Study on Preparation and thermal reflective properties of energy saving pigments with selective solar reflection

Yunlong Li 1, a and Yuanquan Yang 2, b

1 Postgraduate, Shenyang JianZhu University, Shenyang, China
2 Doctoral student, Dalian University of Technology, Dalian, China
E-mail: a yunlong_lee921@126.com, b aquarius0109@163.com

Abstract. Currently, the color of common reflective insulation coating is mainly white, but the white color coating is monotonous and its resistance is poor, moreover, the reflective performance tends to drop after pollution. In addition, color coating has the advantages of anti-dirty and beautiful appearance, so study on colored paint is of great significance. Based on the principle of three-tone color, the effect of thermal reflective pigments on the near-infrared reflectance of color reflective heat-insulating coatings was studied by blending three kinds of color reflective heat-insulating coatings of orange, green and purple with composite inorganic heat-reflective pigments as raw materials. The results show that the thermal insulation effect of heat-reflective pigments is significantly improved, and the near-infrared reflectance of green pigments can be increased by about 25%. The thermal reflection thermal insulation coating of the green system is 2.78 times higher than that of the same color common thermal insulating coating.

1. Introduction
Thermal reflective insulation coating is the most widely used building materials on exterior wall in the direction of energy conservation. In recent years, it has become a hotspot of research[1]. The exterior surface of the building receives solar radiation can be divided into three parts: ultraviolet region (200-400nm), visible light region (400-720nm), infrared light region (720-2500nm). The visible light region and infrared light region occupy 95% energy that the solar radiation to the Earth surface[2]. Due to the absorption of inorganic pigments and organic pigments in the visible light area, the thermal insulation properties of heat-reflective heat-insulating coatings are adversely affected by common pigments. In order to obtain a better visual effect, the multi-color thermal reflective heat-insulating coating is obviously superior to the white paint, so the study of heat-reflective pigments with both reflective insulation effect and good visual effect is the focus of current research.

There are many research results of near infrared reflective heat insulation pigments based on cooling materials of roof and exterior wall in foreign countries[3]. In 1940s, some foreign researchers began entertaining air with low thermal conductivity into multi-layer aluminum film, and then preparing heat insulation coatings after compounding with it, which opened the prelude of heat reflection heat insulation coatings. The Lawrence Berkeley National Laboratory (LBNL) and Oak Ridge National Laboratory (ORNL) began to study the solar reflectance and hemispherical emissivity of pigments in the 1990s, and the pigments were divided into several categories and the effects of the
properties, composition, roughness and purity of the materials on the solar reflectance were studied [4]. In 1998, the American Cold Roofing Association (CRCC) was established to develop accurate, credible evaluation, labeling methods and the dissemination of relevant knowledge for solar and thermal radiation properties of roofing products [5]. Domestic research on the influence of heat reflective pigments on the heat insulation performance of heat reflective insulation coatings is however less. In the 1990s, thermal insulation coatings was introduced into China, and domestic researchers began to conduct in-depth research and development on them [6]. The effect of the optical properties of different color heat-reflective pigments on the thermal insulating properties of the coatings was studied, and the color reflective heat-insulating coating was the same as that of the common reflective heat-insulating coating, and the thermal reflective heat-insulating property was significantly improved.

2 Raw materials and mix ratio

2.1 Materials and mix ratio

Ferric oxide ($Fe_2O_3$) was provided by Hebei Luquan blue color pigment factory. Zirconium red iron (Zr-Si-Fe) was provided by Jingdezhen wonderful Ceramic Pigments Co., Ltd. Titanium nickel Yellow (Ti-Sb-Ni-O) was supplied by Heng Ming New Materials Co., Ltd. PR yellow ($ZrSiO_4-Pr$) from Jingdezhen wonderful Ceramic Pigments Co., Ltd was used here. Phthalocyanine Blue ($C_{32}H_{16}CuN_8$) comes from Yancheng color Tatsu Pigment Co., Ltd. Titanium dioxide ($TiO_2$) was produced by Jinzhou Peng Titanium Dioxide Manufacturing Co., Ltd. Self-crosslinking high-gloss acrylic emulsion was supplied by Jiangyin National Union Chemical Co., Ltd. Silicone modified resin was from Shanghai Summer soil New Materials Co., Ltd. Defoaming agent, hardener, thickener were also used.

2.2 Test instrument.

UV/Vis/NIR spectrophotometer Lambda950, perkinelmer; Automatic Film Drying Machine Afa-iii, Shanghai Worship Force; Coating Thickness gauge QUJ, Tianjin Material Testing Machine Factory; X-ray Diffractometer Uitima-iv, Japan Science Company; Chromatic Aberration Instrument NR110 Shenzhen 3nh Co., Ltd.

Table 1 Basic formulations of white thermal reflective heat-insulating coatings

| Raw material       | m/g     |
|--------------------|---------|
| water              | X       |
| packing            | 85~125  |
| Titanium dioxide   | appropriate |
| latex              | Y       |
| Curing agent       | 3       |
| dispersant         | 3       |
| defoaming agent    | 2.5     |
| Thickening agent   | appropriate |

The amount of titanium dioxide added in the basic formula of white reflective energy-saving paint can be appropriately adjusted according to the needs of color matching. The effect of heat reflective pigments on thermal insulation performance was studied in this experiment. The white base paint with 7% titanium dioxide was not clearly indicated.

2.3 Test Methods
2.3.1 Preparation of White Heat Reflective Heat Insulation Coatings. Paint was prepared according to the mixing proportion in Table 1 for the following process. Sample preparation process: Weigh a proper amount of white powder pigment before and after the heat treatment, add film-forming substances such as emulsion, dispersant, defoamer, water and additives, fully mix for 15 mins under the action of a magnetic stirrer with a rotating speed of 200 r, then add curing agent, and then continue to mechanically stir for 5 min. Cleaning the transparent polyester film with alcohol and placing it flat on the coating base of the automatic film dryer.

2.3.2 Optical Performance Test. Color test: Using colorimeter to test the surface color parameters of pigments and powders $L^*$, $a^*$, $b^*$ values. The chromatic aberration value of different colors $\Delta E$. D65 light source is used for measurement. Colors can be classified according to their lightness. When the value of $L$ is less than 40, it is a dark color. $L$ values between 40 and 80 are medium colors, and $L$ values greater than 80 are light colors [7]. Solar reflectance and near infrared reflectance tests: refer to GJB 2502.2 - 2006 spacecraft thermal control coating reflectance and emissivity test methods part 2: solar absorptivity test, open the vacuum pump to fix it, adjust blade height is 1.00mm, place the mixed pigment in front of the coating device. The coating rate is 6mm/s. After coating is stopped, the heating and drying system is kept at 40 degrees Celsius for 10min. Heat reflective coating was prepared.

3 Results and discussion

3.1 Testing of Optical Properties of Titanium Dioxide

Rutile titanium dioxide is the white pigment with the best heat reflection effect, and it is the key factor affecting the heat insulation performance of the white reflective heat insulation coating base paint. Due to the different surface treatment process of the manufacturer, it will bring about the difference in its performance. The solar reflectance and $L$ (representing brightness, i.e. black and white), $A$ (representing red and green) and $B$ (representing yellow and blue) values of different brands and manufacturers of titanium dioxide pigments were tested. The test results are shown in Table 2 and Figure 1. As can be seen from the data in Table 2, the lightness value $L$ of titanium dioxide pigments is all around 88, and the appearance color is basically the same. The reflectivity curve of rutile-type titanium dioxide pigments to solar light is basically the same except for 2 # domestic samples.

TSR is relatively low, and other titanium dioxide pigments have high solar reflectance (TSR). In the visible region, the solar reflection of 1# and 4# samples is relatively high, about 90%. The 3 # and 4 # samples have relatively high near infrared reflectance in the long-wave near infrared region (1100 ~ 2500 nm). In this study, 4 # titanium dioxide samples were selected to prepare white heat reflective insulating base coating slurry, with titanium dioxide dosage of 7% and PVC of 60%.

Table 2 Optical Performance Data of titanium dioxide pigments

| Serial number | model | $L^*$ | $a^*$ | $b^*$ | TSR/% | NIR/% |
|---------------|-------|-------|-------|-------|--------|-------|
| 1             | PR601 | 88.75 | -0.57 | 1.72  | 88.61  | 90.36 |
| 2             | PR511 | 86.54 | -0.09 | 2.64  | 78.32  | 77.80 |
| 3             | PR521 | 89.99 | -0.41 | 3.67  | 88.98  | 91.71 |
| 4             | PD909 | 88.65 | -0.81 | 3.21  | 88.54  | 92.01 |
3.2 Optical Properties of Heat Reflecting Pigments

Heat-reflective pigments with near-infrared reflectivity are mostly composed of several metal mixtures calcined at high temperatures. The optical data of orange, green and purple heat reflective pigments were tested and shown in Table 3.

| Table 3 | Proportion Scheme of Secondary Color Pigment |
|---------|---------------------------------------------|
| Powder pigment | mass ratio |
| Fe₂O₃: Ti-Sb-Ni-O -- (Orange 1#) | 1:1 1:2 1:3 1:4 |
| | 1:5 1:6 1:7 1:8 |
| Fe₂O₃: ZrSiO₄-Pr -- (Orange 2#) | 1:1 1:3 1:6 1:9 |
| | 1:12 1:15 1:18 1:21 |
| C₃₂H₁₆CuN₈ : Ti-Sb-Ni-O -- (Green 1#) | 1:1 1:2 1:3 1:4 |
| | 1:5 1:6 1:7 1:8 |
| C₃₂H₁₆CuN₈ : ZrSiO₄-Pr -- (Green 2#) | 1:2 1:4 1:6 1:8 |
| | 1:10 1:12 1:14 1:16 |
| C₃₂H₁₆CuN₈ : Zr-Si-Fe -- (purple 1#) | 1:1 1:2 1:3 1:4 |
| | 1:5 1:6 1:7 1:8 |
| Fe₂O₃: C₃₂H₁₆CuN₈ -- (purple 2#) | 1:1.2 1:2 1:3 1:4 |
| | 1:5 1:6 1:7 1:8 |

| Table 4 | Optical Data Of Different Color Heat Reflecting Pigments |
|---------|--------------------------------------------------------|
| Serial number | Color | L* | a* | b* | TSR/% | NIR/% |
| 1 | Orange 1# | 42.54 | 20.06 | 14.32 | 73.8 | 74.0 |
| 2 | Orange 2# | 39.01 | 22.21 | 15.29 | 71.4 | 62.6 |
| 3 | Green 1# | 48.36 | -5.06 | -3.32 | 62.1 | 64.6 |
| 4 | Green 2# | 36.33 | -6.55 | -4.79 | 51.9 | 53.4 |
| 5 | Purple 1# | 28.74 | 1.43 | -1.67 | 47.5 | 48.6 |
| 6 | Purple 2# | 29.29 | 1.59 | -1.20 | 37.7 | 43.5 |

As shown in Figure 2 below, in comparison with orange and green pigments, the TSR effect of...
orange 1# and green 1# is better, the TSR effect of purple pigment is average, and iron red and titanium nickel yellow are better pigment choices. As can be seen from fig. 2, in the near infrared region, the NIR effect of orange 1# and green 1# is better, and the near infrared reflection effect of purple pigment is generally worse. In contrast to orange and green, iron red and titanium nickel yellow are obviously better pigments because they have better $L^*$ and covering ability.

![Fig. 2 TSR of different heat reflecting pigments](image1)

![Fig. 3 NIR of different heat reflecting pigments](image2)

3.3 Comparative Study on Heat Reflective Performance of Heat Reflective Thermal Insulation Coatings and Ordinary Thermal Insulation Coatings

Color reflective heat-insulating paint is blended in the heat-insulating paint base paint, and water-based general color paste is added to the white base paint to prepare common color heat-insulating paint of the same color. The minimum value of color difference that human eyes can distinguish is 1.0. The optical performance data of the color difference $\Delta E \leq 3.2$ kinds of color reflective thermal insulation coatings allowed in this study are shown in Table 5.

| Color classification | Thermal reflective thermal insulation coatings | Common heat insulation coatings | $\Delta E$ |
|----------------------|-----------------------------------------------|--------------------------------|----------|
|                      | Serial number | $L^*$ | NIR/% | Serial number | $L^*$ | NIR/% |        |
| Orange               | 1#            | 42.54 | 74.0  | 1#            | 40.42 | 68.1  | 1.58   |
|                      | 2#            | 39.01 | 65.6  | 2#            | 38.16 | 59.9  | 2.64   |
| Green                | 1#            | 48.36 | 74.6  | 1#            | 48.18 | 50.1  | 2.98   |
|                      | 2#            | 36.33 | 53.4  | 2#            | 35.07 | 26.3  | 1.15   |
| purple               | 1#            | 28.74 | 38.6  | 1#            | 28.91 | 17.4  | 0.59   |
|                      | 2#            | 29.29 | 43.5  | 2#            | 29.23 | 24.9  | 3.15   |

As can be seen from table 5, color-reflective thermal insulation coatings compared to common thermal insulation coating, NIR has different degrees of improvement, the improvement of green
system pigments are particularly obvious, with the increase of the color paste content of the coating color, the value of $L^*$ decreased. The lower the lightness is, the greater difference between the two. Because of the shallowness of orange pigment and the increase of orange pigment amount, the brightness value of orange pigment is not obvious. $L^*$ between 39–42, near infrared reflectance is relatively high, about 65% to 74%. The addition of heat reflective pigment has little effect on the NIR of the coating.

4 Conclusions

(1) White pigment titanium dioxide has the highest visible and near-infrared thermal reflection performance. Yellow heat-reflective pigments have a high thermal reflectance and are formulated as light and medium-color reflective heat-insulating coatings that act the same as ordinary yellow pigments.

(2) Considering the effect of chromatic aberration factor, it can be considered that the orange thermal reflective pigment has the same effect as ordinary pigments. Red and blue thermal reflective pigments, due to their excellent thermal reflectance in the near-infrared light region, can significantly improve the thermal insulation of dark-coloured heat-reflective insulation coatings (generally up to about 10).

(3) Through the rational formulation design and the addition of heat-reflective pigments, color reflective heat-insulating coatings with rich color and high thermal reflectance can be prepared.

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