Article

Fabrication of Nano TiO₂-Polymer Encapsulated Fluorescent Pigments for Weatherability Improvement of Powder Coating

Baowei Yan ¹, Xiao Lv ¹ , Yuanyuan Shao ^{1,2} , Haiping Zhang ^{1,2,*}, Hui Zhang ^{3,*} and Jesse Zhu ^{1,3}

¹ School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China; bwyang@tju.edu.cn (B.Y.); xiaolv@tju.edu.cn (X.L.); yshao@tju.edu.cn (Y.S.); jzhu@uwo.ca (J.Z.)

² Institute of Shaoxing, Tianjin University, Shaoxing 312300, China

³ Department of Chemical and Biochemical Engineering, The University of Western Ontario, London, ON N6A 3K7, Canada

* Correspondence: hpzhang@tju.edu.cn (H.Z.); hzhang1@uwo.ca (H.Z.)

Abstract: Fluorescent coatings have attracted attention due to their bright colors. However, they have fewer outdoor applications due to low stability, especially the poor weather resistance of the fluorescent pigments. In order to improve their weather resistance and maintain the excellent appearance, this study used polymer binders to coat a light shielding agent nano TiO₂ on the surface of the fluorescent pigment to extend the durability. Three organic binders, polyester varnish, polyurethane varnish, and polyvinyl alcohol, were selected. Each binder was dissolved and mixed with pigments and nano TiO₂ particles to make a polymer-TiO₂ layer on the pigment surface. The effects of binder types and loadings were investigated and evaluated by accelerating weather test of corresponding fluorescent powder coatings. According to SEM and ash test, nano TiO₂ was successfully coated on the surface of fluorescent pigments. The modified fluorescent pigment shows a strong ability to absorb ultraviolet rays, and the weather resistance of prepared coatings has been significantly improved compared with the original fluorescent powder coating. When using clear coat PE as a binder and setting the ratio of the binder to the nano TiO₂ of 1:2, the UV exposure time of fluorescent powder coatings can be extended by over twelve times compared to the coatings with original pigment for the same color change. This study provides an effective approach to enhance the weather resistance of fluorescent coatings and thus expand their applications.

Keywords: fluorescent pigments; powder coatings; weather resistance; TiO₂; binder; encapsulation

Citation: Yan, B.; Lv, X.; Shao, Y.; Zhang, H.; Zhang, H.; Zhu, J. Fabrication of Nano TiO₂-Polymer Encapsulated Fluorescent Pigments for Weatherability Improvement of Powder Coating. *Coatings* **2022**, *12*, 315. <https://doi.org/10.3390/coatings12030315>

Academic Editor: Ivan Jerman

Received: 31 December 2021

Accepted: 24 February 2022

Published: 27 February 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

With the development of the coating field, expansion of the coatings market, and, in particular, the tightening of national environmental protection policies, environmentally friendly powder coatings [1–3], with the advantages of no volatile organic compound (VOC) emission, high efficiency, and recyclability, has gradually become an indispensable component of the coating industry. As a branch of high-end powder coating, fluorescent powder coatings [4,5] are given extra characteristics, such as bright color, with the existence of fluorescent pigment. Fluorescent pigment [6] is an excellent functional luminescent pigment that appears to have a more vivid color under the light. However, most fluorescent pigments have disadvantages such as weak UV resistance, poor weather resistance, and low heat stability [7], so they are usually only used in indoor environments. Therefore, in order to expand the application of fluorescent powder coatings, improving the UV resistance of fluorescent pigments is an important subject in the coatings industry.

Generally, UV protecting agents [8–10] are introduced to powder coating systems to improve the UV resistance, which can reduce the transmission of ultraviolet light and protect the internal coating polymer from light damage. Nano titanium dioxide (TiO₂) is one of the widely used UV adsorbers with a good UV shielding effect [11]. It can generate free radicals when irradiated with ultraviolet rays, absorb light with energy

greater than its forbidden bandwidth (about 3.2 eV) [12], and convert it into thermal energy or fluorescence. Modification of pigments with nano TiO₂ would be one of the solutions providing protection to pigments, which can create a barrier and thus protect the internal pigment.

Pigments can be modified by the encapsulation method [13], the inorganic hybrid method [14], and surface modification [15]. A surface treatment that introduces an outside protection barrier on the pigment is one of the promising approaches. Bugnon et al. reported that introducing SiO₂ to the surface of organic pigment through sodium silicate and sulfuric acid activation could improve their UV-resistant capacity [16]. Yuan et al. fabricated SiO₂ [17] and TiO₂ [18] layers by the sol-gel method in the presence of additional polyelectrolytes on the pigment surface (Yellow 109), and successfully enhanced the UV shielding property. Although there are many strategies to make pigment surface modification feasible, it is still urgent to reduce costs, increase production capacity, and simplify processes. Moreover, these encapsulation techniques mainly used continuous inorganic layers, which affected the appearance of the pigments. When introducing the inorganic layer, e.g., sol-gel TiO₂, the film appearance, such as gloss, distinctness of image (DOI) was decreased [19]. Besides the continuous sol-gel TiO₂ film, our previous study showed the introduction of nano rutile TiO₂ could largely enhance the weather resistance of the fluorescent pigments. The replacement of part of sol-gel TiO₂ with nano TiO₂ also improved the film appearance [19].

In fluorescent pigment, resins are one of the main components working as the carrier of the dye. They are also considered as an alternative pigment surface modification encapsulant due to the polymeric substance [20,21], and they can endow pigment stability, dispersion, and weather ability without compromising the pigment brightness [22]. He et al. [23] prepared soap-free nano-pigment composite particles via miniemulsion polymerization encapsulation for fabric printing. The color stability and weatherability of the pigment were significantly improved, and the appearance and brightness were also maintained with the presence of polymer resins on the pigment surface.

In this study, in order to overcome the side effect of the inorganic binder, organic resins were used to bind the rutile nano TiO₂ onto the fluorescent pigment to improve the UV resistance. The added resin polymer could bind nano TiO₂, forming a transparent film on the pigment surface and introducing the UV protection without sacrificing the pigment property. The pigment was applied to powder coatings to investigate the effect of modification through measuring the appearance changes of fluorescent powder coatings under the accelerating UV radiation test. Three different binders, polyester varnish coat (PE), polyurethane varnish coat (PU), and polyvinyl alcohol (PVA), were selected. PE and PU are resins with hardener, which can be cured to form a hard film; PE is the same resin type as the used powder coating, while PU is a similar type to the pigment resin. The effects of the ratios of binder to nano TiO₂ as well as binder types were explored for optimal performance.

2. Materials and Methods

2.1. Methods

Materials for pigment preparation: Fluorescent Pigment (Fluorescent Peach) is K_03 Rose Red from Guangzhou Shancai Chemical Co., Ltd. (Guangzhou, China). Titanium dioxide PGNR408 was provided by Panyan Technology Co., Ltd., Panzhihua, China. Ethyl acetate was produced by Tianjin Yuanli Chemical Co., Ltd. (Tianjin, China). Polyurethane varnish coat (PU) was provided by Tianjin Shengda New Material Co., Ltd. (Tianjin, China). Polyester varnish coat (PE) is from Guangdong Huajiang Powder Technology Co., Ltd. (Zhaoqing, China). Polyvinyl alcohol (PVA) was produced by Guangzhou Liaohua Chemical Co., Ltd. (Guangzhou, China).

Materials for powder coating preparation: Polyester resin, P6310, was supplied by Solvay, Bruxelles, Belgium. The curing agent, TGIC, was produced by Huahui Co., Ltd., Huangshan City, Anhui Province, China. Precipitated BaSO₄ was produced by Fuhua

Chemical Co., Ltd., Weinan, China. Leveling agent GLP588, leveling additive BLC701B, and Benzoin were produced by Nanhai Chemical Co., Ltd., Ningbo, China. Polyethylene wax, PEW0389, was provided by Tianshi New Material Technology Co., Ltd., Nanjing, China. Titanium Dioxide R699 was produced by Baililian Chemical Co., Ltd., Jiaozuo, China.

Coating substrate: Q-panel is an aluminum plate with the dimensions of 51 mm × 82 mm from Q Lab, USA.

2.2. Methods

2.2.1. Preparation of Weather-Resistant Fluorescent Pigment

In this study, ethyl acetate was used to dissolve the binder clear coat polyester (PE) and polyurethane (PU), and water was used to dissolve the binder polyvinyl alcohol (PVA). Firstly, the binder and its corresponding solvent were mixed and stirred continuously with a glass rod for complete dissolution. Then rutile-type nano TiO_2 was added according to the set mass ratio of the binder to nano TiO_2 (1:2, 1:1, 2:1). After continuing stirring with a magnetic stirrer at 600 r/min for 20 min, an appropriate amount of fluorescent pigment was slowly added into the binder solution, controlling the mass ratio of nano TiO_2 to the fluorescent pigment of 2:8. The mixture was heated to 60 °C while stirring, and the solvent was continuously evaporated. When the liquid converted to a paste, the viscous object was heated in an oven at 140 °C for 15 min to make PU and PE fully cured. After that, the modified pigment was pulverized into its original particle size with a jet mill. The preparation process is shown in Figure 1, and experimental conditions are listed in Table 1.

Table 1. Preparation of modified fluorescent pigments under different conditions.

Samples	Binder Type	Binder: TiO_2 Weight Ratio
Control	/	/
PU _{coat} -2:1	PU	2:1
PVA-2:1	PVA	2:1
PE _{coat} -2:1	PE	2:1
PE _{coat} -1:2	PE	1:2
PE _{coat} -1:1	PE	1:1

Figure 1. Preparation process of modified fluorescent pigment.

2.2.2. Preparation of Powder Coating

An appropriate amount of modified fluorescent pigment; polyester resin P6310; curing agent TGIC; filler BaSO_4 ; and additives 588, 701B, PEW0389, benzoin, and TiO_2 R699 were taken according to the formula (Table 2) and added to a swing stainless steel pulverizer to be crushed and pre-mixed. The mixture was then transferred to a twin-screw extruder

(SLJ-10, Donghui Co., Yantai, China) and melt-extruded at 110 °C. After cooling and rolling, a flaky powder coating was obtained. The flakes were put into a crusher (BJ-150, Sufeng Industry Co., Ltd. Zhengzhou, China), crushed for about 80 s at a voltage of 250 V, and then sieved to obtain a fluorescent powder coating with a medium particle size of less than 40 µm.

Table 2. Fluorescent powder coating formula.

Chemicals	Model	Proportion wt %
Polyester resin	P6310	51.40
TGIC(Hardener)	/	3.93
BaSO ₄	/	30.84
General leveling agent	GLP588	0.93
Leveling additives	BLC701B	0.93
Polyethylene wax	PEW0 389	0.37
Benzoin	/	0.37
Titanium Dioxide	R699	1.87
Fluorescent pigment	K_03 Rose red	9.35

A small amount of fluorescent coating powder was put into a venturi funnel of an electrostatic powder spray gun (Surecoat, Nordson Co., Westlake, OH, USA), and sprayed uniformly on a Q-panel substrate at a voltage of 60 kV. The sprayed Q-panel was cured at 180 °C for 15 min in an oven to form a coating film.

2.3. Characterization and Weatherability Assessment

2.3.1. Characterization of Modified Fluorescent Pigments

In order to determine the content of TiO₂ in the modified fluorescent pigment, the ASTM D5630-13 ash test method [24] was used to determine the content of inorganic substances in the sample, thereby calculating the content of TiO₂ in modified fluorescent pigments. To exclude the effect of the substances contained in the raw materials on the experimental results, the original fluorescent pigment, binders, and TiO₂ were subjected to an ash test. The content of TiO₂ was calculated after eliminating their effect.

The ash content of the sample (ω) is defined as Equation (1), where M_1 is the mass before calcination, and M_2 is the mass after calcination.

$$\omega = \frac{M_2}{M_1} \times 100\% \quad (1)$$

The identification of TiO₂ in the modified samples was performed by X-ray diffraction spectroscopy (XRD, D/MAX2500, Rigaku, Tokyo, Japan). The original and modified fluorescent pigments were scanned in the scanning range of 10°–60°, and their XRD phase analysis was performed by comparison with the standard spectrum of TiO₂.

An Ultraviolet-visible spectrophotometer (UV2600, Shimadzu, Tokyo, Japan), which can provide monochromatic light in the range of 190–800 nm, was used to study the absorption capacity of ultraviolet and visible light by the samples. The absorption ability reflects the ultraviolet resistance of the pigment samples.

The microscopic morphology of the fluorescent pigment particles was obtained using a scanning electron microscope (SEM, ZEISS SIGMA 300, Carl Zeiss AG, Oberkochen, Germany). The field emission transmission electron microscope (FE-TEM, JEM2100F, JEOL, Tokyo, Japan) was used to analyze the microstructure of pigments. The chemical compositions and element distributions were obtained from energy dispersive spectrum (EDS, JEM-F200, JEOL, Tokyo, Japan).

2.3.2. Characterization of Fluorescent Powder Coatings

The particle size of the prepared fluorescent powder coating was measured by a Bettersize 2000B laser analyzer (Dandong Baxter Instrument Co., Ltd., Dandong, China).

The medium particle size D_{50} and span were used to represent the particle size and size distribution, respectively. Span was calculated according to Equation (2); the smaller the value, the narrower the distribution.

$$Span = (D_{90} - D_{10}) / D_{50} \quad (2)$$

where D_{10} , D_{50} , and D_{90} are the particle diameters that 10, 50, and 90 volume % of the particles are smaller than, respectively. In order to prevent the inconsistency of particle size from affecting the gloss and other properties of the film, the medium particle size of all the powder coating was kept the same, at the D_{50} of $32.6 \pm 1.3 \mu\text{m}$ and span of 1.95 ± 0.05 .

The weather resistance of the coating film was evaluated by the UV accelerated aging test. The prepared films were placed in a UV aging box (KC-UV, Shanghai Kece Experimental Instrument Co., Ltd. Shanghai, China), and the UV-B irradiation intensity was set as 0.68 W/m^2 . The film samples were taken out at different time periods and the surface appearance was measured to evaluate their weather-resistant performance. The tested surface properties include gloss, distinctness of image (DOI), and color change.

Gloss is a surface property of a coating film, which depends on the specular reflection ability of the film surface to light and can well evaluate the appearance performance of a film. A gloss meter (IQ206085, Rhopoint Components Ltd., East Grinstead, UK) was used to measure the gloss values at angles of 60° , which is usually used to evaluate the coating surface. The average was calculated based on nine tests on each coating film.

DOI is used to reflect the roughness of the coating surface through the reflection or refraction of light by the coating. Poor DOI indicates that orange peel, micropores, wrinkles, and other phenomena exist on the surface of the film, which directly affects the appearance of the coating film. The DOI value of the film was measured by the gloss meter to analyze the degree of orange peel of the film prepared under different schemes.

The color change of the coating films was measured with an iWAVE Precision Color Difference Meter (iWAVE, Shenzhen Weifu Optoelectronic Technology Co., Ltd. Shenzhen, China). The color difference of the films at different time periods was obtained by comparing with the coating surface before the aging test, which can be calculated by Equation (3). The total color difference can be used to assess the UV resistance of the fluorescent powder coating. At the same UV irradiation time, the smaller the color difference changes, the stronger the UV resistance of the coating.

$$\Delta E = \sqrt{DL^2 + Da^2 + Db^2} \quad (3)$$

where ΔE is the total color difference, DL indicates brightness varying from black (0) to white (100), Da exhibits the changes from red (+) to green (−), and Db represents the changes from yellow (+) to blue (−).

3. Results and Discussion

3.1. Characterization of Modified Pigment

3.1.1. Analysis of TiO_2 Content

In theory, organic substances in fluorescent pigments will decompose and gasify at high temperatures, and the remaining components are inorganic substances, because the fluorescent pigment is composed of amino resin, dye, and additives. Its main component is organic matter, which will be decomposed by calcination at 500°C for 3 h. The ash test results of the original materials are shown in Table 3. The inorganic purities in pigments and binder are all less than 4%.

Table 3. Ash test results of raw materials and binders.

Samples	Original Pigment	PE	PVA	PU	Commercial TiO_2
Ash content (%)	3.25 ± 0.11	0.79 ± 0.02	2.42 ± 0.19	0.42 ± 0.01	94.51 ± 0.08

Three types of binders were used to coat the fluorescent pigment. It can be seen from Figure 2 that different binder contents and types have different effects on the content of nano TiO_2 in modified fluorescent pigments. Among different types of binders, the coating effect of PVA is the worst. This is because PVA is a pure resin without a curing agent, thus it cannot form a hard film and tightly bind TiO_2 nanoparticles on the surface of the fluorescent pigment. On the contrary, the TiO_2 content of the fluorescent pigment coated with clear coat PU and PE is high, indicating that the surface of the fluorescent pigment is coated with a certain amount of nano TiO_2 . Clear coat PU and PE containing curing agents, which can be cured at the treating temperature, would provide high binding ability and form a firm layer on the surface of the pigment. The content of nano TiO_2 in the PU coating is slightly higher than that in the PE coating, which may be due to the higher similarity of PU and pigment resin. When the binder to TiO_2 ratio is 1:2, the nano TiO_2 content in the pigment is the most, because the TiO_2 addition is the highest.

Figure 2. TiO_2 content in modified pigments.

3.1.2. Analysis of X-ray Diffraction Results

The crystals contained in the modified fluorescent pigment were analyzed by XRD. It can be seen from Figure 3 that the original fluorescent pigment has a clear broad peak at 21.5° . After coating with resin binders, the original peak of the fluorescent pigment is weakened, and new diffraction peaks appear at 27.4° , 36.1° , 41.3° , 44.1° , 54.3° , 56.7° , 62.7° , 64.1° , and 69.1° , corresponding to (110), (101), (200), (210), (211), (220), (002), (310), and (301) of rutile nano-titanium dioxide crystals [25] (ICDD file No. 03-065-1118), indicating the successful binding of rutile nanocrystals- TiO_2 on the pigment surface. Among three binders, the TiO_2 peaks in PE and PU are more obvious than that in PVA, indicating that more TiO_2 is bound on the pigment when using PE and PU coat with resin and hardener rather than bare resin PVA. At different PE binder ratios, the TiO_2 peaks of pigment at a PE-to- TiO_2 ratio of 1:1 are much smaller than that at ratio of 1:2 and 2:1.

Figure 3. XRD patterns of fluorescent pigments under different conditions. (a) different types of binders (b) different ratios of PE to TiO_2 .

3.1.3. Morphology of Modified Fluorescent Pigments

The morphology of the original fluorescent pigment is observed by electron microscopy. As shown in Figure 4, SEM images of the original fluorescent pigment particles at different magnifications are presented, respectively. The pigment particles are distributed evenly, and most of them are of spherical structures, while some of them contain irregular aggregates. As can be seen from Figure 4b,c, the original fluorescent pigment particles are regular spheres with a particle size of approximately $2\ \mu\text{m}$ and a clear surface texture. It is also observed that some fine particles are distributed on the local surface of spherical particles, and some coarse particles are aggregated to form irregular clusters (Figure 4d).

Figure 4. SEM images of the original fluorescent pigment at different magnifications: (a) magnification of 6 k; (b) magnification of 20 k; (c) magnification of 50 k; (d) magnification of 20 k.

By comparing fluorescent pigments coated with the nano TiO_2 and binders, it can be found that the surface of the pigment is covered with clusters, because PVA is not able to form a continuous film on fluorescent pigment due to the lack of hardener, and nano TiO_2 particles are weakly attached to the surface of the fluorescent pigment. On the other hand, the clear coat PU and PE can form a good paint film on the surface of fluorescent

pigments, as seen from Figure 5d,f (in red circles). Under the heating condition, PU or PE resins reacted with hardener, forming a crosslinked polymer layer, which benefits the binding of TiO_2 . Compared to PU coated pigment, PE coated pigment shows thinner and more uniform film.

Figure 5. SEM images of pigments with different binders. (a,b): PVA coated; (c,d): PU coated; (e,f): PE-coated fluorescent pigments.

The influence of binder content on the morphology of modified pigment was further analyzed in consideration of the uniformity of the PE coating. As seen from Figure 6, the surfaces of the fluorescent pigments are all covered with resin at all three ratios (1:2, 1:1, and 2:1), but with small different morphologies. The fluorescent pigments at the ratio of 1:2 are covered with a large amount of nano TiO_2 , and distinct clusters of particles can be observed in Figure 6a, d. The clusters decrease when polyester varnish to nano TiO_2 ratio increase to 1:1. Larger resin films and fewer clusters are observed when increasing binder addition to 2:1, which indicates most of the fluorescent pigment particles are well coated with the resin film containing nano TiO_2 . With the increase of binder addition, TiO_2 particles are more likely embedded in the continuous binder film instead of small clusters. From the enlarged view of the local particles, it can be seen that the outer layer of the film obviously contains a small number of nano TiO_2 particles, indicating that this experiment successfully coated the nano TiO_2 on the surface of the fluorescent pigment.

Figure 6. SEM results of pigments with different ratios of binder and nano TiO_2 . (a,b) 1:2; (c,d) 1:1; (e,f) 2:1.

Figure 7 shows TEM images of the modified pigments, which are uniform spherical particles with few clusters on the surfaces. In the enlarged TEM images (Figure 7e,f), nanosized particles can be observed, confirming that the TiO_2 particles can be well bound by PE coating. Fewer nanoparticles and smoother surfaces can be observed in Figure 7a,c,e at the binder-to- TiO_2 ratio of 2:1, which is in accordance with lower TiO_2 loading (Figure 2), and the smoother surfaces indicates the formation of a continuous resin film, which is beneficial to the uniform dispersion of nano TiO_2 particles. On the other hand, it can be seen from 7d,f that the pigment has more TiO_2 and less smooth structure at a higher binder-to- TiO_2 ratio of 1:2. The nanostructure of modified pigments is also consistent with the SEM results. The mapping results, in Figure 7e,f, both show the overall coverage of Ti on the pigment, which further proves that resin is a good binder for the adhesion of nanoparticles.

Figure 7. TEM and mapping results of pigments with different ratios of binder to nano TiO_2 . (a,c,e,g) 2:1; (b,d,f,h) 1:2.

3.1.4. Analysis of UV Absorption

Figure 8 shows the UV-Vis spectrum of the original pigment and modified fluorescent pigments. It can be seen that the original pigment and modified fluorescent pigments show the absorption of ultraviolet rays and have large absorbance at the 270 nm band in Figure 8. The absorbances of fluorescent pigments coated with different binders increase significantly compared with the original one and are in the order of PU, PE, and PVA. There are functional amine groups in the PU, so this may be because the compatibility of the PU and the amino resin in the pigment endows the maximum absorption of ultraviolet rays. The absence of the curing agent in PVA causes the loss of the titanium dioxide in the

preparation process, thus leading to the small UV absorption. The results are consistent with the ash test, which showed that pigment coated with PU contains more TiO_2 at the same binder-to- TiO_2 ratio.

Figure 8. UV-visible absorption results of pigments coated under different conditions: (a) different types of binders; (b) different ratios of polyester varnish to TiO_2 .

The effect of PE content on UV absorption was investigated. The ultraviolet absorption of the modified fluorescent pigment is similar when the ratios of the binder to the nano TiO_2 are 1:1 and 1:2, while the ultraviolet absorption of the pigment is significantly increased when the ratio increased to 2:1. From the SEM and TEM images, we can see at this higher binder ratio that PE forms a better film layer on the pigment surface and TiO_2 is expected to be dispersed more evenly when there are more resins in the fluorescent pigments. The results suggest UV absorption is not only affected by TiO_2 amount, but also by its state and dispersion.

From the characterization of modified pigments, we can see that, for different binder types, pigments with PU and PE coatings show higher TiO_2 content with higher TiO_2 XRD peaks, more film-like encapsulation, and also higher UV absorption ability compared to PVA. These results indicate binders that can form crosslinked film are beneficial to the binding of nano TiO_2 particles. PU of a higher similarity to pigment resin ensures a higher TiO_2 binding ability than PE, as seen from the ash test results. On the contrary, PE forms a better film on the pigment surface, and of the same type of resin as the coating resin; it may also lead to a better dispersion of pigment in the powder coatings and be beneficial to the coating anti-weathering performance. When investigating the different loadings of PE binder, we find that pigment with the lowest binder-to- TiO_2 ratio (1:2) has the highest TiO_2 content, and nano TiO_2 is bound to the pigment in both continuous film and clusters, while at the highest binder addition of 2:1, pigment has a lower TiO_2 content, but a better dispersion of TiO_2 in a resin film. This leads to a higher UV adsorption, which may be good for the coating weatherability.

3.2. Analysis of Fluorescent Powder Coating

3.2.1. Coating Surface Properties

Gloss is a surface property of the film, which depends on the specular reflection ability of the coating surface to light. In this experimental process, the gloss of the film at an angle of incidence of 60° is selected for data analysis. Distinctness of image (DOI) reflects the degree to the sharpness of the image, and to some extent, the degree of orange peel of the film.

According to the comparison of the gloss of different coating films at 60° , it can be seen in Figure 9 that the pigment wrapped by the binder (PE coat) has little effect on the gloss of the film, which is basically maintained at around 83. However, the fluorescent pigment wrapped by the binder (PVA and PU coat) has a greater impact on the film's gloss. Compared with the original pigment, the gloss of the coating is reduced by approximately 20. Therefore, from the perspective of the gloss of the film, the PE-coated fluorescent pigment has the least influence on the gloss compared to the original coating. Similar to gloss, it can be clearly observed that the DOI value of the film with the pigment coated by PE is around or higher than 50. This is even better than the original fluorescent powder coating, whose DOI is approximately 40. On the other hand, the DOI value of the film coated with PVA and PU decreased greatly. The better performance of the PE binder is due to the good compatibility with the base PE coating. Introducing the same material binder with the base coating not only binds the nano TiO_2 onto the pigment surface but also enhances the dispersion and compatibility of the pigment, leading to a better coating appearance.

Figure 9. Gloss and DOI results of fluorescent powder coatings.

The effect of UV-B irradiation on the coating surface was also examined, and the weathering test results are shown in Figure 10. After a long time of ultraviolet irradiation, the gloss and DOI of different powder coatings have almost been maintained at the starting level, with a slight fluctuation. The gloss and DOI values reflect the property of the coatings, which indicates that the base powder coatings are not affected by UV light irradiation within the investigating time.

Figure 10. Gloss and DOI results of fluorescent powder coatings: (a) gloss; (b) DOI.

3.2.2. Coating Surface UV Resistance Test

The effect of pigment modification was determined by UV accelerated aging test. Samples were taken at different time periods, and the surface color change of the film was measured and compared with the unirradiated UV film. The effect of binder type (PE coat, PU coat, PVA) on the nano TiO_2 coated fluorescent pigments was discussed. The time for the same color difference ΔE of the fluorescent powder coating after PE and PU coating is extended 4 to 6 times longer compared to the control sample, which indicates that the ultraviolet resistance of the modified fluorescent pigment is greatly improved. In particular, as seen from Figure 11, when the original coating is exposed to UV-B irradiation for 0.2 h, the color change of the coating film is 10, while the time extends to 1.2 h for the coating with the PU coated pigments to reach the same color change. Within the UV-B irradiation time of 0~2 h, coating with PU coated pigments is slightly higher than that with PE coated, and the PVA binder exhibits the least effect on enhancing UV resistance. When the exposure time increases to over 80 h, the fluorescent film coated with PE binders shows the highest UV inhibition ability. When the color change reaches 25, coating with PE bonded pigments requires 17.6 h, which is over 5 times as for the original coatings with unmodified pigment (3.4 h).

Figure 11. Changes in color difference of coatings affected by UV under different formulations: (a,c) samples coated with different resins; (b,d) samples coated with different resin loadings.

The effects of different binder to TiO_2 ratios (1:1, 1:2, and 2:1) on the UV-resistance of the pigments were determined by comparing the color change of the corresponding fluorescent powder coating. It can be seen from Figure 11 that within 0 to 2 h, as the time of UV irradiation continues to increase, the color difference of the film continues to increase. Compared with the original film, the modified fluorescent film has stronger UV resistance. When the color difference ΔE of the fluorescent film reaches 10, the UV-B irradiation time for original coating is 0.2 h, while the time is extended to 0.9 h when the PE binder to TiO_2

ratio is 1:2 or 2:1. The lower enhancement with the ratio of 1:1 may be due to the lower content of TiO_2 . With the continuous extension of the UV irradiation time to over 2 h, it can be observed that the color difference of the fluorescent film coated with the binder and titanium dioxide in the ratio of 2:1 and 1:1 is substantially the same. The fluorescent pigment with the ratio of binder to nano TiO_2 of 1:2 has the best weather resistance, with the exposure time (42.1) over twelve times longer than original coatings (3.4) at ΔE of 25. This may be due to the high content of nano TiO_2 bonded on the surface of the pigment surface.

4. Conclusions

This paper proposes a facile method to coat anti-ultraviolet material nano TiO_2 onto fluorescent pigments to enhance their UV resistance. The organic transparent resins of good adhesion ability and film forming properties were used as binders. Through the experiment, it was found that when the ratio of the binder PE to the nano TiO_2 is 1:2, the nano TiO_2 content of the fluorescent pigments was the highest. SEM morphologies show that all the fluorescent pigment particles are well coated with the resin and nano TiO_2 at different conditions. The UV absorption is all enhanced compared to the original pigment. By analyzing the gloss and DOI of the modified coating, it can be found that coatings with PE bonded pigments show the best surface performance. Moreover, when the ratio of the PE to the nano TiO_2 is 1:2, the UV exposure time of fluorescent powder coatings can be extended over twelve times compared to the coatings with original pigment for the same color change, which indicates that the UV resistance of the fluorescent pigments can be greatly improved through the organic binding method without scarifying the coating aesthetics. The method of resin-binding nanoparticles provides an effective and promising approach for the UV resistance improvement of fluorescent pigments. The compatibility and interaction between organic resin and pigment, as well as the bonding of nanoparticles, will be further investigated.

Author Contributions: Conceptualization, H.Z. (Haiping Zhang) and H.Z. (Hui Zhang); data curation, X.L.; formal analysis, Y.S.; funding acquisition, H.Z. (Hui Zhang); investigation, B.Y. and X.L.; methodology, B.Y., Y.S., H.Z. (Haiping Zhang), and H.Z. (Hui Zhang); project administration, Y.S. and J.Z.; supervision, H.Z. (Haiping Zhang), H.Z. (Hui Zhang), and J.Z.; validation, Y.S.; writing—original draft, B.Y.; writing—review and editing, X.L., H.Z. (Haiping Zhang), H.Z. (Hui Zhang), and J.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Natural Sciences and Engineering Research Council of Canada (NSERC), Discovery Grant RGPIN-2018-06256.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Hughes, J.F. *Electrostatic Powder Coating*; US Defense Technical Information Center: Fort Belvoir, VA, USA, 1984.
2. Huang, Q.; Zhang, H.; Zhu, J. Flow properties of fine powders in powder coating. *Particuology* **2010**, *8*, 19–27. [[CrossRef](#)]
3. Bailey, A.G. The science and technology of electrostatic powder spraying, transport and coating. *J. Electrosat.* **1998**, *45*, 85–120. [[CrossRef](#)]
4. Du, Z.; Wen, S.; Wang, J.; Yin, C.; Yu, D.; Luo, J. The review of powder coatings. *J. Mater. Sci. Chem. Eng.* **2016**, *4*, 54–59. [[CrossRef](#)]
5. Ring, J.; Cassidy, S.P.; Cordiner, A.G.; Morgan, A.R.; Handyside, T.M.; Sinclair-Day, J.D. Powder Coating Compositions. U.S. Patent 5856378A, 5 January 1999.
6. Gürses, A.; Açıkyıldız, M.; Güneş, K.; Gürses, M.S. Dyes and pigments: Their structure and properties. In *Dyes and Pigments*; Springer: Cham, Switzerland, 2016; pp. 13–29.
7. Zeng, W.; Zhou, Q.; Zhang, H.; Qi, X. One-coat epoxy coating development for the improvement of UV stability by DPP pigments. *Dye. Pigment.* **2018**, *151*, 157–164. [[CrossRef](#)]
8. Ibrahim, N.; Gouda, M.; Husseiny, S.M.; El-Gamal, A.; Mahrous, F. UV-protecting and antibacterial finishing of cotton knits. *J. Appl. Polym. Sci.* **2009**, *112*, 3589–3596. [[CrossRef](#)]

9. Abou Elmaaty, T.M.; Mandour, B.A. ZnO and TiO₂ nanoparticles as textile protecting agents against UV radiation: A review. *Asian J. Chem. Sci.* **2018**, *4*, 1–14. [[CrossRef](#)]
10. Reinert, G.; Fuso, F.; Hilfiker, R.; Schmidt, E. UV-protecting properties of textile fabrics and their improvement. *Text. Chem. Color.* **1997**, *29*, 12.
11. Pinnell, S.R.; Fairhurst, D.; Gillies, R.; Mitchnick, M.A.; Kollias, N.J.D.S. Microfine zinc oxide is a superior sunscreen ingredient to microfine titanium dioxide. *Dermatol. Surg.* **2000**, *26*, 309–314. [[CrossRef](#)] [[PubMed](#)]
12. Birch, J.; Burleigh, T. Oxides formed on titanium by polishing, etching, anodizing, or thermal oxidizing. *Corrosion* **2000**, *56*, 1233–1241. [[CrossRef](#)]
13. Xu, Z.; Li, K.; Hu, H.; Zhang, Q.; Cao, L.; Li, J.; Huang, J. From bulk to nano metal phthalocyanine by recrystallization with enhanced nucleation. *Dye. Pigment.* **2017**, *139*, 97–101. [[CrossRef](#)]
14. Li, M.; Liu, X.; Xu, Z.; Yeung, K.W.K.; Wu, S. Dopamine modified organic-inorganic hybrid coating for antimicrobial and osteogenesis. *ACS Appl. Mater. Inter.* **2016**, *49*, 33972–33981. [[CrossRef](#)] [[PubMed](#)]
15. Parazak, D.P. Ink-Jet Inks Comprising Pigment Precursors. U.S. Patent 6,102,996, 18 August 1999.
16. Bugnon, P. Surface treatment of pigments. Treatment with inorganic materials. *Prog. Org. Coat.* **1996**, *29*, 39–43. [[CrossRef](#)]
17. Yuan, J.; Zhou, S.; Gu, G.; Wu, L. Encapsulation of organic pigment particles with silica via sol-gel process. *J. Sol-Gel Sci. Technol.* **2005**, *36*, 265–274. [[CrossRef](#)]
18. Yuan, J.; Zhou, S.; Wu, L.; You, B. Organic pigment particles coated with titania via sol-gel process. *J. Phys. Chem. B* **2006**, *110*, 388–394. [[CrossRef](#)] [[PubMed](#)]
19. Yan, B. Preparation and the Improvement of Weather Resistance of New Fluorescent Powder Coatings. Master's Thesis, Tianjin University, Tianjin, China, 8 May 2020.
20. Hakeim, O.A.; Abdelghaffar, F.; Haroun, A.A. UV-curable hyperbranched polyester acrylate encapsulation of phthalocyanine pigments for high performance synthetic fabrics printing. *Dye. Pigment.* **2020**, *177*, 108307. [[CrossRef](#)]
21. Ibrahim, N.; Eid, B.; Abd El-Aziz, E.; Abou Elmaaty, T. Functionalization of linen/cotton pigment prints using inorganic nano structure materials. *Carbohydr. Polym.* **2013**, *97*, 537–545. [[CrossRef](#)] [[PubMed](#)]
22. Agbo, C.; Jakpa, W.; Sarkodie, B.; Boakye, A.; Fu, S. A review on the mechanism of pigment dispersion. *J. Dispers. Sci. Technol.* **2018**, *39*, 874–889. [[CrossRef](#)]
23. He, Y.; Zhang, J.; Cai, Y.; Yi, L. Encapsulation of organic pigment via a facile dispersion approach and soap-free miniemulsion polymerization. *Prog. Org. Coat.* **2021**, *159*, 106403. [[CrossRef](#)]
24. ASTM D5630–13; Standard Test Method for Gel Time of Thermosetting Coating Powder. ASTM International: West Conshohocken, PA, USA, 2013.
25. Wategaonkar, S.; Pawar, R.; Parale, V.; Nade, D.; Sargar, B.; Mane, R. Synthesis of rutile TiO₂ nanostructures by single step hydrothermal route and its characterization. *Mater. Today Proc.* **2020**, *23*, 444–451. [[CrossRef](#)]