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The influence of nano-silica sol on the performance of iron chromium black for the building energy-saving coating

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The nano-silica sol was modified by a silane coupling agent KH560 for the building energy-saving coating. The effect of the modified silica sol dosage on coating properties was discussed. Increasing the amount of modified silica sol can enhance the reflective properties of the coating and improve the ageing resistance and stain resistance of the coating. However, the excessively modified silica sol can cause film formation difficulties, but reduce the performance of the coating. When the mass ratio of the modified silica sol to the pure acrylic emulsion is 1:1, the overall performance of the coating is the best; the solar reflectance and the near-infrared reflectance of the coating without the modified silica sol increased by 7.41 % and 8.33 %, respectively, the rate of change of solar reflectance after aging and pollution is reduced by 2.67 % and 1.30 %, and the static water contact angle is increased by 29.2°. Water resistance, adhesion, pencil hardness, flexibility and impact strength have all been improved to some extent.
Keywords: building energy-saving coating, silica sol, modification.

Золь нанокремнезема модифицирован силановым связующим агентом KH560 для получения энергосберегающего покрытия из железо-хромовой сажи. Обсуждается влияние дозировки модифицированного золя кремнезема на свойства покрытия. Увеличение количества модифицированного золя кремнезема может улучшить отражающие свойства покрытия и улучшить устойчивость к старению покрытия. Однако чрезмерно модифицированный золь диоксида кремния может вызывать трудности формирования пленки и снижать характеристики покрытия. Когда массовое отношение модифицированного золя кремнезема к чистой акриловой эмульсии составляет 1:1, общие характеристики покрытия являются наилучшими: коэффициент отражения солнечного света и ближнего инфракрасного света покрытия без модифицированного золя кремнезема увеличился на 7,41 % и 8,33 %, соответственно. Скорость изменения солнечной отражательной способности после старения и загрязнения уменьшается на 2,67 % и 1,30 %, а статический угол контакта с водой увеличивается на 29,2°.

Вплив золю кремнезему на характеристики залізо-хромової сажі будівельного енергозберігаючого покриття. *Q.Gao, J.Wen*.
Золь нанокремнезему модифікований силановим сполучним агентом KH560 для отримання енергозберігаючого покриття з залізо-хромової сажі. Обговорюється вплив дозування модифікованого золю кремнезему на властивості покриття. Збільшення кількості модифікованого золю кремнезему може поліпшити відбивальні властивості покриття і поліпшити стійкість до його старіння покриття. Проте надмірно модифікований золь діоксиду кремнію може викликати труднощі формування плівки і знижувати характеристики покриття. Коли масове відношення модифікованого золю кремнезему до чистої акрилової емульсії становить 1:1, загальні характеристики покриття є найкращими; коефіцієнт відбиття сонячного світла і ближнього інфрачервоного світла покриттям без модифікованого золю кремнезему збільшився на 7,41 % і 8,33 %, відповідно. Швидкість зміни сонячної відбивної здатності після старіння і забруднення зменшується на 2,67 % і 1,30 %, а статичний кут контакту з водою збільшується на 29,2°.

1. Introduction

Ordinary synthetic resin architectural coatings are easy to adsorb dust and have poor stain resistance. After a long time, the coating is easy to age, resulting in a significant reduction in the reflectance, which greatly affects the energy-saving effect of heat insulation. Inorganic coatings use silica sol, sodium silicate/potassium as raw materials, are easy to produce, are characterized by low energy consumption and low cost. For example, the inorganic silica sol coating has the Si–O bond which does not easy accumulate charge after curing, does not easy generate static electricity, and does not easy adsorb dust; the bond energy of Si–O–Si bond is high, it is very good against ultraviolet rays, corrosive waste, etc., shows a good anti-erosion effect and good weather resistance. Therefore, the use of the silica sol as the main film-forming binder will extend the service life and functional durability of building energy-saving coatings. Most of the energy-saving coatings reported at present are organic resins or emulsions with excellent film-forming properties as film-forming binders. Although building energy-saving coatings prepared with inorganic film-forming binders have been reported [1], they are limited to the proportioning experiments, and there are few reports on the modification of inorganic film-forming binders in advance. When the silica sol is used as a film-forming material alone, the film forming property of the coating is extremely poor, and the internal dry shrinkage force after curing is large; this causes the inside of the coating to be filled with cracks and pores [2, 3]. Therefore, the synthetic resin emulsion is often selected to be used as a film-forming binder. Commonly used synthetic resin emulsions are pure acrylic emulsions and styrene-acrylic emulsions. Although the price of the styrene-acrylic emulsion is relatively low, the durability and stain resistance are rather poor, and it is not suitable for exterior wall applications.

The authors of [4] show that the surface of colloidal silica nanoparticles usually has a small charge to stabilize the nano-silicon dispersion. However, when mixed with an emulsion, the surface charge property of the colloidal SiO_2 particles changes due to the addition of a new medium; and the pH value of the system changes. When the pH value of the system is in the range of $3 < pH < 7$ or $pH > 11$, the colloid can stick together, which will lead to the system becoming unstable and becoming viscous. Therefore, the pH value of the recommended coating system should be guaranteed in the slightly alkaline range (pH:815–1010). In [5], it is noted that nano-silicon sols are widely used in the coating industry to improve the adhesion of coatings and to strengthen weak substrates; It can also be used as a refractory binder, with strong adhesion and high temperature resistance (1200 ~ 1600°). In [6], it was found that sol particles of nano-silica are small, and silica exhibits high activity during gel formation and can form a new silicate inorganic polymer compound with some inorganic salts and metal oxides to form a very hard film. Small particles have a strong penetrating ability to the substrate, and the small particles can penetrate into the substrate under the action of capillaries.

The innovation of this paper is to modify the surface compatibility of silica sol with a silane coupling agent to improve its compatibility with emulsion; then to introduce it into the iron-chrome black of the energy-saving coating system for buildings, and to determine the addition amount of modified silica sol. The influence of layer performance provides a reference for the preparation of the energy-saving coatings with excellent aging resistance and stain resistance.

2. Experimental

The following materials were used: pure acrylic emulsion RS-6733 (solid content 48 %±2 %, average particle size 0.8 ~ 1.2 μm, Guangdong Baidefu Chemical Co., Ltd.); silica sol JN-30 (solid content 30 %, average particle size 5 ~ 10 nm, Qingdao Ocean Chemical Co., Ltd.); iron chrome black A2901 (average particle size is about 2.5 μm, Hunan Jufa Technology Co., Ltd.); thickener SN-162 (Japan Nopko Group); defoamer L-1311, (American Ashland Co., Ltd.); dispersant BYK-163, (Germany Bi Ke Chemical Co., Ltd.); film forming aid Texanol (American Eastman Co., Ltd). The above materials are all of industrial grade. The silane coupling agent KH560 [γ-(2, 3-epoxypropoxy) propyltrimethoxysilane] was of analytical grade and was supplied by Hubei Wuda Silicone New Material Co., Ltd. Deionized water was homemade [7].

Studies were carried out on four groups of samples A, B, C, D. The basic composition of the iron chrome black energy-saving coatings for buildings is shown in Table 1 (A). In the experiments (B, C, D), it was found that continuing to increase the silica

Table 1. Compositions of iron-chrome black energy-saving coatings for buildings

Recipe number	m (Pure acrylic emulsion), g	m (Silica sol), g	m (KH560), g	m (Iron chrome black), g	m (Filming aid), g	m (Dispersant), g	m (Defoamer), g	m (Thickener), g	m (water), g
A	300	0	0.00	36	4	3	3	3	60
B	200	100	0.75	30	10	3	2	2	0
C	100	100	0.75	20	5	3	1	1	0
D	100	200	1.50	30	5	3	2	2	0

sol content would make the coating film difficult, so no more experiments were carried out on the amount of silica sol.

The mixture of KH560 and silica sol was heated in a water bath at a constant temperature 60°C and mechanically stirred for 4 h. The pH of the system was adjusted to about 8 with ammonia water to discharge, and the modified silica sol was obtained [8].

A pure acrylic emulsion was added to the modified silica sol according to the dosage. After mixing, the filming aid, dispersant, antifoaming agent and thickener were added. After mechanical stirring for 5 min, the iron-chrome black was added and dispersed at low speed for 15 min. After filtration, the iron chrome black energy-saving coating was obtained. To facilitate spraying, the viscosity of the coating was adjusted to about 30 mm^2/s. It was injected into the spraying device with controlling the spraying pressure to 0.3 MPa; the coating was sprayed evenly on the surface of the aluminum alloy plate (maintaining the gun at the distance of 300 mm vertically from the substrate); then under the standard curing conditions [temperature (23±2)°C, relative humidity 50 %±5 % for 168 h, the thickness of the coating after drying was about 40 μm [9].

The silica sol before and after the modification was dried at 120°C in vacuum for 2 h to obtain a silica sol powder. The group structure was analyzed by Fourier transform infrared spectroscopy (FT-IR) using a Nicolet 6700 instrument (Thermo Fisher Company, USA). The microstructure of the silica sol powder before and after modification was observed by SN-3700N scanning electron microscope (SEM) of Hitachi.

The reflectance spectra of the coatings in the solar (400 to 2500 nm) and near-infrared (780 to 2500 nm) bands were measured using an Agilent Cary-5000 UV/Vis/NIR spectrophotometer. The infrared emissivity of the coating in the band of 8 to 14 μm was measured by the HWF-2 infrared emissivity measuring instrument of the North Chihong Optoelectronics. The brightness of the coating, L, the red-green property, a, and the yellow-blue property, b, were measured by an HP-200 precision colorimeter of Shanghai Hanpu Optoelectronics Technology Co., Ltd.

To characterize the quality of the coatings, the following parameters were measured: the solar reflectance of the coating (TSR), the near infrared reflectivity (NIR), the rate of change of the solar reflectance (ΔTSRW), the chromatic aberration and infrared radiation of the coating after contamination and artificial exposure to the atmosphere (ΔTSRL), ΔE^* and $\Delta\varepsilon$, respectively. Among them:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}.$$

Let us measure the mass m_0 of the dried 125 mm×25 mm rectangular test piece (accurate to four decimal places), and then immerse it in a water bath incubator at 25°C for 48 h. After taking out, the surface is dried with a dry towel to weigh. For m_1, the water absorption rate is

$$q = [(m_1 - m_0)/m_0]\times 100\ \%.$$

3. Results and discussion

3.1. Morphology and structure of silica sol

As can be seen from Fig. 1 (1), the absorption bands of 1111 cm^{-1} and 796 cm^{-1} correspond to the absorption peak of the vibration against expansion and the absorption peak of the symmetric tensile vibration of the Si–O–Si bond; the band 2841 cm^{-1} is the characteristic peak of methylene, the band 2943 cm^{-1} is the characteristic peak of absorption of methyl, the band 3435 cm^{-1} is the peak of vibration absorption when the surface of nanosilica is stretched with hydroxyl [10]. The addition of KH560 attenuates the hydroxyl absorption peak at 3435 cm^{-1}, and the appearance of new methyl and methylene absorption peaks indicates that KH560 not only physically mixes with the silica sol, but also with hydroxyl groups on the surface of nano-silica. This confirms that the addition of KH560 successfully modified the silica sol.

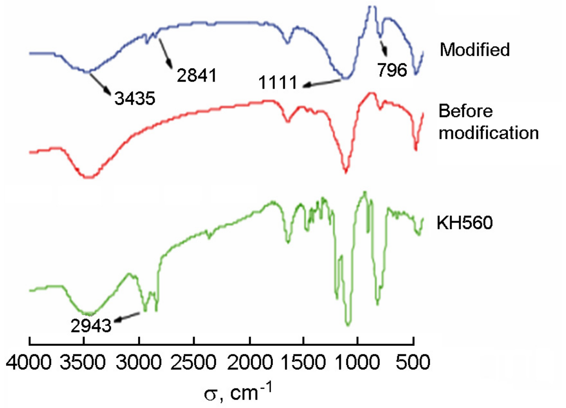

Fig. 1. Infrared spectrum of KH560 before and after modification of silica sol powder.

3.2. Effect of KH560 modified silica sol on the reflective properties of iron chromium black energy-saving coatings on buildings

The solar reflectance can indirectly indicate the thermal insulation effect of the building energy-saving coating: the higher the solar reflectance, the more energy the coating reflects, the less energy is absorbed, and the better the heat insulation effect. Fig. 2 and Table 2 show the reflection of the iron-chromium black energy-saving coating with different modified silica sol contents.

When the amount of modified silica sol increases, the reflection coefficient of the visible light of the coating first increases and then decreases. This is due to the fact that nanosilica in the modified silica sol increases the effective reflection of the coating in visible light, however, an excess of silica reflects irregular light and is mainly scattered inefficiently. Compared with coating A (without a modified silica sol), a coating with a modified silica sol (B and C) has stronger reflective properties in the near infrared region, which is due to the reflection properties of nanosilica in the near infrared region. Compared to coatings B and C, coating D (with the highest content of modified silica sol) has a lower reflection coefficient. However, coating D is difficult to form.

The increased content of modified silica sol has a great influence on the reflection performance of the coating in the visible and near-infrared long-wavelength bands, but the solar spectral energy is mainly concentrated in the visible and near-infrared short-wavelength bands (wavelength 780 ~ 1200 nm), near-infrared long-wavelength. The solar spectrum energy distribution of the band is small, so the average value of the solar energy reflected by the coating is mainly determined by the visible light reflectance, so it also tends to increase first and then decrease. The average values of the solar energy reflected by the B and C coatings are 0.25 W/(m^2·nm) and 0.24 W/(m^2·nm) respectively with small differences.

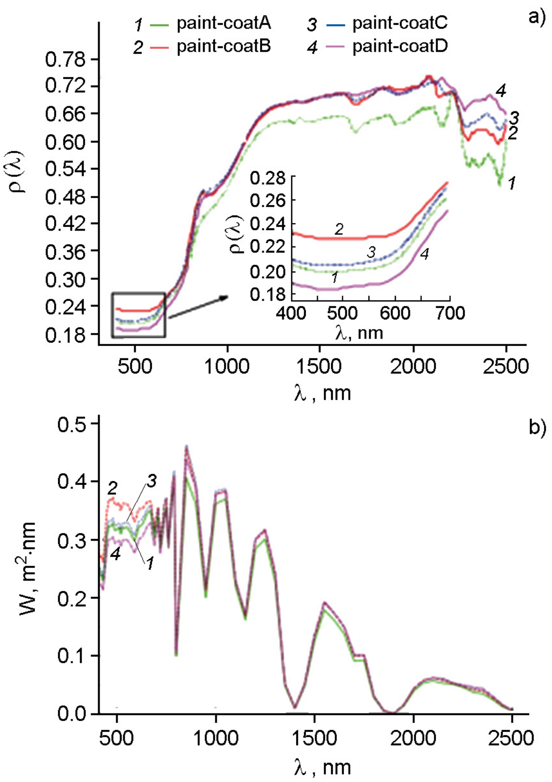

Fig. 2. Effect of the amount of modified silica sol on the reflective properties of the coating.

Table 2. Reflectance of coatings prepared by different amounts of modified silica sol

Coating	TSR	NIR	Average reflected energy, W/(m^2·nm)
A	0.54	0.60	0.23
B	0.58	0.65	0.25
C	0.58	0.65	0.24
D	0.58	0.66	0.22

Studies have shown that the mass ratio of the pure acrylic emulsion is preferably 1:1. In this case, the solar reflectance and near-infrared reflectance of the coating are increased by 7.41 % and 8.33 % respectively, compared with the A coating without the modified silica sol.

3.3. Effect of KH560 modified silica sol on artificial weathering aging performance of iron-chromium black building energy-saving coatings

It can be seen from Table 3 that the brightness of the coating is improved after

Table 3. Performance of coatings after aging treatment of different modified silica sol additions

Coating	ΔTSRL, %	ΔL^{*D}	ΔE^*	ε (after aging)	Δε	Coating appearance
A	4.89	2.85	2.88	0.86	−0.07	Powdering
B	2.36	0.61	2.23	0.85	−0.05	No abnormality
C	2.22	0.49	1.08	0.87	−0.02	No abnormality
D	2.24	0.38	0.48	0.86	−0.01	Slightly powdered

the aging treatment. Increasing the amount of modified silica sol can reduce the change rate of the solar reflectance and the change rate of the brightness after the aging of the coating, so that the chromatic aberration is gradually reduced to a trace. This is because after the xenon lamp is irradiated, the pure acrylic molecules gradually start to break, and then decompose, and the density of the portion entangled in the amorphous region decreases, and the short-chain molecules migrate toward the surface of the coating, eventually causing an increase in the brightness of the coating. In addition, the oxidation and decomposition of the pure acrylic molecular chain will also produce some chromophoric groups, resulting in discoloration of the coating.

The more pure propyl molecules is, the greater the decomposition will be, the more defects on the surface of the coating is, the stronger the scattering of light and the weaker the reflection will be. The modified silica sol replaces a part of the pure C molecule in the coating is, and the more the amount used, the less the pure C molecule will get, which will cause the decomposed chromophore group reduced, so that the solar light reflectance change rate and the brightness change rate become smaller and smaller, and the chromatic aberration becomes less and less obvious. According to Kirchhoff's law, a good absorber is also a good emitter. In other words, an object with a low infrared reflectance has more infrared absorption and a higher infrared emissivity. After the coating is aged, the pure acrylic molecules on the surface decompose, and the reduction of the organic matter with higher infrared absorption causes the infrared emissivity of the coating to decrease, and the more the organic content is, the more the infrared emissivity of the coating will decrease. Therefore, the D coating with the most inorganic content has the smallest change in infrared emissivity. Despite the aging, the infrared emissivity of all coatings is still greater than 0.85. However, the D coating has a poor film forming property due to excessive content of the modified silica sol, and there is a slight pulverization phenomenon after aging, which is not suitable for practical application. The change rate of solar reflectance after aging of C coating was less, only 2.67 percentage points lower than that of A coating, and the appearance did not change much, and the aging resistance was relatively good.

3.4. Effect of KH560 modified silica sol on stain resistance and water resistance of iron-chromium black building energy-saving coatings

The reflectance and water absorption of the coating are reflected by the change rate of the solar reflectance after the coating is contaminated, the static water contact angle and the water absorption rate. It can be seen from Table 4 that as the content of the modified silica sol in the coating increases, the rate of change of the solar reflectance after the coating is contaminated decreases. Moreover, the static water contact angle of the coating becomes large, and both hydrophobicity and water resistance are improved. This is because the surface of the coating inevitably has more bubbles, pores and defects during the preparation and curing process, which is beneficial to the infiltration of water. The nano-silica particles in the modified silica sol are filled into these defects and pores during curing, which improves the compactness and cross-linking of the coating, thereby enhancing the hydrophobicity and water resistance of the coating. After the hydrophobicity is enhanced, the contaminant does not easily adhere to the surface of the coating, and it is easy to roll off with the liquid, thereby reducing the rate of change of the solar reflectance after the coating is contaminated. Continue to increase the amount of modified silica sol, the coating's stain resistance and water resistance will be slightly reduced, which is caused by the excessive mass fraction of the modified silica sol and cracking of the coating. When the mass ratio of the modified silica sol to the pure acrylic emulsion is 1:1, the coating has the best stain resistance and water resistance.

Table 4. Performance of coatings prepared by different modified silica sol additions

Coating	ΔTSRL, %	Static water contact angle, °	Water absorption rate, %	Water resistance(96 h)
A	3.20	60.3	10.4	Slightly white
B	2.10	69.1	6.1	Basically not white
C	1.90	89.5	5.2	Not white
D	2.20	86.4	5.6	Slightly white

Table 5. Mechanical properties of coatings prepared with different silica sol additions

Coating	Adhesion/level	Pencil hardness	Flexibility, mm	Impact strength, kg·cm
A	2	H	1	58
B	1	2H	2	62
C	1	3H	2	62
D	2	4H	3	60

3.5. The effect of modified silica sol by KH560 on the basic mechanical properties of iron-chrome black building energy-saving coatings

The effect of modified silica sol on the basic mechanical properties of iron-chrome black building energy-saving coatings is shown in Table 5. As the amount of modified silica sol increases, the adhesion of the coating increases slightly, and the pencil hardness and impact resistance gradually increase, but the flexibility decline. The rigidity of the nano silica particles in the modified silica sol increases the pencil hardness of the coating, so that the impact resistance is also improved, but at the same time the flexibility is lowered. The mechanical properties of organic-inorganic composite coatings are related to the degree of microphase separation. Silica sol modified by KH560, on the one hand, it reacts with pure acrylic molecules, on the other hand, it hydrolyzes itself to form a certain spatial network structure, with strong hydrogen bonding and high degree of cross linking, thus enhancing the mechanical properties of the coating. When the number of inorganic nanoparticles is too large, the interaction between the soft segment and the hard segment is weakened, and the mechanical properties are decreased, but the requirements for the use of the architectural coating can still be met.

4. Conclusions

The silica sol was modified with silane coupling agent KH560 to improve its compatibility with pure acrylic emulsion, and an iron chrome black building energy-saving coating was prepared on this basis. Increasing the amount of modified silica sol can increase the static water contact angle of the coating as well as the solar and near-infrared reflectance, decreasing the solar reflectance change rate, chromatic aberration, brightness change rate, and infrared emissivity change rate after aging of the coating, and the change rate of the solar reflectance after the coating is contaminated and the water absorption rate, and the aging resistance and stain resistance of the coating are improved. However, too much modified silica sol will cause film formation difficulties, and the coating will be easily pulverized after aging. Considering the film formation, economy and coating properties, the mass ratio of the modified silica sol to the pure acrylic emulsion is 1:1, and the coating has good comprehensive properties.

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