A Cost-effective Method to Fabricate a Super-non-wetting Self-cleaning Transparent Emulsion Paint Coating

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Abstract. The procedure to fabricate an industrially-producible, practically-applicable and easily-reconstructible transparent paint coating with luminescence is introduced step-by-step in this paper. Without chemical modification, an ultrahydrophobic transparent paint coating with luminescence can be readily created using cost-effective commercially available materials. Grinding the ultrahydrophobic transparent paint coating surfaces using appropriate emery papers can generate appropriate surface roughness and thereby endows the coating surfaces with super-non-wettability and self-cleaning property. The applications of the coating to the external walls of buildings can provide the walls with self-cleaning property, decorate the walls and save outdoor illumination power during the night.

1. Introduction

Wettability of solid surfaces has aroused worldwide interest during the past three decades. It is widely accepted that a surface with a water contact angle greater than 90° is referred to as a hydrophobic surface[1], a surface with a water contact angle (WCA) greater than the maximum observable on a flat surface (≈120° for polytetrafluoroethylene) is originally regarded as an ultrahydrophobic surface, and a surface with a minimum water contact angle of 150°, a maximum contact-angle hysteresis of 10° and a sliding angle less than 10° is considered to be a super-non-wetting surface[1-4], which generally causes water to roll off easily leaving little or no residue and carry away any resting surface contamination[2-3].

Non-wettability of super-non-wetting surfaces endows them with many functionally practical and valuable properties[1], including self-cleaning [1,4-7], water repellency[1], anti-fogging[4-5,7], anti-icing[1,5], anti-sticking[1], anti-contamination[1,5], anti-fouling[1,5], anti-bacteria, corrosion resistance, drag reduction[5], among others. Because of these unique capabilities, super-non-wetting surfaces have inspired many fundamental and applied investigations since Tsujii and co-workers[8] first demonstrated artificial super-non-wetting surfaces in the mid-1990s[3,7,9], although the basic ideas of super-non-wettinity were initially developed by Wenzel[2] and Cassie and Baxter[2]. Subsequently, a plethora of techniques have been successfully developed to fabricate super-non-wetting surfaces on different types of substrates[1,3,5], using various materials from metal to polymers[3].

In this work, a novel, simple and cost effective method to manufacture a super-non-wetting transparent emulsion paint coating with luminescence was explored.
2. Experimental Section

2.1. Selection of materials
To prepare the super-non-wetting transparent paint coating with luminescence, a styrene-acrylic emulsion was selected as a water-based binder. A luminous pigment with yellow-green luminescence and a commercially available zinc stearate were also selected as pigment and extender, respectively. In addition, appropriate paint additives, including a wetting agent, a dispersant, an antifoaming agent, a suspending agent, a leveling agent and a coalescent, were selected to improve the quality and performance of the coating. All the above materials were used as received to prepare the transparent coating with luminescence.

2.2. Preparation of the coating
The preparation process of the super-non-wetting self-cleaning transparent coating with luminescence was as follows: the styrene-acrylic emulsion, luminous pigment, zinc stearate and a prescribed amount of water were first added into 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 additional 30 min and the transparent coating was obtained and sprayed onto fiber cement boards for a variety of measurements. The dry coating thickness was approximately 200 μm, as measured by a PosiTector 200-Ultrasonic coating thickness gauge.

2.3. Surface roughening
In the present work, a pneumatic angle grinder equipped with silicon carbide emery papers having various grit numbers (80, 120, 180, 240, 320 and 600) was used for surface roughening to obtain super-non-wetting self-cleaning transparent coating surfaces.

2.4. Wettability characterization
The wettability of the final super-non-wetting transparent coating surfaces was systematically evaluated by the static WCA, the dynamic contact angle hysteresis (CAH) and sliding angle (SA). To this end, a video-based contact angle measurement system (OCA 15EC, DataPhysics Instruments GmbH, Germany) was used to measure the WCA, CAH and SA of the transparent coating surfaces. The volume of water droplets was 7 µL for the measurements of WCA and CAH and it was 10 µL for the measurements of SA. The WCA, CAH and SA values are reported as the average of five parallel measurements at different places on the surfaces. The measured WCA values were employed to compute the surface free energy (SFE) of coatings using the equation-of-state model.

3. Results and discussion

3.1 The effects of coating composition on the wettability
Basically, the chemical constitution and the physical topology of surfaces are two key surface parameters that are essential to fabricate super-non-wetting surfaces[5,10-11]. The chemical composition of a material dominates the surface free energy and thereby plays an important role in achieving the desired super-non-wettability[5]. Consequently, the first step for the fabrication of super-non-wetting surfaces is to select appropriate materials and subsequently optimize the coating composition.

Of the commercially available emulsions claimed to have “lotus effect”, the styrene-acrylic emulsion, grade EC0702, manufactured by BASF Corporation was confirmed to do have low SFE and thus used as the binder of the coating. The CA value of the specimen singly painted with the binder was approximately 97° with an apparent SFE of 24.85 mN/m.
3.1.1 The effects of the luminous pigment on the wettability. To isolate the impact of the luminous pigment from that of the zinc stearate, the effects of the weight content of the luminous pigment on the wettability of the coating was preliminarily investigated. Fig. 1 shows the variation of the measured average WCA, together with the standard deviation, and the apparent SFE as a function of the weight content of the luminous pigment. As indicated in Fig. 1, the average WCA initially increases rapidly as the weight content of the luminous pigment increases up to 13 wt% and then reaches a plateau value between 13 wt% and 15 wt%, subsequently, the average WCA of the coating decreases and levels off as the weight content of the luminous pigment continuously increases. Accordingly, the apparent SFE initially decreases sharply as the weight content of the luminous pigment increases up to 13 wt% and then levels off between 13 wt% and 15%, subsequently, the apparent SFE increases and reaches a plateau value as the weight content of the luminous pigment continuously increases. The maximum WCA that can be observed on a flat surface was originally reported to be approximately 120º for polytetrafluoroethylene (PTFE)[3]. This upper limit of WCA that can be achieved on a flat substrate was further improved to approximately 130º by assembling fluorinated organosilanes[10]. To increase the substrates’ non-wettability beyond this limit, the surface roughness should be increased[10].

Therefore, the addition of luminous pigment increases the roughness of the transparent coating surface. Consequently, the WCA of the transparent coating surface initially increases from 97º for the specimen singly painted with the binder to 121.5º for the specimen filled with 13-15 wt% of luminous pigment, corresponding to a decrease of the apparent SFE values from 24.85 mN/m to 11.41 mN/m. Above 15 wt%, as the weight content of luminous pigment further increases, the apparent SFE of the coating increases to a plateau value most likely because the coating surfaces’ roughness does not match with the chemical composition of the surfaces, accordingly, the average WCA decreases and stabilizes at a lower value. The optimum concentration of 13 wt% of the luminous pigment was chosen for further coating formulation.

![Graph showing the dependence of contact angle and surface free energy on the weight content of luminous pigment.](image)

**Fig. 1.** The dependence of contact angle and surface free energy on the weight content of luminous pigment.

3.1.2 The effects of the zinc stearate on the wettability. Because of the presence of long-chain-alkyl group, the zinc stearate has low surface free energy and thus is generally used to fabricate super-non-wetting surfaces. In this work, the zinc stearate was selected to further decrease the apparent SFE of the coating to fabricate the desired non-wetting surface. In this subsection, at the given luminous pigment content of 13 wt%, the effects of the weight concentration of the zinc stearate on the wettability of the coating were studied.
The variation of the measured average WCA, along with the standard deviation, and the apparent SFE values as a function of weight content of zinc stearate is presented in Fig. 2. As observed in Fig. 2, the WCA value initially increases markedly to the maximum value of approximately 150° and the apparent SFE accordingly decreases pronouncedly to the minimum value of approximately 1.41 mN/m as the weight content of zinc stearate increases up to 5 wt% and subsequently the WCA decrease and levels off at a lower value and the apparent SFE increase and reaches at a plateau value as the weight content of zinc stearate further increases. Clearly, the super-non-wetting surfaces at the edges of the specimens can be achieved simply by changing the surface chemistry. The increase in the WCA and the decrease in the apparent SFE are mainly ascribed to the addition of zinc stearate with low SFE. Above 5 wt%, as the weight content of low density zinc stearate increases, the coating’s viscosity becomes very high and thereby the dispersion of the fillers of the coating becomes less homogeneous. Consequently, the apparent SFE of the coating surface starts to increase and the measured WCA decreases.

![Graph showing variation of contact angle and surface free energy](image)

**Fig. 2.** The variation of contact angle and surface free energy as a function of the weight content of zinc stearates.

At this point, the composition of the transparent coating might be optimized as follows: styrene-acrylic emulsion (40 wt%), luminous pigment (13 wt%), zinc stearate (5 wt%), water (37 wt%), wetting agent (0.2 wt%), dispersant (0.3 wt%), antifoaming agent (0.8 wt%), suspending agent (2.5 wt%), leveling agent (0.5 wt%) and coalescent (0.7 wt%).

Note that the WCA was measured along the edges of the specimens in order to obtain a clear profile of a water droplet and thus an accurate measurement. The specimens need to be broken when the WCA values at the center places of the specimens were measured. Consequently, the average WCA measured for the entire coating specimen with the optimized composition is approximately (147.5 ± 3.2)°, with some data at the edges of the specimen greater than 150° and the others of the specimen smaller than 150°. Organic transparent coating surfaces are inherently heterogeneous because the pigments and fillers are not homogeneously distributed in the matrix. Air flow of the spray gun generally makes pigments and fillers of coatings deposit more at the edges of the transparent coating surfaces than in the centers of the transparent coating surfaces, resulting in rougher edges and smoother centers of specimens. After all, the polymer surface roughness cannot be readily created via self-assembly[12]. Clearly, to fabricate ideal super-non-wetting surfaces, the transparent coating surfaces need to be roughened.
3.2. The effects of grinding on the wettability

The roughness of a surface is essential in fabricating super-non-wetting surfaces[1] because the appropriate roughness may provide a capillary force to prevent liquid from entering into the grooves on the surfaces[5]. Therefore, the second step to manufacture super-non-wetting surfaces is the generation of appropriate surface roughness. To this end, a pneumatic angle grinder equipped with silicon carbide emery papers having various grit numbers was employed in this work to roughen the transparent coating surfaces. The effects of grit numbers of emery papers at a specific grinding depth was investigated to identify the optimum roughening conditions. Note that only when the average WCA of the specimens was bigger than or equal to 150° were the CAH and SA measured and presented because this paper mainly focuses on super-non-wettability.

Fig. 3 presents the change of the measured average WCA, as well as the standard deviation, as a function of grit number of emery papers. As shown in Fig. 3, the average WCA measured for the coating surfaces ground using emery papers with grit numbers of 180, 240 and 320 are 150.7, 150.2 and 151.7°, respectively. The average WCA values measured for the specimens ground using emery papers with grit numbers of 80, 120 and 600 are smaller than 150°. The appropriate surface roughness can be created by grinding the coating surfaces using emery papers with grit numbers of 180, 240 and 320. The surfaces grounded using emery papers with grit numbers of 80 and 240 seem to be too rough and the surface grounded using emery papers with grit numbers of 600 appears to be too smooth to generate super-non-wetting coating surfaces.

![Figure 3. The grit number dependence of the average WCA values, together with the standard deviation, measured for the transparent coating specimens ground using emery papers with different grit numbers.](image)

4. Conclusions

Based on the new findings presented above, the main conclusions can be drawn as follows:

- Without chemical modification, an ultrahydrophobic transparent paint coating with luminescence can be fabricated using low-cost commercially available materials via tailoring the coating composition.
- An industrially-producible, practically-applicable and easily repairable super-non-wetting self-cleaning transparent paint coating with luminescence may be manufactured through grinding the ultrahydrophobic coating surfaces using emery papers with appropriate grit numbers.
- Grinding the coating surfaces using emery papers with the grit numbers of 180, 240 and 320 created micro-grooves, with micro-particles exposed on the coating surfaces, resulting in the super-non-wettability and self-cleaning property of the coating surfaces.
- When applied to the external walls of buildings, the transparent paint coating with yellow-green luminescence can provide the external walls with super-non-wetting self-cleaning property, decorate them during the night and save outdoor illumination power.
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