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Influence of Metallic Oxide Pigments on Optical Performance of Energy Saving Coating

Guang Yang[a], Anzhong Deng[b]

[a] Department of Chemistry & Material Engineering, Logistical Engineering University of PLA, Chongqing 401311, China
[b] Department of Military Engineering Management, Logistical Engineering University of PLA, Chongqing 401311, China
GuangYang@126.com

Based on the requirement of reducing energy supplies and relieving urban heat island mitigation, influence of six different types of metal oxide pigments and its dosage of color paste on near infrared reflectance, long wave emissivity and CIE color value of the coatings were investigated. UV/VIS/NIR spectrophotometer, infrared radiance gauge and precision chromatic meter were used to characterize optical performance of pigments and its coatings. The result reveals that, Compared with traditional pigments, Nickel iron chromite black spinel, Cobalt green and Titanium chrome yellow has higher near infrared reflectance, thus, is more appropriate to be the pigments of energy saving coating; Near infrared reflectance of energy saving coating can be influenced by color paste, when applied, the proper proportion of color paste of Nickel iron chromite black spinel coating is 10%wt while other pigments coating is 20%wt; Long wave emissivity of energy saving coating can hardly be influenced by color paste; Lightness of energy saving coating can be increased by Titanium chrome yellow and Iron oxide yellow color paste while lightness of other pigments coating can hardly influenced by color paste; In order to obtain good color performance coating, proper proportion of color paste is 20%wt.

1. Introduction

Traditional building energy saving system such as thermal mortar, wall built-in insulated board suffers complicated construction and high price and is easy to cause fire (Buratti et al., 2015). Which restricts the wide application of energy saving building materials. Therefore, considering the increasingly tight energy consumption, it is extremely necessary to research and develop straticulate building energy saving coating. Akbari (Akbari and Bretz, 1997) thought that relying on the high solar reflectivity, energy saving coating could reduce the room temperature by reflecting some solar heat, so as to save energy and reduce cost. Shi (Shi and Zhang, 2011) studied impact of building envelope structure on the annual energy consumption based on the simulation software, the results indicated that appropriate increases in solar reflectivity and long wavelength emissivity could greatly lower the annual energy consumption.
As presented in Literature (Zhao et a., 2016; Guo et al., 2012) energy saving coating matrix resin should have high infrared permeability and low absorptivity, and styrene-acrylic emulsion and fluorocarbon resin were considered to be the proper matrix resin of building energy saving coatings. Literature (Thongkanluang et al., 2012; Liang et al., 2015) develops preparation of near-infrared new pigment with high reflectance and analyzes change impacts of crystalline form, lattice parameters and chromatic value of pigment.
However, researches seldom investigated pigments used in building energy saving coating. Metal oxide pigments is a type of complex inorganic color pigment (Naddeo et al., 2017). Near infrared reflectance was increased in the process of preparation through the method of solid phase reaction at high temperature which would obtain the goal of decreasing temperature and energy saving (Zhang et al., 2010; Zhang et al., 2013). However, research on the key factors of properties of energy saving coating, that is to say, pigments, was seldom reported. Thus, investigating porperties of pigment itself and influence on its coating is necessary, which will provide theoretical guidance on preparing energy saving coating with high near infrared reflectance and high long wave emissivity.

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2. Experimental

2.1 Materials

Modified silica sol-styrene acrylic composite emulsion property parameters were shown in Table 1;

Table 1: Property parameters of silica sol-styrene acrylic nanocomposite emulsion

Solid content (by mass)/%	Tg /°C	MFT/°C	Average size/μm	Stable	PH value
45±2	63±1	20	0.2-0.3	Anionic	8

Nickel iron chromite black spinel, Chrome green and Titanium chrome yellow were productions of Jufa Science and technology co., LTD of Hunan; Iron oxide black, Cobalt green and Iron oxide yellow were productions of Hongte Chemical industry co., LTD. of Guangzhou; coalescing agent:Texanol were productions of Eastman co., LTD. of United States;
Dispersing agent: BYK-163 were the productions of BYK chemical co., LTD. of Germany; antifoaming agent: L-1311 were productions of Ashland co., LTD., of the United States; multi-functional agent: AMP-95 were productions of ROHM HARS co., LTD., of the United States; deionized water were prepared in lab;
Aluminium plate were productions of Hongfa stainless steel co., LTD., of Chongqing; asbestos cement plate were productions of Kedun experiment equipment company of Congqing; basic formulation of energy saving coating were shown in Table 2.

Table 2 : Basic formulation of energy saving coating

Material	Mass/g
Silica sol	200
KH560	0.3
Styrene-acrylic emulsion	400
Coalescing agent	8
Pigments	30-120
Dispersing agent	4-6
Wetting agent	2-4
Antifoaming agent	4-8
Deionized water	Several
Multi-functional agent	2-4

2.2 Methods

Preparation of color paste: Pigments and deionized water was mixed with ratio of 1:1 so as to improve dispersibility in coating, reduce particle of pigments and prevent conglomerating. Appropriate amount of dispersing agent was mixed when homogeneous mixing, making revolving of grinding miller was 800r per minute. Mixture was filtrated after 15 minutes and then we obtained color paste.
Preparation of coatings: aluminium sheet pretreatment: Sand papered, water washed, absolute ethyl alcohol for oil removed and dried at last; Certain amount of color paste and modified silica sol styrene-acrylic composite emulsion were mixed. Making revolving speed of grinding miller was 400r per minute and stirred 5 minutes and then mixed dispersing agent and multi-functional agent. Increasing revolving speed to 800r per minute and stirred 15 minutes and then filtered. Controlling proper spraying pressure and making distance between spray gun and substrate was 30cm. Spraying paint evenly on aluminium sheet. Putting these sheets in lab at indoor temperature for 7days. Dried film thickness was about 150μm.

2.3 Characterization techniques

U-4100 UV/VIS/NIR spectrophotometer of Japanese hitachi Co. Ltd. was used to test near infrared reflectance of metal oxide pigments and its coatings, $BaSO_4$ was the standard white plate; The solar reflectance (R*) in the wavelength range from 700 to 2500nm could be figured out according to GB/T 235-2014 Architectural reflective thermal insulation coating and the formula was as follows:

$$R^* = \frac{\int_{700}^{2500} r(\lambda) i(\lambda) d(\lambda)}{\int_{700}^{2500} i(\lambda) d(\lambda)}$$

where *r(λ) and i(λ)* represented the spectral reflectance at the wavelength of λ and the standard intensity of radiation ($W \cdot m^{-2} \cdot nm^{-1}$) of the samples respectively; According to the CIE 1976 L* a* b* color coordinate system regulation, L* was the lightness axis[black(0) to white(100)], a* was the green(-) to red(+) axis and b* was the blue(-) to yellow(+) axis; The parameter c (Chroma) presented saturation of the color and was dedined as $c=[(a^*)^2+(b^*)^2]^{1/2}$; HWF-2 infrared radiance gauge of Yunnan Kiro-Ch Photonics Co.Ltd. was used to test the long wave emissivity of coating in the waveband of 8~14μm; HP-200 precision chromatic meter of Shanghai Hanpu photoelectric technology co.LTD was used to analysis pigments and coatings CIE color value.

3. Results and discussion

3.1 Analysis of metal oxide pigments

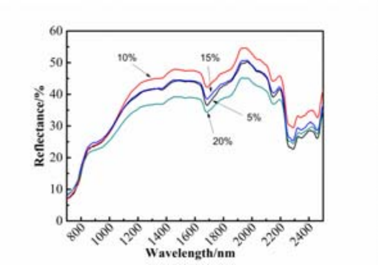
Table 1 shows the average value, maximum value and minimum value of the near infrared (with the waveband of 780-2500nm) reflectance of six metallic oxide pigments, based on which, the near infrared reflectance of three inorganic mixed-phase pigments are all higher than common traditional pigments. Nickel iron chromite black spinel sees near infrared reflectance 56.38% higher than that of common iron oxide black. Nickel iron chromite black spinel is a complex inorganic color pigment prepared with solid phase reaction of chrome green (Cr_2O_3) and hematite (Fe_2O_3) at high temperature, with chrome green occupying large proportion in its crystal structure. The near infrared reflecting performance of nickel iron chromite black spinel enhances as Cr^{3+} is replaced by Fe^{3+} in crystal structure, making it more suitable for being building energy saving coating-used pigments than common iron oxide black. Also, average near infrared reflectance of nickel iron chromite black spinel is 13.86% than that of chrome green without ion doping. Titanium chrome yellow sees the highest near infrared reflectance of 101.39%, 14.8% higher than common iron oxide yellow. Thus, titanium chrome yellow is a better pigment of building energy saving coating than common iron oxide yellow. The average near infrared reflectance of cobalt green and chrome green is 48.02% and 45.3% respectively. In despite of the small difference, chrome green is more suitable for being applied in the building energy saving field as cobalt green suffers toxicity.

Table 3: Near infrared reflectance of metallic oxide pigments

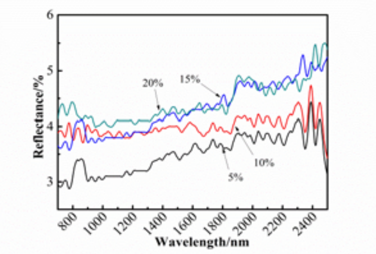
Pigments type	Average reflectance	Max reflectance	Min reflectance
Nickel iron chromite black spinel	59.16	77	13.70
Iron oxide black	3.94	5.40	3.30
Cobalt green	48.02	72.7	19.10
Chrome green	45.30	55.80	7.20
Titanium chrome yellow	101.39	123.20	76.00
Iron oxide yellow	86.59	103.70	58.90

3.2 Influence of metallic oxide pigments on near infrared reflectance

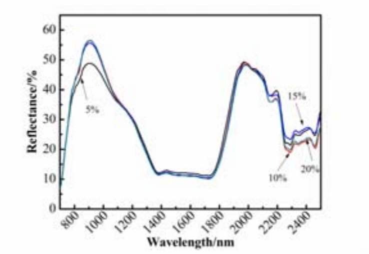
Figure 1 shows the near infrared (with the waveband of 780-2500nm) reflectance of dried coatings adding common traditional pigments and complex inorganic color pigment. Black pigments are used to lower lightness of coating, however, green and yellow pigments are used to enrich the color and covering power of coating. According to the analysis of (a) and (b), iron oxide black has strong absorptivity on near infrared waveband, leading to low near infrared reflectance. While nickel iron chromite black spinel has high near infrared reflectance due to chromium ions doping after solid-phase reaction at high temperature. Under the condition of same color paste, the average near infrared reflectance of nickel iron chromite black spinel coating is 4.3 times higher than that of iron oxide black coating. According to the analysis of (c) and (d), as for cobalt green coating, color paste has small impacts on the near infrared reflectance. Coatings with different color paste all have strong absorptivity within waveband of 1400-1700nm and enjoy strong reflectance in the wavelength of 900nm and 1900nm, however, chrome green coating sees strong reflectance in the waveband of 780nm-2200nm. Although reflectance decreases from wavelength of 2200nm, it is still higher than that of cobalt green coating in this waveband. According to the analysis of (e) and (f), both titanium chrome yellow coating and iron oxide yellow see higher near infrared reflectance in near infrared waveband. The average near infrared reflectance of iron oxide yellow coating does not follow the increase trend of color paste which is possibly because that color paste cannot obviously change the distribution of particle of iron oxide yellow pigment which suffers small density. Also, iron oxide yellow coating sees the highest average near infrared reflectance when color paste reaches 10%. On the contrary, along with the increase of color paste, near infrared reflectance of titanium chrome yellow coating increases, with the average growth rate of 4.66%. When color paste is 20%, near infrared reflectance reaches the highest 68.69%.



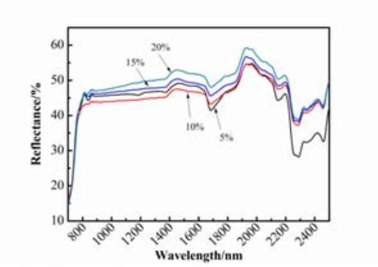
(a) Nickel iron chromite black spinel



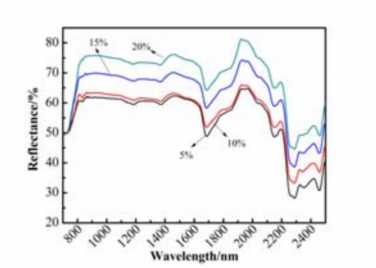
(b) Iron oxide black



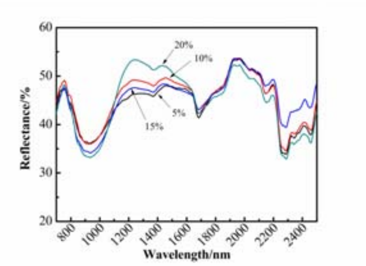
(c) Cobalt green



(d) Chrome green



(e) Titanium chrome yellow



(f) Iron oxide yellow

Figure 1: The near infrared (with the waveband of 780-2500nm) reflectance

3.3 Influence of metallic oxide pigments on long wave emissivity

Table 3 shows long wave emissivity of modified silica sol styrene-acrylic composite emulsion after dried on aluminium sheet (with the emissivity of 0.05) and asbestos cement sheet (with the emissivity of 0.95) respectively, based on which, long wave emissivity of coatings can be hardly influenced by substrate with different long wave emissivity such as aluminium sheet and asbestos cement sheet. Somehow, long wave emissivity of cement-based coatings is a little higher than that of aluminium-based coatings. Table 4 shows long wave emissivity of coatings prepared with six types of pigments, based on which, long wave emissivity of iron oxide black coating is a little higher than that of nickel iron chromite black spinel. Long wave emissivity of cobalt green coating and chrome green coating, iron oxide yellow coating and titanium-chrome yellow coating is basically the same.

Table 3: Spectral emissivity of modified silica sol-styrene-acrylic composite emulsion

Film thickness/μm	Emissivity (aluminium sheet)	Emissivity (asbestos cement sheet)
150μm	0.88	0.89

Table 4: Spectral emissivity of different kinds of pigment coatings

Film type	Pigment content/%							
	Aluminum sheet				Asbestos cement sheet			
	5	10	15	20	5	10	15	20
Nickel iron chromite black spinel	0.88	0.88	0.88	0.88	0.89	0.89	0.90	0.90
Iron oxide black	0.91	0.92	0.94	0.97	0.91	0.91	0.93	0.95
Chrome green	0.87	0.87	0.88	0.88	0.88	0.87	0.88	0.89
Cobalt green	0.86	0.88	0.88	0.89	0.88	0.88	0.88	0.90
Iron oxide yellow	0.87	0.89	0.89	0.89	0.88	0.89	0.90	0.90
Titanium-chrome yellow	0.88	0.88	0.90	0.90	0.88	0.88	0.90	0.91

According to the comparison of Table 3 and Table 4, long wave emissivity of coating is not obviously affected after mixed with metallic oxide pigments. There is a little difference among long wave emissivity of different types of metallic oxide pigments, with all remain a high level of 0.86. Amount of admixture metallic oxide pigments also has small impacts on long wave emissivity of the same type of coating. Increase in mixing amount of metallic oxide pigments can slightly improve long wave emissivity of coating, with the emissivity reaching the highest when color paste is 20%, what's more, maximum emissivity of iron oxide black coating up to 0.97.

3.4 Influence of metallic oxide pigments on CIE color value

Table 5 shows CIE 1976 (L*, a*, b*, c*) color value of different types of coatings, tested by precise colorimeter, prepared with six different types of pigments mixed with modified silica sol styrene-acrylic composite emulsion in different color paste of 5%, 10%, 15% and 20%. Lightness of nickel iron chromite black spinel coating and iron oxide black coating can be slightly influenced by increasing color paste and both belong to low lightness coatings regulated in GB/T 235-2014 Architectural Reflective Thermal Insulation Coating(L*≤40). In spite of different color paste, lightness of nickel iron chromite black spinel coating is higher than that of iron oxide black coating. The possible reason is that color ion Cr^{3+} improves lightness of coating somewhat. Both two types of coatings see extremely low color saturation. As for chrome green coating and cobalt green coating, certain color paste coatings have medium lightness in accordance with GB/T 235-2014 Architectural Reflective Thermal Insulation Coating (40 < L* < 80). With the increase of color paste, a* of two coatings decreases and coating turns to the green phase possibly due to accumulation of Cr; b* of chrome green coating remains unchangeable while that of cobalt green increase slightly when increasing color paste. When color paste reaches 10%, the maximum growth rate is 3.54%, showing that increasing color paste leads to coating color transferring from blue phase to red phase, which is possible caused by the accumulation of Co^{3+}.Color saturation of cobalt green coating is higher than chrome green coating in spite of color paste. Titanium chrome yellow coating and iron oxide yellow coating are both coating with medium lightness in accordance with the GB/T 235-2014 Architectural Reflective Thermal Insulation Coating (40 < L* < 80). As for titanium chrome yellow coating, when titanium chrome yellow pigments mixing amount increases, a* increases gradually with the average growth rate of 4.11%, indicating that coating turns to red phase when increasing color paste because of accumulation of color ion; When titanium chrome yellow pigments mixing amount increases, a* increases, indicating that coating turns to yellow phase. Because Cr^{3+} is green, increasing Cr^{3+} and Fe causing coating turns to yellow phase. As for iron oxide yellow coating, increase in color paste mixing amount impacts a* slightly but impacts b* greatly, based on which coating will turn to yellow phase when increasing color paste. According to experimental data, iron oxide yellow coating turns to yellow phase while titanium chrome yellow turns to red phase. Color paste should be 20% in order to get coatings with better color saturation.

Table 5: Influence on CIE value of coating prepared with different amount and types of pigment

Pigments	Content (wt%)	Color performance			
		L*	a*	b*	c
Nickel iron chromite black spinel	5	28.18	1.27	-0.71	1.46
	10	27.77	1.61	-0.68	1.75
	15	27.94	2.34	-0.13	2.34
	20	28.14	2.42	-0.12	2.42
Iron oxide black	5	18.25	1.02	-0.69	1.23
	10	18.01	1.28	-0.61	1.42
	15	17.78	1.85	-0.48	1.91
	20	16.88	1.98	-0.4	1.94
Chrome green	5	40.28	-8.12	8.68	11.89
	10	39.86	-10.24	8.72	13.45
	15	38.27	-12.04	8.88	14.96
	20	39.23	-14.3	8.81	16.8
Cobalt green	5	42.01	-6.67	10.28	12.25
	10	41.15	-7.82	13.82	15.88
	15	40.88	-9.05	15.73	18.15
	20	39.79	-10.28	18.25	20.95
Iron oxide yellow	5	46.67	5.03	32.36	32.75
	10	53.29	6.35	37.83	38.36
	15	55.86	6.72	43.45	43.97
	20	56.02	6.98	49.87	50.36
Titanium-chrome yellow	5	48.82	8.01	30.02	31.07
	10	55.72	12.43	34.48	36.65
	15	58.1	17.52	36.23	37.1
	20	60.62	20.34	40.42	45.25

4. Conclusions

In conclusion, nickel iron chromite black spinel, cobalt green and chrome yellow pigments, with the average near infrared reflectance 56.38%, 2.72% and 14.8% higher than those of traditional iron oxide black, chrome green and iron oxide yellow respectively, are more suitable for being used in energy saving coating due to strong near infrared reflectivity. The conclusion is applied equally to coating. Color paste can impact near infrared reflectance of coating. Nickel iron chromite black spinel coating sees the highest reflectance when color paste is 10% and 20% for the other five pigments coating. Emissivity of substrate, color paste and pigments do not impact long wave emissivity of coating obviously. Long wave emissivity of coatings prepared with these pigments is no less than 0.86. Lightness of coating can be improved with increase in color paste of two yellow pigments. Lightness of coating cannot be influenced obviously with color paste of black and green pigments. Nice color saturation can be obtained when color paste of coating reaching 20%.

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