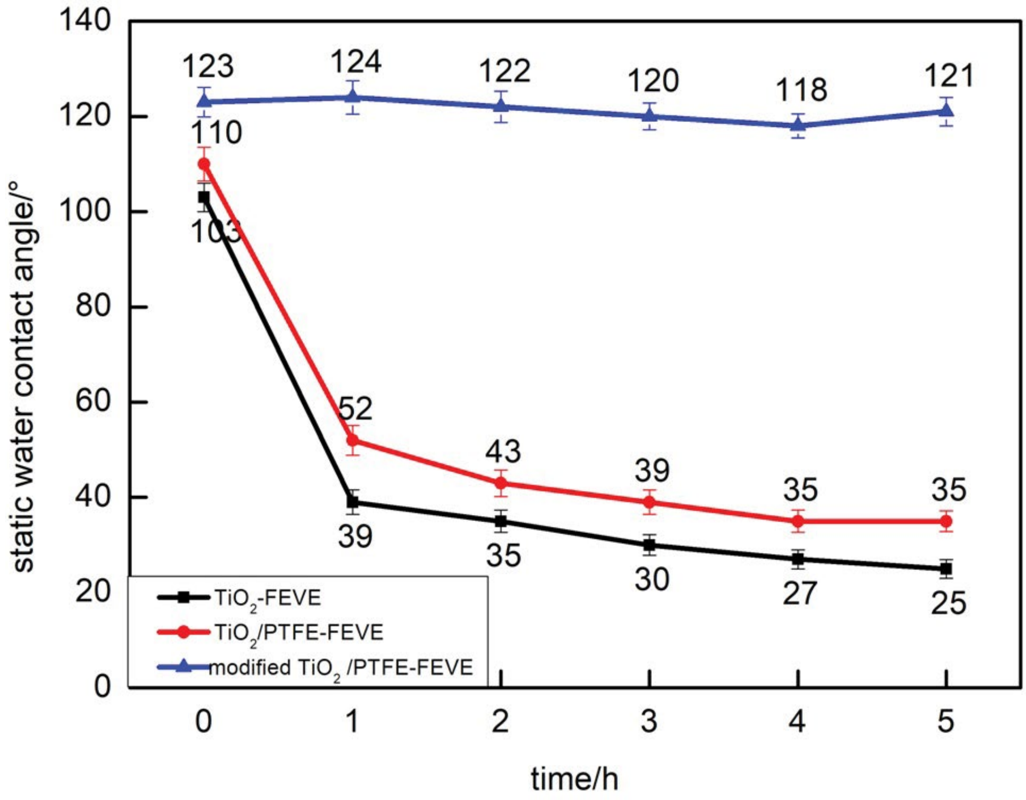

Figure 4: Change trend of static water contact angle of each sample under ultraviolet light irradiation.

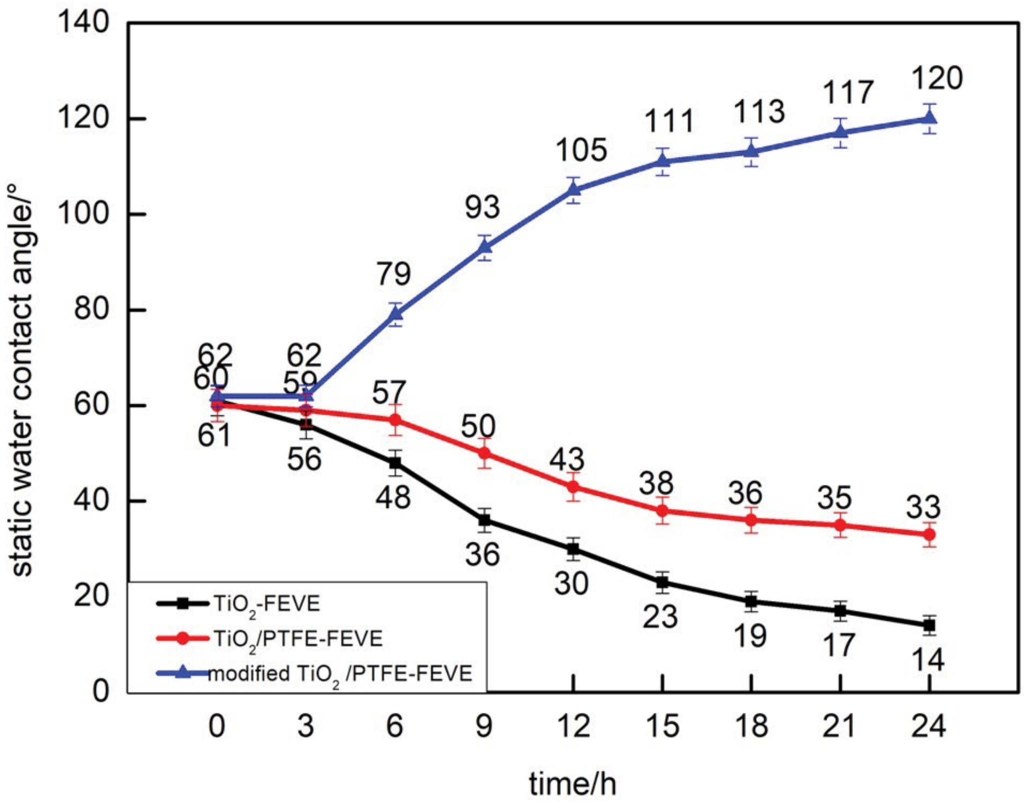

Figure 5: Change trend of static water contact angle of each sample adsorbed oleic acid under ultraviolet light irradiation.

is 110°, and the static water contact angle of modified nano TiO_2/PTFE-FEVE coating surface is 123°. The three coatings are hydrophobic. After UV irradiation for 5 h, the static water contact angle of the modified nano TiO_2/PTFE-FEVE coating surface remained basically at 121°, while the static water contact angle of the TiO_2-FEVE coating surface decreases rapidly to 25°, and the static water contact angle of the TiO_2/PTFE-FEVE coating surface decreased rapidly to 35°. The TiO_2-FEVE coating and TiO_2/PTFE-FEVE coating change from hydrophobic state to hydrophilic state. The micro-nano composite structure formed by modified nano-TiO_2 and micro-PTFE increased the surface roughness of the coating. In addition, the migration of low surface energy groups of fluorosilane to the coating surface resulted in the enrichment of F and Si to the coating surface, which reduced the surface energy of the coating. The surface hydrophilic groups were reduced accordingly, which was conducive to maintaining high hydrophobicity.

After the three coatings are adsorbed with oleic acid, they are irradiated with ultraviolet light for 24 h again. The static water contact angle changes of the surface are shown in Table 2 and Figure 5. It can be seen that the surface static water contact angles of TiO_2-FEVE coating, TiO_2/PTFE-FEVE coating and modified TiO_2/PTFE-FEVE coating are 61°, 60° and 62°, respectively, when oleic acid is adsorbed without UV irradiation. After 24 h of UV irradiation, due to the photo induced hydrophilicity effect, the surface static water contact angle of TiO_2-FEVE coating is finally 14°, and the surface static water contact angle of TiO_2/PTFE-FEVE coating is 33°, showing hydrophilicity. The static water contact angle of the modified TiO_2/PTFE-FEVE coating gradually increases from 62° to 120°, restoring its hydrophobicity. This is because the TiO_2 particles in the modified TiO_2/PTFE-FEVE coating can produce free radicals with strong oxidation ability through a series of photocatalytic reactions, so that oleic acid occurs bond breaking reaction, and is finally degraded into environmentally friendly carbon dioxide, water, inorganic acid and other products, to remove the adsorption of oleic acid on the surface of the coating. Therefore, the photocatalytic self-cleaning performance of modified TiO_2/PTFE-FEVE coating is better.

Anti-ultraviolet aging property test of the coating

The rutile nano TiO_2/PTFE-FEVE coating is used as a control, and the rutile nano TiO_2/PTFE-FEVE coating and the modified rutile nano TiO_2/PTFE-FEVE coating are subjected to an 8-week UV aging test. It can be seen from the results of the gloss loss test in Table 3 that the TiO_2/PTFE-FEVE coating has a 3-level gloss loss, and the modified TiO_2/PTFE-FEVE coating has a 2-level gloss loss. Among them, the gloss loss rate of the TiO_2/PTFE-FEVE coating gradually increases from 24% to 51% as the number of test weeks increases. With the increase of the number of test weeks, the light loss rate of the modified TiO_2/PTFE-FEVE coating increases slowly from 9% to 16%, and the light loss rate is much lower than that of the TiO_2/PTFE-FEVE coating. It can be seen from the test results of the discoloration test in Table 4 that the TiO_2/PTFE-FEVE coating shows a second-order discoloration, and the modified TiO_2/PTFE-FEVE coating does not show discoloration. Among them, the color difference of the TiO_2/PTFE-FEVE coating increases from 4.7 to 6.0 with the increase of the number of test weeks. The color difference of the modified TiO_2/PTFE-FEVE coating increases from 0.2 to 1.0 with the increase of the number of test weeks, and the color difference is much smaller than that of the TiO_2/PTFE-FEVE coating.

This is because nano TiO_2 can absorb or scatter part of the ultraviolet light, which can effectively prevent the ultraviolet light from destroying the methyl group on the coating side during the chain initiation, chain growth, self-cross linking and other stages of the ultraviolet aging free radical reaction of the coating, thereby inhibiting the formation of the hydrophilic group C=O [17,18]. In addition, the compatibility of modified TiO_2 nanoparticles with PTFE makes the chemical bonding force more stable, so the anti-ultraviolet aging performance of the modified TiO_2/PTFE-FEVE coating is better.

Physiochemical and electrical insulation properties test of the coating

The physical, chemical and electrical insulation properties of rutile nano TiO_2/PTFE-FEVE coating and modified rutile nano TiO_2/PTFE-FEVE coating are tested, as shown in Table 5. The results show that the adhesion of the prepared modified TiO_2/PTFE-FEVE coating to the substrate can reach level 0, which is due to the fact that the modified TiO_2 and PTFE as composite fillers can enhance the bonding force between the coating material and the substrate and make up for the deficiency of PTFE bonding force. At the same time, the hardness, water resistance, chemical reagent resistance, salt spray resistance and other physical and chemical properties of TiO_2/PTFE-FEVE coating and modified TiO_2/PTFE-FEVE coating are better and stable. In addition, compared with the TiO_2/PTFE-FEVE coating, the volume resistivity of the modified TiO_2/PTFE-FEVE coating measured under the same experimental conditions can reach 2.7×10^{10} Ω·m, the breakdown field strength can reach 23.7 kV/mm, the TMA2.5 level, the maximum electrical erosion depth can reach 1.23~2.65 mm, and the electrical insulation is better. In summary, the modified TiO_2/PTFE-FEVE coating has better anti-pollution flashover performance.

Conclusion

In this paper, a new type of nano TiO_2/PTFE fluorocarbon anti-pollution flashover coating is prepared by using FEVE as film-forming material, modifying rutile nano TiO_2 with fluorosilane coupling agent and PTFE as composite filler. The properties of the coating are tested and studied. According to the above results and discussions, the following conclusions can be drawn:

- The surface hydrophobicity of fluorocarbon coatings can be improved by adding rutile nano TiO_2 modified by fluorosilane coupling agent. The optimal addition amount of modified nano TiO_2 is 4%. At this time, the adhesion of fluorocarbon coatings can reach grade 0, and the static contact angle is up to 121°. At the same time, it has little effect on the electrical insulation of the coating.
- After 5 h of UV irradiation, the static water contact angle of the newly prepared modified rutile nano TiO_2/PTFE fluorocarbon anti-pollution flashover coating remained at about 120°. After 24 h of UV irradiation, the oleic acid adsorbed on the coating surface could be successfully removed, and the static water contact angle could be restored from 62° to 120° when the oleic acid is adsorbed without UV irradiation. The photocatalytic self-cleaning performance is good.
- After 8 weeks of anti-ultraviolet aging test, the newly prepared modified rutile nano TiO_2/PTFE fluorocarbon anti-pollution flashover coating has grade 2 loss of light, no discoloration, loss of light rate and color difference, which are also better than the reference sample. At the same time, there are no other aging phenomena such as pulverization, crack, foaming and shedding, and its anti-ultraviolet aging performance is relatively better.
- The newly prepared modified rutile nano TiO_2/PTFE fluorocarbon anti-pollution flashover coating has good physical and chemical properties such as water resistance, chemical reagent resistance and salt spray resistance. At the same time, its electrical insulation performance is better. The volume resistivity can reach 2.7×10^{10} Ω·m, the breakdown field strength can reach 23.7 kV/mm, and the maximum electric erosion depth can reach 1.23~2.65 mm. It has excellent anti-pollution flashover performance.

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