Research Article

Preparation of Antibacterial Color-Coated Steel Sheets

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1. Introduction

The menace of infection caused awareness around the world by the suddenly globally spreading epidemic disease, such as avian influenza [1], SARS, H1N1, and other unexpected multiplication of germs or other bacteria that pose serious health problems [2, 3]. Great deals of antibacterial products appeared in the cases of antibacterial ceramics [4–7], antibacterial glasses [8–10], antibacterial textiles [11–13], antibacterial plastics [14–16], antibacterial stainless steels [17–20], and so forth. These applications mainly involve the methods of adding antibacterial agents into the overall substrate, modifying the surface of substrate, or directly coating the antibacterial agents. However, the development of antibacterial products in a wide range of areas was still hindered due to the low effective utilization rate of the antibacterial agents, the high cost, and the poor binding force, which existed between antibacterial agents and the substrates restrict. In this paper, the antibacterial agent was firstly poured into steel coating before being made into the antibacterial color-coated sheet. Sequent research findings demonstrated that antibacterial agents presented a comfortable dispersive distribution on the surface of color-coated sheet, which could remarkably reduce the cost by attributing to the less addition of antibacterial agents and the simple manufacturing technological process. It was also found that the binding force among the antibacterial agents and substrate got much stronger than ever due to the integration of antibacterial agents into the coil coating.

Served as one category of antibacterial agent, titanium dioxide is the most preferred material to be served as pigment. Unfortunately, the antimicrobial activity of pure TiO$_2$ is merely valid when it is irradiated under UV light. In addition, the low electron transfer rate to oxygen and high recombination rate of electron-hole employed in UV light impose further limits to the effective photocatalytic sterilization rate of TiO$_2$ [21–23]. These drawbacks strongly restricted the practical applications of TiO$_2$ as an effective and promising antimicrobial material. Silver (including Ag ions and Ag nanoparticles) is a well-known and effective inorganic antimicrobial material that has been applied in many fields. However, the high-cost and dark color are two notable obstacles during its applications as large-scale antimicrobial coatings [24–26]. Nevertheless, Ag can act as both an antimicrobial auxiliary agent and a sink for electrons and redox catalyst that may enhance the overall photooxidation ability of TiO$_2$ [27–30]. Thus, it is reasonable and rational to combine Ag with TiO$_2$ during antimicrobial coatings production.

This study focused on the manufacture of antibacterial color-coated sheet using Ag-loaded TO$_2$ as antibacterial agent. The antibacterial agent was firstly poured into steel
coating with some additives and made into the antibacterial coil coating. And then, the antibacterial color-coated sheet was manufactured in a normal process. It delivered a technology of less addition of antibacterial agents and simple procedure.

2. Experimental

2.1. Materials. Ag-loaded TiO\(_2\) was purchased from Jingui Group (Chenzhou, China). The grain size was 48 nm and the Ag particle size was 10 nm. Coil coatings (including polyester topcoat and epoxy priming paint) and diluents (the main components were ethyl acetate, butyl acetate, benzene, toluene, acetone, ethanol, butanol, etc.) were provided by Center Group (Changshu, China). The additives including plasticizer, wetting dispersant, and flow agents were purchased from Yongyan Ltd. (Shanghai, China).

2.2. Preparative Method of Antibacterial Color-Coated Sheet. The preparative process of antibacterial color-coated steel plate is shown in Figure 1. A certain amount of coil coatings, coil coating diluents, silver-loaded titanium dioxide, and some additives including plasticizer, wetting dispersant, and flow agents were added into the paint grinder running in high speed, and then filtered through the paint filter. Finally, the color-coated steel plate was achieved by roller coating, baking and curing.

The Ag-loaded TiO\(_2\) used in this study was produced by Jingui Group using the technological process developed in our previous studies [31–35].

2.3. Antibacterial Properties Testing. Antibacterial properties of products were tested according to "Antibacterial Coating—Antibacterial Performance Test Method, the appendix A of "the People’s Republic of China Chemical Standard HG/T 3950-2007". In the tests, nutrient agar media (Luria Broth, LB) was prepared in water by mixing tryptone, NaCl, agarose gel powder and yeast extract in the volume percent of 1%, 0.5%, 1.5%, and 0.5% to total of media, respectively. The mixture was put into a conical flask and autoclaved for 45 min at 120°C. The conical flask was kept in room temperature for 2 h for cooling and then poured into separate Petri dishes. A 5 cm × 5 cm sample was cut from the antibacterial color-coated sheets for bacterial culture and the surface of all samples was cleaned with absolute ethanol soaked tissue paper before antibacterial test. The samples were placed in separate Petri dishes on top of the pre-deposited LB. A clean soda-lime glass piece was used as a control sample. After placing the antibacterial color-coated sheets samples, a thin layer of LB was further deposited on top. These plates were kept for 1 h for complete gelation of the agar, and after that quantitative solution of E. coli was evenly spread over each gel plate in the respective Petri dishes. The plates were incubated for 24 hours to allow the completion of bacterial growth. The bacterial colonies formed in each plate were observed and the bacterial number on each sample was counted with colony counting method. The antibacterial efficiency of the color-coated sheet was calculated in

\[
\text{Antibacterial efficiency} = \frac{A_0 - A}{A_0},
\]

where \(A_0\) and \(A\) are the antibacterial number of the control sample and antibacterial color-coated sheet sample, respectively.

2.4. Photocatalysis Properties. The methyl orange solution with 3 of pH value was poured into the culture. The photocatalytic activity of the antibacterial color-coated sheet was evaluated on the degradation of methyl orange in an aqueous solution under illumination of UV light (mercury vapor lamp, 40 W, 40 cm long, predominant wavelength 253.7 nm) in a photoreactor system. The degradation of methyl orange was calculated in

\[
\text{Degradation} = \frac{B_0 - B}{B_0},
\]

where \(B_0\) and \(B\) are the absorbance of the primal and remaining methyl orange, respectively. The absorbance was measured with UV/vis spectrophotometer (UV-2450, Japan).

2.5. Duration Properties. The antibacterial color-coated sheet was made of the white gray coil coating with 2% silver-loaded titanium dioxide, cutting into 5 cm × 5 cm pieces. Forty-five pieces were placed into the \(\varnothing\) 9 cm culture dish, respectively, with three parallel samples each day. Then each culture dish was poured 30 mL ultra-pure water, and sampled every day. The silver content in the water and the antibacterial properties of the sheets would be tested.

3. Results and Discuss

3.1. Antibacterial Properties. Addition of antibacterial agent and effective utilization rate are key factors influencing on antibacterial properties of the color-coated sheet. The more antibacterial agents used, the higher antibacterial efficiency obtained, but the cost also increased thereupon. The best dose should satisfy antibacterial requirement and low cost. Ag-loaded TiO\(_2\) should be highly dispersed under stirring and function of additives to get well compatibility with coil...
Table 1: Effect of agent amount on antibacterial property of color-coated steel.

<table>
<thead>
<tr>
<th>The dose of Ag/TiO2/wt%</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bacterial count of 1#/cfu</td>
<td>$1.88 \times 10^6$</td>
<td>$2.40 \times 10^5$</td>
<td>172</td>
<td>29</td>
<td>$&lt;20$</td>
<td>$&lt;20$</td>
</tr>
<tr>
<td>Bacterial count of 2#/cfu</td>
<td>$1.86 \times 10^6$</td>
<td>$2.36 \times 10^5$</td>
<td>166</td>
<td>27</td>
<td>$&lt;20$</td>
<td>$&lt;20$</td>
</tr>
<tr>
<td>Bacterial count of 3#/cfu</td>
<td>$1.91 \times 10^6$</td>
<td>$2.48 \times 10^5$</td>
<td>180</td>
<td>35</td>
<td>$&lt;20$</td>
<td>$&lt;20$</td>
</tr>
</tbody>
</table>

coating. So, the rotation speed and stirring time are considered.

Table 1 shows the effects of different antibacterial agent dosages on the antibacterial properties of color-coated sheet. As from Table 1, the antibacterial properties increased with the increase of addition of antibacterial agents. The antibacterial efficiency reached about 87% when 1% (wt) of Ag-loaded TiO2 was added. Obviously, the antibacterial efficiency reached 99.99% when the antibacterial agents addition was higher than 2%. This could be ascribed to the reactive oxygen antibacterial mechanism. In the presence of water and oxygen, the antibacterial agents containing TiO2 can adsorb water and oxide, producing HO* with high oxidative and reactive capacity. HO* can infiltrate and destruct coenzyme A and also degrade endotoxin, protein lipids and mineralize into CO2 through particles on the cell surface binding of the hydroxyl groups. Ag+ in the antibacterial agents can be firmly attached to the bacteria, and further penetrate into the bacterial cell wall when contacting the negatively charged cell membrane. This responds to OH in bacteria and results in bacterial proteins coagulation, cell synthesize enzyme activity destruction, and therefore, loss of reproduce ability and death. Besides, Ag+ can also destroy bacteria electronic transmission system, respiratory system, and mass transport system for killing bacteria. Silver-loaded titanium dioxide agents have the advantages of both above at high temperature, high security, long-term sterilization, and high antibacterial property even in dark condition. Therefore, the 2% dosage of silver-loaded titanium dioxide in coil coating is determined.

Silver-loaded titanium dioxide was added to the mixture of paint at high speed, and then an original speed. The effects of different rotation speeds on the fineness of the coil coating and gloss of the color-coated steel sheet were investigated. As seen from Figures 2 and 3, the fineness of the coating decreased and the gloss of color sheet increased gradually with the increase of speed. The fineness of coating is the range of 10–20 μm and the gloss 35 ± 5 according to “evaluation method of dispersion of pigments.” The fineness of coating is about 19 μm and the gloss approximately 32 under speed 4000 r/min, both of which meet the required standards. Antibacterial agents dispersed in the coil coating passes through three processes, namely, wetting, grinding, and dispersion and stability. Wetting is defined as the solvent taking the place of the air and water on the surface of paint. Solvent-based paint is not a problem as the surface tension of paint is always lower than that of the general. The silver-loaded titanium dioxide is a nanopowder, but the particles of antibacterial agents would get together due to van der waals force. Therefore, it is required to redisperse under shearing or impact forces. When the shear rate (D) is constant, the shear force (τ) and viscosity (η) is proportional as

$$τ = D_ν.$$ (3)
The higher the speed, the greater the shearing force under certain viscosity, which is helpful for the grinding. In summary, silver-loaded titanium dioxide is added to the coil coating under the speed of 4000 r/min.

The effects of stirring time on fineness of the coil coating and gloss of the color-coated sheet were studied under 4000 r/min of rotation speed after adding silver-loaded titanium dioxide to the coil coating.

Figures 4 and 5 show the effects of stirring time on fineness and gloss of coil coating. It is evident that the fineness decreased and the gloss improved with the increase of stirring time. The fineness and the gloss were about 19 μm and 32, respectively, after stirred for 3 h. Both values reached the pigments and the grinding fineness requirements based on “the evaluation method of dispersion of pigments” mentioned above. Consequently, the final choice of grinding time is 3 h.

The surface morphology of color-coated sheet was observed by using SEM in order to detect the effect of antibacterial agent in the coil coating. SEM analysis results of precoated layer of color-coated sheets with and without Ag-loaded TiO₂ are shown in Figure 6. The coated particles after adding antibacterial agents were well distributed except a small part of the reunion, and the particle sizes were about 10 μm, which is quite similar to the ordinary color-coated sheet. The results were in accordance with the measurement results and achieved the required fineness. It was indicated that Ag-loaded TiO₂ almost became the part of coil coating under the function of additives. There was nearly no difference between ordinary color-coated sheet and antibacterial color-coated sheet in appearance and morphology. This was beneficial to the dispersion of antibacterial agents and the improvement of the antibacterial property.

Ag in the antibacterial agent plays an important role in antibacterial property. The most distinguished feature of the ordinary color-coated sheet and antibacterial color-coated sheet lies in the function of silver and titanium dioxide. Although the addition was little, the change of the elements in the ordinary color-coated sheet and antibacterial color-coated sheet should be observed. EDX analysis of color-coated sheet with and without antibacterial agents was undertaken to analyze the change of their elements. The results are showed in Figure 7.

It can be seen from the figures that the elements Ti and Ag in color-coated sheet adding antibacterial agents appeared as compared to those without adding antibacterial agents. However, the dosage of elements was relatively small so that the increase of elements Ti and Ag were not significant. Nonetheless, it also can be indicated that silver-loaded titanium dioxide has been incorporated into the precoated layer of antibacterial color-coated sheet.

3.2. Photocatalysis Properties. Figure 8 shows the methyl orange degradation ability of color-loaded sheet. The concentration of methyl orange decreased with time and came to the equilibrium finally. The speed of degradation is not fast with the degradation efficiency of 25% in the first 1 h. However, the degradation efficiency reached about 80% after 2 h. Methyl orange concentration tends to be stable with the degradation efficiency of about 88% at 4th hour. In conclusion, the color-coated sheet synthesized in the present study possesses high degradation of methyl orange. The color-coated sheet adding antibacterial agents has the capability of “self-cleaning.”

Photocatalytic degradation of methyl orange mechanism is as follows: the valence band electrons of silver-loaded titanium dioxide are excited under UV, then they jump across the forbidden band into the conductive band and form the highly reactive negative-charged electron e⁻, while producing a corresponding hole h⁺ in the valence band. Then electrons and holes separate and migrate to different positions on the surface of particles and reduction and oxidation happens on the surface of materials. The main reactions are as follows:

\[ \text{OH}^- + h^+ \rightarrow \cdot \text{OH} \]
\[ \text{H}_2\text{O} + h^+ \rightarrow \cdot \text{OH} + \text{H}^+ \]
\[ \text{e}^- + \text{O}_2 \rightarrow \text{O}_2^- \]
3.3. Stability and Duration Properties. The stability of antibacterial coil coating was evaluated using the centrifugation settling time and gravity settling time. The settling time of antibacterial agents is equal to the storage period of antibacterial agents in the coil coating under gravity. The time for appearing 10 mm supernatant is the centrifugal settling time $t_C$. Gravity settling time $t_G$ can be calculated by

$$t_G = \frac{4\pi^2 R N^2}{g}. \quad (5)$$

As shown in Table 2, the storage period of coil coating is about 2 years without antibacterial agents and 16 months with antibacterial coil coating. The silver-loaded titanium dioxide particles make Brownian motion in the coil coating, which could result in the decline of stability. Flocculation appears under the particles’ kinetic energy over the repulsive force when particles contact to each other. Therefore, adding antibacterial agents makes the stability of the coil coating decreased.
Table 3: Results of pilot-scale run and practical application (average values).

<table>
<thead>
<tr>
<th></th>
<th>Chromatic aberration</th>
<th>Impact/J</th>
<th>MEK/times</th>
<th>Glossiness/°</th>
<th>T-bend/T</th>
<th>Film thickness/µm</th>
<th>Antibacterial Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hand sample</td>
<td>DL 0.09 Da 0.06 Db 0.10 DE 0.21</td>
<td>9</td>
<td>&gt;100</td>
<td>33</td>
<td>3T</td>
<td>14</td>
<td>&gt;99.99%</td>
</tr>
<tr>
<td>Bulk sample</td>
<td>DL 0.07 Da 0.03 Db 0.07 DE 0.10</td>
<td>9</td>
<td>&gt;100</td>
<td>32</td>
<td>2T</td>
<td>14</td>
<td>&gt;99.99%</td>
</tr>
<tr>
<td>First batch of commercial product</td>
<td>DL -0.23 Da -0.18 Db 0.01 DE 0.28</td>
<td>9</td>
<td>&gt;100</td>
<td>34</td>
<td>3T</td>
<td>14</td>
<td>&gt;99.99%</td>
</tr>
<tr>
<td>Second batch of commercial product</td>
<td>DL -0.09 Da -0.11 Db 0.06 DE 0.16</td>
<td>9</td>
<td>&gt;100</td>
<td>33</td>
<td>3T</td>
<td>14</td>
<td>&gt;99.99%</td>
</tr>
</tbody>
</table>

4. Conclusions

A simple way to manufacture antibacterial color-coated sheet using Ag-loaded TiO₂ is developed. The optimal technical parameters are 2% of silver-loaded titanium dioxide, 4000 r/min of stirring speed, 3 h for stirring time. The silver-loaded titanium dioxide is dispersed well in color-coated sheet and the antibacterial efficiency reaches 99.99%. The efficiency of methyl orange degradation reaches 88% in 4 h. The duration of antibacterial color-coated sheet is long enough. The products of antibacterial color-coated sheet meet the first class standard of prepainted steel sheet and have excellent properties of antibiosis, photocatalysis, and duration.

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