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Superhydrophobic self-cleaning solar reflective orange-gray paint coating

Xiao Xue[a,b], Zhuo Yang[a,c], Yanwen Li[a,d], Pengcheng Sun[a], Ya Feng[e], Zhongyu He[a], Tiejun Qu[c], Jian-Guo Dai[b,*], Tao Zhang[a], Jie Qin[a], Lijin Xu[d], Weidong Zhang[a,*]

[a] Technical Center, China State Construction Engineering Co., Ltd., Beijing 101300, PR China
[b] Department of Civil and Environmental Engineering, The Hong Kong Polytechnic University, Hung Hom, Hong Kong, PR China
[c] School of Civil Engineering, North China University of Technology, Beijing 100144, PR China
[d] Department of chemistry, Renmin University of China, Beijing 100872, PR China
[e] China Southwest Architectural Design and Research Institute Co., Ltd., Chengdu 610042, PR China

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ABSTRACT

A method of fabricating an industrially scalable, widely applicable, and easily repairable superhydrophobic self-cleaning cool orange-gray coating using commercially available materials and following a simple industrial procedure is introduced. Grinding the coating surfaces using an appropriate emery paper creates microgrooves with suitable widths and exposes micro- and nanoparticles on the coating surface. Both factors together endow the coating surfaces with superhydrophobic self-cleaning properties. The hydrophobicity of the coating possesses good resistance to alkali, acid and mechanical abrasion. Grinding the coating surfaces using emery papers also increases the solar reflectance of the coating. The cooling effect of the superhydrophobic coating, which has a solar reflectance of 0.815, is estimated to be 23 °C relative to concrete on a typical clear summer sunny day. Although the superhydrophobic self-cleaning property and solar reflectance of the coating may be compromised by artificial accelerated weathering, the superhydrophobic self-cleaning property can be easily and fully re-established and the inclined solar reflectance may be partially restored after the coating surfaces are ground using an appropriate emery paper.

1. Introduction

Well-designed chromatic cool gray coatings [1] generally combine the aesthetics of dark-colored coatings [2] with the high solar reflectance of light-colored coatings [1,2] and thereby are preferred by building owners [1] to improve thermal comfort [2] and/or reduce cooling energy use in summer [3].

The solar reflectance of cool light-colored coatings exposed to outdoor conditions may attenuate over time, owing mainly to soiling of the surface [4,5] rather than weathering [4] because more than 90% of the initial solar reflectance can be restored by washing [6]. However, nearly all conventional architectural coatings are hydrophilic and hence tend to be contaminated by water-soluble pollutants [7] and dust deposition [4,5]. Cleaning the coating surfaces requires manpower and thus is not cost-effective [4,7].

Clearly, to maximize the benefits of chromatic cool gray coatings, it is of practical significance to make them self-cleaning. A superhydrophobic coating surface with a minimum water contact angle (WCA) of 150°, a contact angle hysteresis (CAH) less than 10°, and/or a maximum sliding angle (SA) of 10° may effectively allow water and water-soluble pollutants to roll off easily and carry away any resting surface contamination [8,9]. This self-cleaning behavior, termed the lotus effect [10], has inspired numerous scientists to develop many techniques to fabricate superhydrophobic surfaces on different substrates using various materials during the past three decades [8–10].

Essentially, a superhydrophobic surface can be fabricated either by roughening a surface with inherently low surface free energy (SFE) or by chemically modifying an intrinsically rough surface using low-SFE materials [8–10]. In the former case, many surface roughening techniques require numerous procedures and/or specialized, complicated, and sometimes expensive equipment [8,9]; in the latter case, fluoroalkylsilanes are the most commonly used chemicals because of the extremely low SFE and simple reaction between the hydroxyl group and the silane group [11] However, most of fluoroalkylsilanes are less cost-effective and probably harmful to human health and the environment [12]. Moreover, most previous works focused on the fabrication of superhydrophobic film coatings rather than superhydrophobic paint coatings [7]. In addition, in the literature to date, there are relatively few reports on combining superhydrophobic performance with other functions including antireflective [13], fluorescent [14] and reflective

* Corresponding authors.
E-mail address: zwdpt@sohu.com (W. Zhang).

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[15] properties in a single coating. Although the authors of the last report claimed that they had fabricated highly reflective superhydrophobic white coatings inspired by poplar leaf hairs [15], the coatings are actually a series of hollow fibrous polymer films manufactured using coaxial electro-spinning technology. Moreover, the reflectance of the white coatings between 400 and 950 nm was reported to be 0.6. However, the spectral reflectances of the coatings in the entire ultraviolet (UV, 250–400 nm) and partial near infrared (NIR, 950–2500 nm) regions were not investigated. More precisely speaking, these white coatings are not solar reflective coatings. Additionally, to our knowledge, the long-term performance of superhydrophobic coating surfaces has not been fully investigated yet.

Therefore, a superhydrophobic solar reflective orange-gray paint coating has been carefully formulated using commercially available low-cost materials. In this paper, the superhydrophobic self-cleaning property and surface morphology of the coating surface are investigated. Moreover, the optical and thermal properties of the coating are studied, and the cooling effect is estimated. Additionally, the long-term performance of the coating is predicted, and an easy method to reestablish the superhydrophobicity of the weathered coating surface is presented.

2. Materials and methods

2.1. Selection of materials

To prepare the coating, the following materials were selected: a styrene–acrylic emulsion binder, grade EC0702, purchased from BASF Corporation; commercially available titanium dioxide rutile (TiO_2), cobalt aluminate blue ($CoAl_2O_4$), Cromophtal Orange, octyltriethoxysilane, and paint additives including a wetting agent, dispersant, antifoaming agent, suspending agent, leveling agent, and coalescent.

2.2. Chemical modification

TiO_2 and $CoAl_2O_4$ powders were separately added to mixing setups containing an appropriate amount of octyltriethoxysilane, and the mixtures were stirred for 60 min. Subsequently, the mixtures were filtrated, and the obtained powders were dried at 110 °C.

2.3. Preparation of the coating and samples

The optimized composition of the coating was as follows: styrene–acrylic emulsion (40 wt%), TiO_2 (28 wt%), $CoAl_2O_4$ (0.18 wt%), Cromophtal Orange (0.02 wt%), water (27 wt%), wetting agent (0.2 wt %), dispersant (0.3 wt%), antifoaming agent (0.6 wt%), suspending agent (2.5 wt%), leveling agent (0.5 wt%), and coalescent (0.7 wt%).

The cool orange-gray paint coating was fabricated as follows: the styrene–acrylic emulsion, chemically modified TiO_2 and $CoAl_2O_4$, Cromophtal Orange, and a prescribed amount of water were first added to the mixing setup, followed by the addition of the wetting agent, dispersant, antifoaming agent, and suspending agent. The mixture was stirred at high speed for 60 min. Subsequently, the antifoaming agent and coalescent were added, and the mixture was continuously mixed at high speed for an additional 30 min. The obtained coating was sprayed onto fiber cement boards with white basecoats developed in our laboratory, whose UV, visible (VIS), NIR, and solar reflectance values are 0.064, 0.964, 0.909, and 0.892, respectively [16]. The dry coating thicknesses of the basecoats and topcoats were approximately 200 and 100 µm, respectively.

2.4. Characterization of hydrophobic property

A Dataphysics Contact Angle System OCA 15EC was employed to measure the WCA, CAH, and SA of the coating surfaces. Water droplets (3, 5, and 7 µL) were used to measure the static water contact angles of the coating surfaces with contact angles much smaller than 150°, approximately 150°, and larger than 150°, respectively. The results are reported as the average of six parallel measurements at different places on the surfaces, unless otherwise indicated.

The CAH was determined as the difference between the advancing and receding angles measured using the "needle-in-drop" technique to increase or decrease the volume of the droplet at a speed of 1 µL step^{-1}. The initial volume of the water droplets was 7 µL. The reported advancing and receding contact angles were the average of six measurements performed at different positions on the coating surfaces.

Water droplets (10 µL) were used to examine the sliding angle of the coating surfaces. The results are reported as the average of six parallel measurements at different places on the surfaces.

2.5. Roughening treatment of coating surfaces

The coating surfaces were roughened using an angle grinder equipped with emery papers having various grit numbers.

2.6. Morphological characterization

The surface morphologies of the coatings were examined using a Zeiss-supra 55 field emission Scanning Electron Microscopy (SEM).

2.7. Measurements of optical properties

Following ASTM E903-12 (Standard test method for determining the solar absorbance, reflectance, and transmittance of materials using integrating spheres), a UV/VIS/NIR spectrophotometer (Perkin Elmer Lambda750) equipped with an integrating sphere (150 mm diameter, Labsphere RSA-PE-19) was used to determine the spectral reflectance of the coating. The solar reflectance was computed by integrating the measured spectral data weighted with the air mass 1.5 beam-normal solar spectral irradiance, as described in ASTM E891-87 (Tables for Terrestrial Direct Normal Solar Spectral Irradiance for Air Mass 1.5).

2.8. Measurement of thermal emittance

Following ASTM C 1371 (Standard test method for determining the emittance of materials near room temperature using portable emissometers), a portable differential thermopile emissometer was employed to measure the thermal emittance.

2.9. Artificial accelerated weathering tests

Following ISO 11341-2004 (Paints and varnishes – Artificial weathering and exposure to artificial radiation – Exposure to filtered xenon-arc radiation), artificial accelerated weathering tests were conducted for 400 h using a xenon lamp in a weather-resistant test chamber (SN-66, Beijing Beifang Lihui Test Instrument Equipment Co., Ltd.). During the tests, the upper surfaces of the coating specimens were exposed to the light source and sprayed with water using an 18/102 spray cycle (18 min of water spray/102 min of dryness). The chamber temperature, black panel temperature, and relative humidity (RH) during the dry period were (38 ± 3) °C, (63 ± 2) °C, and (40–60%), respectively.

3. Results and discussion

3.1. Hydrophobicity before surface roughening

In general, low SFE and enhanced surface roughness are essential for fabricating superhydrophobic surfaces [10,17]. TiO_2 and $CoAl_2O_4$ pigments are inherently hydrophilic because of the presence of hydroxyl groups (-OH$^-$) on the powder surfaces [4]. To decrease the SFE of the coating, the hydrophilic TiO_2 and $CoAl_2O_4$ were treated with