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The Effect of Silica Sol on the Stain Resistance of Exterior Wall Latex Coatings through Natural Exposure to Sunlight

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Abstract: Stain resistance is one of the important characteristics of exterior wall latex coatings in cities. Adding silica sol to the coating can increase its stain resistance. However, there is currently limited research on the long-term natural exposure test of latex coatings. This paper first investigates the influence of different amounts of silica sol on the elongation, water absorption, and stain resistance of coatings and obtains a better percentage of silica sol addition. Then, heat storage tests were conducted to obtain the viscosity and pH changes of the coating. Afterwards, outdoor natural exposure tests were conducted for up to 12 months to obtain the stain resistance of the coating with the addition of silica sol. The results indicate that the stain resistance value of the coating with added silica sol was significantly better than that without added silica sol after 12 months of natural exposure to sunlight, increasing by 65.8%. The formation of a network structure of Si O-Si bonds in the silica sol enhances the hardness and rigidity of the coating while also allowing it to enter the capillary tubes of the coating caused by prolonged exposure to sunlight, avoiding cracking of the coating and preventing the entry of dust and impurities. Therefore, the stain resistance of the coating is improved. These research results will contribute to the better application of exterior wall latex coatings in architecture.

Keywords: silica sol; stain resistance; exterior coatings; latex coatings; natural exposure to sunlight

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1. Introduction

Exterior wall coatings have become the protagonist in decorating and protecting building exterior walls due to their light weight, safety and environmental protection, and simple construction [1,2]. They gradually replace exterior wall decoration materials which pollute the environment and have poor safety. Latex coatings have good elasticity and can cover capillary cracks in exterior walls and place concrete to prevent carbonization, and have received popularity in the market [3,4]. The film formation of latex coatings requires a process of forming a whole layer from dispersed polymer particles and pigment particles. These particles maintain a dispersed state in the latex coating through a double layer and shielding stability. After being applied as a wet film, the water gradually evaporates, and the dispersed particles gradually draw closer to each other. When approaching a certain degree of closeness, the adjacent particles will be tightly squeezed together, losing the freedom of movement and becoming gel-like. At this stage, water can still be redispersed, and when the water further evaporates, the volume of the wet film shrinks. When water is about to evaporate, capillary force plays a significant role, and the contraction of volume and capillary attraction are enough to outweigh the dispersion and stable repulsion of these particles, causing them to contact, attract, flow, and condense with each other to form a complete paint film.

The latex coating used on exterior walls is constantly exposed to the outdoor natural environment and is constantly subject to various external pollution [5]. Therefore, stain resistance is an important characteristic of architectural coatings in cities [6–8]. However, latex coatings are relatively soft. In hot and rainy summer weather, the surface of the

coating is prone to becoming soft or even sticky, easily adhering to dust and impurities in the air, greatly reducing its stain resistance [9]. In addition, if water enters the wall, the alkaline substances precipitated from the concrete due to the erosion of water will seep out through the coating in the form of aqueous solution from the cement pores [10]. This will cause the coating to lose its proper color and cause spots to appear. Adding silica sol to the coating will reduce the probability of the above problems occurring. The silica sol particles are fine, and the silica during gel precipitation has high activity and can form new silicate inorganic polymer compounds with certain inorganic salts and metal oxides [11,12]. This causes a very hard film to be formed. After the formation of silica sol film, a network structure of silica oxide, which is not phobic towards acid or alkali, is formed, improving the corrosion resistance of the coating. Some scholars have conducted research on the application of silica sol in coatings [13,14]. However, most studies focus on the production of synthetic coatings or silica sol materials, and stain resistance tests are conducted in the laboratory [15–17]. Compared to laboratory testing, a more reliable method for testing the stain resistance of coatings is to use natural exposure to sunlight. There is currently limited research on the long-term natural exposure test of latex coatings with the addition of silica sol.

This paper first investigates the influence of different amounts of silica sol on the elongation, water absorption, and stain resistance of coatings and obtains a better percentage of silica sol addition. Then, heat storage tests are conducted to obtain the viscosity and pH changes of the coating. Afterwards, outdoor natural exposure tests are conducted to obtain the stain resistance of the coating with the addition of silica sol, and its stain resistance principle is elucidated. This article clarifies the influence of silica sol on the stain resistance of latex coatings, making contributions to the better application of exterior wall latex coatings in buildings.

2. Materials and Experimental

The main formulation of exterior wall latex coating is shown in Table 1. The technical specifications of silica sol are shown in Table 2. Silica sol was added into latex coating in proportion, and PVC was adjusted to 38%. Afterwards, the elongation, water absorption, and stain resistance of the coating were measured. Elastic emulsion (POLYSOL AP-5085) was produced by Showa Polymer Co., Ltd., in Shanghai, China. It is an acrylate copolymerized elastic emulsion, and its Tg value is 10 °C.

Table 1. The main formulation of exterior wall latex coating.

Raw Material Name	Elastic Emulsion	Dispersant	Defoamer	Wetting Agent	Titanium Dioxide	Heavy Calcium Carbonate	Coalescent	Preservative	Thickener
Mass fraction/%	30	0.5	0.3	0.1	15	20	0.5	0.2	0.5

Table 2. The technical specifications of silica sol.

Name	SiO_2 Content/%	Stabilizer Type/%	PH Value	Density at 20 °C	Average Particle Size/nm
Data	30	$NaO_2 \leq 0.5$	9–10.5	1.21	12

The weight of the sample after drying is measured, and then it is immersed in water for 24 h before weighing. The percentage of the difference in mass between the latter and the former in the weight of the coating is the water absorption rate. The elongation of the coating is measured using a tensile machine, and the sample is stretched at a speed of 200 mm/min until cracks appear. The distance between the jaws during the elongation test is 25 mm. The sample preparation method for elongation is as follows: The coating was thoroughly stirred and mixed evenly in the container and poured into the steel coating mold three times to make the film. Mold A, with a size of 230 mm × 100 mm × 1 mm, was used for the first film's production. The mold was removed after 24 h of film formation.

When making the second film, Mold B, with a size of 235 mm × 105 mm × 1.2 mm, was removed after 24 h of film formation. When making the third film, Mold C, with a size of 240 mm × 110 mm × 1.5 mm, was removed after 24 h of film formation. Afterwards, the prepared coating was placed in a curing box with a temperature of 23 °C and a humidity of 50 for 48 h. Then, the coating was flipped over and placed in an 80 °C drying oven for insulation for 96 h. Afterwards, the coating sample was cut into dumbbell-shaped specimens with a length of 115 mm, a maximum width of 25 mm, and a minimum width of 6 mm. The samples were cured for 7 days with each side facing upwards, for a total of 14 days. After the above steps, the sample preparation of coating elongation was completed. The elongation of the coating was tested at three different temperatures (−10 °C, 25 °C, 80 °C). These three temperatures represent typical temperatures of low temperature, room temperature, and high temperature, respectively. The stain resistance test is conducted using a self-made testing machine, as shown in Figure 1. The 15 L water in a 2 m high water tank is used to rinse the coating on the sample for 1 min, and then the reflection coefficient is recorded. The difference in reflection coefficient before and after the experiment can characterize the stain resistance of the coating.

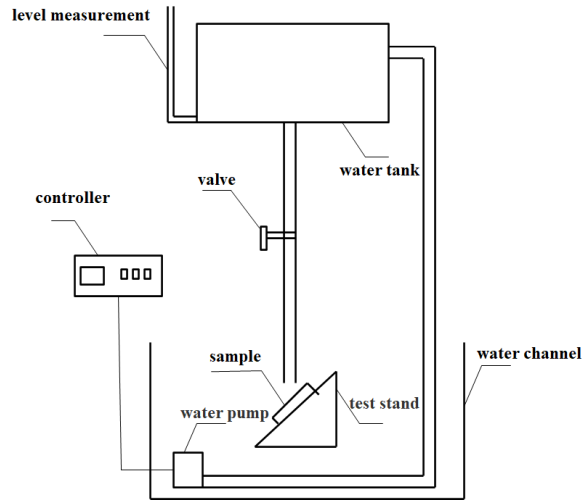


Figure 1. The self-made stain resistance testing machine.

After storage, the viscosity of the coating will increase, while the pH value will decrease. The decrease in pH value may lead to the condensation of silica sol. Therefore, in order to study the stability of coatings with silica sol added, different proportions of pH value regulator 15% NaOH solution were added and then placed in a 50 °C oven for thermal storage testing to determine the changes in viscosity and pH value of the coating over a certain period of time.

The sample preparation method for exposure test is as follows: The substrate was made of asbestos cement flat plates, with a size of 150 mm × 70 mm × 5 mm. The wire rod applicator was used to brush paint. The test panel was placed in an environment with a temperature of 23 °C and a relative humidity of 50 for 7 days. The samples for the exposure test were made. The natural exposure test was completed using an exposure rack, which forms a 45° angle between the sample and the ground (Figure 2). This exposes the sample completely to sunlight. The total duration of the natural exposure test is 12 months. Natural exposure to sunlight starts in January and ends in December. The location of the exposure is located in the southeastern region (Xinyu City, Jiangxi Province) of China. The altitude of this area is between 500 and 1000 m. The region belongs to a subtropical monsoon climate with sufficient sunlight and abundant rainfall. The minimum temperature is −2 °C, the maximum temperature is 39 °C, and the annual average temperature is 11.6 °C–19.6 °C. More than 50% of the annual precipitation is concentrated in April to July. The natural exposure test uses at least 5 samples, and after exposure for a period of time, the

reflection coefficient of the same sample was measured to demonstrate the stain resistance of the coatings.

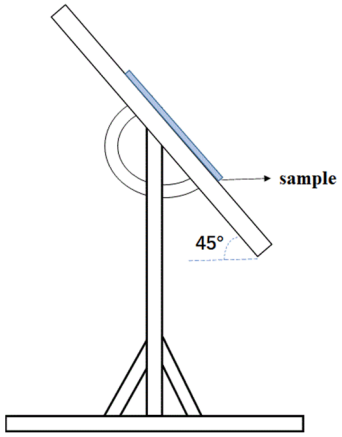


Figure 2. Schematic diagram of exposure rack.

Before the exposure test, the reflection coefficient was measured at the top, middle, and bottom three positions of each test panel. Their average value was recorded as the original reflection coefficient A. After the exposure test, the above steps were repeated to obtain the reflection coefficient B. Reduction rate of reflection coefficient of coating ($X = (A - B) \times 100\%/A$) was the stain resistance value of the coating. When the exposure reached a certain period of time, the sample was taken off for reflection coefficient measurement and the stain resistance value was calculated. Afterwards, it was exposed to sunlight until the scheduled time was reached. Finally, the stain resistance values at different stages within the year were obtained.

A viscometer is used to measure viscosity with an accuracy of 0.1. The pH meter is used to measure the pH value with an accuracy of 0.01. All tests were repeated at least 4 times.

3. Results and Discussion

3.1. The Effect of the Amount of Silica Sol Added

Figure 3 shows the elongation rate of coating with different addition amounts of silica sol. Figure 4 shows the water absorption rate of coating. Figure 5 shows the staining resistance value of coating. At different temperatures (low temperature, room temperature, and high temperature), the elongation of the coating decreases with the increase in silicon addition. For the three temperatures, the elongation is highest at 25 °C, second-highest at 80 °C, and lowest at −10 °C. As the addition amount of silica sol increases, the water absorption decreases, and the stain resistance is improved. The addition of silica sol is beneficial for improving the density and rigidity of the coating film while also introducing more hydrophilic groups [18]. The impact of density on water absorption is significantly greater than that of rigidity, resulting in a decrease in water absorption. The decrease in water absorption rate contributes to the improvement of stain resistance, and there is a linear relationship between the two. When the addition amount of silica sol is 10%, the stain resistance value is 17 and the elongation can meet the requirements. After 15% addition, the stain resistance value decreased to 14, but the low-temperature elongation significantly decreased and was unable to meet the requirements. Therefore, the optimal amount of silica sol addition was determined to be 10%.

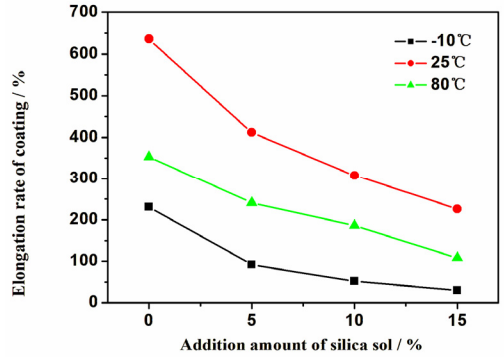


Figure 3. Elongation rate of coating.

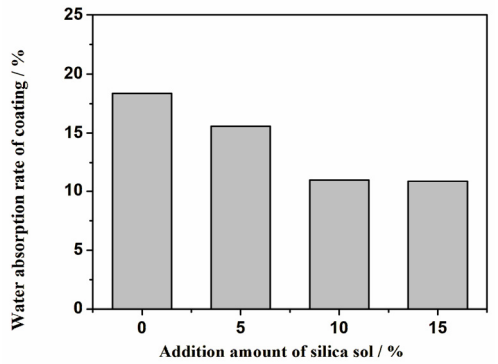


Figure 4. Water absorption rate of coating.

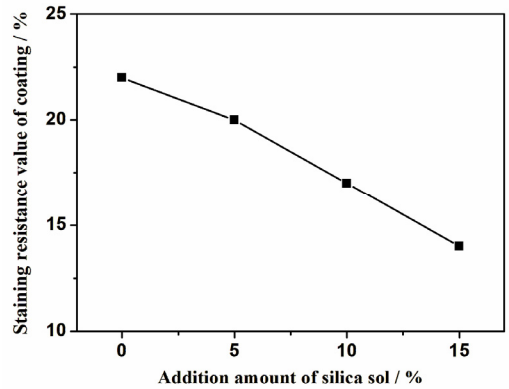


Figure 5. Staining resistance value of coating.

3.2. Heat Storage Test

Table 3 shows the viscosity fluctuations of coating at 50 °C, and Table 4 presents the pH value fluctuations of coating at 50 °C. When the addition amount of NaOH is 0.2% and the initial pH value of the coating is 8.39, the viscosity of the coating increases from 73.1 to 91.2 after 3 days of hot storage, and the phenomenon of increasing viscosity is very obvious. When the amount of NaOH is greater than 0.4% and the initial pH value is above 8.7, the rate of viscosity of the coating increases, and after 3 days of hot storage, it decreases. Especially when the amount of NaOH added is greater than 0.8% and the initial pH value is above 9, not only does the viscosity of the coating decrease after 3 days of hot storage, but the viscosity of the coating also remains basically unchanged during storage for 30 days. During the experiment, it was found that when the amount of NaOH added was 3.2%, the viscosity of the coating increased rapidly and a large amount of agglomeration was generated. After further stirring for a period of time, the agglomeration of particles could disappear. The surface of colloidal particles in silica sol generally carries

a small amount of charge to stabilize its nanodispersion system. However, when silica sol is mixed with coating, the pH value of the system is changed due to the addition of new media, and the surface charge property of SiO_2 colloidal particles will change. When the pH value is between 3–7 or greater than 11, the colloid itself is prone to coalescence, leading to instability and thickening of the system. In the case of 3.2% NaOH, the initial pH value is 11.86, higher than 11. Therefore, the viscosity of the system increases rapidly and becomes unstable during the preparation process. Although the thermal storage results of the coating are stable at this condition, its initial pH value is 11.85, which is already higher than the non-stationary pH value of 11. Due to the rapid increase in viscosity and instability during the preparation of coatings, the pH value of the coating should be controlled below 11. Therefore, based on a comprehensive analysis of the data in Tables 3 and 4, the thermal storage stability of the coating can meet the requirements when the initial pH value is controlled between 8.7–10.93, i.e., the amount of NAOH added is 0.4%–2.4%.

Table 3. Viscosity (KU) fluctuations of coating at 50 °C.

15% NaOH Content/% / Heat Storage Time/Day	0.2	0.4	0.8	1.6	2.4	3.2
0	73.1 ± 0.2	82.2 ± 0.1	108.9 ± 0.3	98.1 ± 0.2	97.5 ± 0.1	99.8 ± 0.2
3	91.2 ± 0.1	84.4 ± 0.3	113.3 ± 0.1	99.2 ± 0.2	97.4 ± 0.1	100.7 ± 0.1
7	93.2 ± 0.1	86.5 ± 0.1	114.5 ± 0.1	98.5 ± 0.1	97.4 ± 0.1	100.5 ± 0.1
14	92.0 ± 0.2	85.9 ± 0.2	114.3 ± 0.1	97.7 ± 0.3	96.9 ± 0.1	100.6 ± 0.1
30	95.4 ± 0.1	87.7 ± 0.1	113.7 ± 0.2	97.1 ± 0.5	96.9 ± 0.1	100.0 ± 0.2

Table 4. pH value fluctuations of coating at 50 °C.

15% NaOH Content/% / Heat Storage Time/Day	0.2	0.4	0.8	1.6	2.4	3.2
0	8.39 ± 0.21	8.7 ± 0.18	9.02 ± 0.17	9.79 ± 0.19	10.93 ± 0.26	11.85 ± 0.24
3	8.08 ± 0.07	8.39 ± 0.24	8.73 ± 0.10	9.48 ± 0.14	10.36 ± 0.15	10.98 ± 0.20
7	8.15 ± 0.04	8.33 ± 0.12	8.65 ± 0.08	9.32 ± 0.12	10.19 ± 0.14	10.68 ± 0.17
14	8.05 ± 0.06	8.29 ± 0.12	8.47 ± 0.11	9.19 ± 0.07	9.97 ± 0.09	10.45 ± 0.17
30	7.95 ± 0.05	8.17 ± 0.17	8.31 ± 0.13	9.11 ± 0.04	9.80 ± 0.07	10.25 ± 0.12

3.3. Natural Exposure to Sunlight Test

Figure 6 presents the staining resistance of coating after natural exposure to sunlight test. After adding silica sol, the stain resistance value of the coating was lower than that of the coating without silica sol, which indicates that the stain resistance was significantly improved. Through a comparison of 12 months of exposure test data, the increase in stain resistance of the coating with the addition of silica sol was much smaller than that of the coating without the addition of silica sol. Especially after 12 months of natural exposure to sunlight, the stain resistance value of the coating with added silica sol was only 13%, which increased by 65.8% compared to the coating without added silica sol.

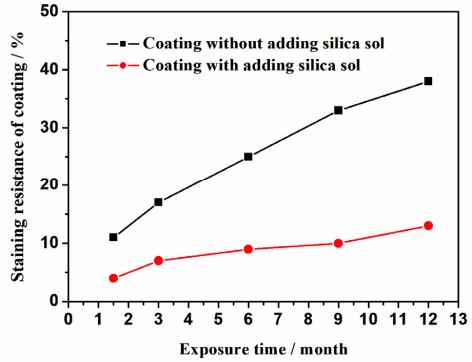


Figure 6. Staining resistance of coating after natural exposure to sunlight test.

3.4. Staining Resistance Mechanism

The silica sol is a dispersion system of amorphous silica colloidal particles in water, with a molecular formula expressed as $mSiO_2 \cdot H_2O$. Its appearance is a milky white translucent liquid. After dehydration, the silica sol particles undergo dehydration and condensation to form a rigid microporous framework structure. This structure exhibits high compressive strength, high hardness, and breathability in terms of physical properties. In terms of chemical properties, it is inert, non-toxic, and stable. As shown in Figure 7, the internal structure of silica sol particles is a siloxane bond (-Si-O-Si-). Its surface layer is covered by many siloxane groups (-SiOH) and hydroxyl groups (-OH), which together with alkali metal ions present in the colloidal solution—form a diffusion double layer [19]. The electrostatic interaction between particles plays an important role in the stability of the colloidal solution. Silica sol is a sol with colloidal properties, particle-like spheres, and negative charges. The three major factors of ζ potential, Brownian motion, and sufficient solvent barrier endow it with aggregation stability and kinetic stability [20]. However, the colloidal particles are metastable and always exhibit a tendency for spontaneous aggregation. As long as one of the three stabilizing factors is weakened, it will automatically coalesce to produce gel or coalescence. When the silica sol condenses into gel, it cannot be heated or added with solvent to make it become a sol again, so it is an irreversible colloid.

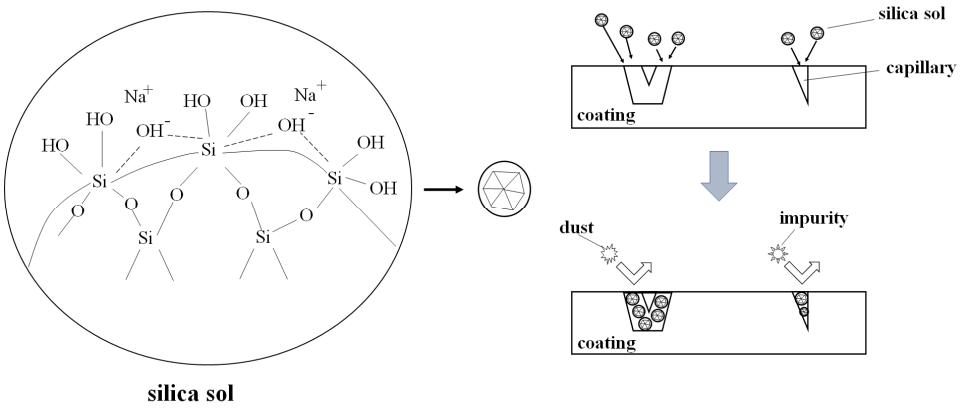


Figure 7. Schematic diagram of silica sol enhancing the stain resistance of coatings.

The Si-O-Si bond in silica sol has a high bonding energy and good bonding stability. Its ultrafine particles have a large specific surface area and are prone to form irreversible silica network structures after film formation (Figure 7). The coating with the addition of silica sol is hard and has strong rigidity, which does not easily generate electrostatic adsorption and has good stain resistance. This is because silica sol increases the surface density of the elastic coating and reduces the inhalation pollution of the coating [21,22]. The latex coatings exposed to prolonged sunlight are prone to cracking and producing capillaries. The tiny capillaries of the coating continue to expand under long-term sunlight exposure, which can easily hide dust and impurities inside. Over time, the stain resistance gradually weakens, and even the capillaries expand to form cracks, shortening the service life of the coating. Adding silica sol to the coating will likely reduce the occurrence of this situation. The silica sol particles have fine size and strong permeability to the substrate. Fine particles can penetrate into the interior of the substrate through capillary action, thus sealing the pores on the surface of coating. Because of this, it will be difficult for dust and impurities to enter the interior of the coating, thereby improving the stain resistance of the coating.

4. Conclusions

This paper concentrates on the stain resistance of exterior wall latex coatings with added silica sol through natural exposure to sunlight. The main conclusions arising from this paper are as follows:

(1) As the addition amount of silica sol increases, the elongation of the coating significantly decreases, while the water absorption also decreases and the stain resistance is improved.
(2) When the amount of NAOH added is 0.4%–2.4%, the pH value of the coating is controlled between 8.7–10.93 and the thermal storage stability of the coating can meet the requirements.
(3) After 12 months of natural exposure to sunlight, the stain resistance value of the coating with added silica sol was significantly better than that without added silica sol, increasing by 65.8%.
(4) The formation of a network structure of Si O-Si bonds in the silica sol enhances the hardness and rigidity of the coating, while also allowing it to enter the capillary tubes of the coating caused by prolonged exposure to sunlight, avoiding cracking of the coating and preventing the entry of dust and impurities. Therefore, the stain resistance of the coating has been improved.

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