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The progress of TiO_2 photocatalyst coating

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Abstract: *- TiO_2 photocatalyst coating is a kind of environmental friendly coatings. It has been widely applied to many fields, such as water treatment, cosmetics, ceramic, plastic, architecture etc.. The major mechanism of titanium dioxide photocatalyst coating is that photocatalyst absorbs light and then occurs a series of photocatalytic reactions. In this article, the synthesis method and application of photocatalytic coating were introduced, in order to provide references for other scholars. Concluding bactericidal (mildew-proof) coating, NOx degradation coating, formaldehyde and benzene degradation coating, self-cleaning coating and so on.*
Keywords: *- Photocatalyst; photocatalytic; TiO_2; paint; coating*

I. INTRODUCTION

Photocatalytic coating, as a kind of environmental friendly coatings, has been widely developed and applied in many fields, and fully displayed its value in domestic and abroad markets. In the "Chinese paint industry in the 12th Five Year Plan" promulgated at 2012, the average annual growth rate of total production value of paint industry were pointed out at 10%, and coating production is expected to reach 12 million tons in the 2015. The key and direction of the structural adjustment of coating industrial is encouraging the production of environment-friendly, resource-conserving coating; urging the production of TiO_2 which annual capacity more than 30,000 tons, as well as the content of TiO_2 is not less than 90%. After absorbing energy, photocatalyst can become a material with catalytic characteristics, and during this process, light is the catalyst. Although ZnO as the photocatalyst was documented as far back as 1930s, TiO_2 was the favorite material as photocatalyst since its characteristics was discovered by Japanese scholar To Aki. At present, the academic definition of photocatalyst is a semiconductor material made by TiO_2 [1]. Photocatalyst coating is an environmentally friendly coating which is combined by photocatalytic material and coating. It can eliminate harmful substances in the environment because of its photocatalytic activity. Now, photocatalytic coating such as bactericidal (mildew-proof) coating, formaldehyde degradation coating, self-cleaning coating and so on were widely used in many fields. The current researches are focused on the photocatalyst coating whit high light energy utilization rate, the ability of pollutant degradation and the weatherability of photocatalyst coating. In this paper, the application status of photocatalyst in various function coatings were introduced, and some advices about the development direction were proposed in order to make references to the research in this field.

II. MECHANISM OF PHOTOCATALYST

Two kinds of change of nanometer titanium dioxide occur after absorbing light surface: strong oxidation and super hydrophilicity.

2.1 STRONG OXIDATION

Photocatalysis reactions are activated by the absorption of photon, the absorption leads to a charge separation due to promotion of an electron (e^-) from the valence band of the semiconductor catalyst to the conduction band, and then a hole (h^+) in the valence band will be obtained. The recombination of the electron and the hole must be prevented as much as possible if a photocatalyzed reaction must be favored. Electrons whit negatively charged combines with oxygen to produce negative oxygen ion (O^{2-}), and holes whit positively charged are combined with water to produce hydroxyl radicals (·OH), they are both highly unstable substances. When organic matters contact with the photocatalyst surface, they will combine with the negative oxygen ions and hydroxyl radicals respectively, and reconfigured into carbon dioxide and water [2].

2.2 SUPER HYDROPHILICITY

After activated by the photon, the formed hole will diffuse to the surface and reaction with oxygen, then hydroxyl radical and chemical absorbing will formulate. Chemical adsorption water will continue adsorbing water, and this leads to the formation of many hydrophilic micro areas. The contact angle between titanium dioxide surfaces and water will be substantially reduced. When water is added to the titanium dioxide surface, it will not form a droplet, but a uniform film. Consequently, dirt or dust adsorbed on the surface could be removed only by water flushing. Water will soon be adsorbed by TiO_2 surface and penetrate to the below of pollutants due to the super hydrophilicity. In this way, contaminants could be removed [3].

III. THE CURRENT SITUATION OF PHOTOCATALYST'S APPLICATION IN COATING

Many kinds of nano photocatalyst coating have been reported, and some of them have realized industrialization. Function paint can be made by nanometer titania and ordinary paint through mixing method in order to apply into which has been polluted such as outdoor, indoor, surface of furniture, tunnel, parking and so on. Harmful gases and bacterial will be eliminate and inhibit by photocatalyst coating, so as to improve people's living environment.

3.1 PHOTOCATALYST BACTERICIDAL (MILDEW-PROOF) COATING

Nanometer titania not only can inhibit the reproduction of bacterial, but also can decompose the bacterial cells at the same time. A thorough research on the sterilization mechanism of photocatalyst coating were made ZhengHuang et al. They concluded that the cell wall will be wrecked first, and lead to the change of osmotic pressure, the intracellular structures will be destroyed subsequently, and make the bacteria's disintegration finally. William A•Jacoby et al have also proved this theory—organic matters in cells can be decomposed completely by photocatalyst. They also demonstrate the escherichia coli cell fractions were mineralized into CO_2 by (14) Carbon Isotope Tracer Method [4]. More and more researches on the application of photocatalyst in bactericidal (mildew-proof) coating were carried out in recent years.

Dai Wenxin [5] et al developed a TiO_2 sol coating with sterilization function. In his study, Zn^{2+}, Cu^{2+}, Ag^+ and I^- was introduced in the sol respectively. And the final study showed that Ag^+ can significantly improve the performance of TiO_2. So a Fungicidal Latex Coatings with good comprehensive properties were prepared by mingling Ag^+ into TiO_2 sol. And its sterilization rate can reach a maximum of 97%. He Tianshu [6] prepared Ce-TiO_2 photocatalyst by impregnation, and made Zn as the carrier to obtain the supported TiO_2 photocatalysts. Then add it to the coating. The antibacterial property was evaluated by inhibition zone method. Huang Anna [7] developed a kind of visible light response TiO_2 photocatalytic coatings. It is doped by iron. And the experimental results show that the coating has good photocatalytic antibacterial properties. Luo Junxuan [8] prepared a kind of nanometer Cu-TiO_2 antibacterial coating. And the results showed that the sterilization and weather resistance of this coating are perfect. The sterilization rate is more than 99.9% before aging, and still can reach more than 95% after aging.

L.Caballero [9] et al composited the titanium dioxide photocatalyst into acrylic paint and this coating can kill Escherichia coli. The first photocatalyst coatings brand in Japanese: ARC-FLASH has obtained the approval and support of public. The photocatalyst coating produced by ARC-FLASH can effectively sterilize mildew, deodorizing purification, and the sterilization rate as high as 99.99%.

In addition, antibacterial metal can be combined with potocatalyst, and it has been developed by some scholars. A new coating made by nanometer titanium dioxide particles and gold nanoparticles was prepared by Dai Wenxin [10] et al. It can sterilize under light condition because of the potocatalyst, and take advantage of the bactericidal function of gold nanoparticles at dark condition.

3.2 PHOTOCATALYST SEWAGE RESISTANCE COATING

Two characteristic are used in this type potocatalyst, strong oxidation and super hydrophilicity. The pollution on the surface can be degraded owing to the strong oxidation, and the dust is easy to be swilled out science the super hydrophilicity.

Shi Yuying [11] et al excogitated a self cleaning coating. Expect the two characteristic mentioned above, the characteristic that easy to pulverize was utilized, and the dust on the wall will be abscised together with TiO_2. Kuai Qin [12] prepared TiO_2/Al by liquid phase deposition, and then blended it in coating. The self-clean performance was evaluated in the end and oleic acid was as the pollution simulation. Zhang Anjie [13] made nanometer TiO_2/SiO_2 by sol gel method, and made transparent coating. This coating can be smeared on the glass, and make glass have the ability to tolerance pollution. Nowadays, stain resistance coatings has entered industrialized, for example, Beijing ShouChuang Company has successfully developed a stain self-cleaning coatings. This painting can be used on the surface of material or building, so as to achieve the effect of self-cleaning.

Kaishu Guan composited nanometer SiO_2 with nanometer TiO_2, and added the mixture into coating. The persistence of super hydrophilicity of paint film will be improved significantly because of nano silica, and the damage from light catalytic also can be reduced. Japan's Dai Nippon Toryo company developed an indoor water-based coating: Novoclean Bio. Photocatalyst is added in the resin, and the resistance was enhanced greatly.

3.3 PHOTOCATALYST HARMFUL DEGRADATION COATING

Photocatalyst has many specific advantages, such as non-toxic, non-corrosive, low preparation cost, and can react at room temperature. It can be stimulated not only by visible light, but also ultraviolet light. Carbon dioxide, water and inorganic salt were the products of photocatalysis reaction, and they are all non-

polluting. Therefore, the harm from NOx, formaldehyde, toluene and other pollutants in the air will be alleviated greatly if the photocatalyst was made full use of.

3.3.1 PHOTOCATALYTIC OXIDATION OF NOX FUNCTIONAL COATINGS

Nanometer TiO2 was made with sol-gel method by Li Yanwen [14] et al, and then mixed with the organic silicon resin to obtain photocatalysis coating. Consequently NOx degradation rate of this kind coating was up to 85%. Qiu, et al developed another photocatalysis coating which made NOx degradation rate up to 97% in the sunlight after 7 days. The photocatalysis coating will restore activity after it touched water. Guan Youjun [15] et al invented the TiO2 coating to paint inter wall of tunnels and underground parking in order to degrade the NOx of automobile exhaust. This TiO2 coating not only remove the automobile exhaust pollution, but also release the negative air ion to improve the air quality in the tunnel and underground parking. J.E.Maltby developed an organic binder containing nano-titanium dioxide particles, which will photocatalytic the NOx without pre-activation. J Siteladeng syntheses a NOx degradation coating with high weather-resistance and transparency.

3.3.2 THE FUNCTIONAL COATING OF PHOTOCATALYTIC OXIDATION OF FORMALDEHYDE AND BENZENE.

C.A'guia [16] et al invented a photocatalytic coating, and studied its properties factor. The TiO2 P25 is added in a high-quality vinyl coating, and made of the film, then the property of NOx degradation is tested. Cong burn mixture of the partical of PTFE acetic and titanium dioxide to calender it into sheet. the NOx and other waste gas in tunnel and park were removed by photocatalysis. European scientists developed an environmental coating which can effectively remove automobile exhaust, especially nitrogen oxides. The coating is applied in parking lot or building surfaces for cleaning air. The weather resistance of this coating was very good, and sustained five years.

Lin Jindong [17] based on the anatase TiO_2 to make the Fe-TiO_2 photocatalytic by metal ion doping, and this photocatalytic was added to potassium silicate inorganic coating to test the degradation properties of formaldehyde. The results showed that the coating in the fluorescent environment can effectively degrade formaldehyde. Zhao Yanli [18] coated a layer of photocatalyst in the conventional paint surface to form a photocatalytic coating, and the degradation rate of formaldehyde can be as high as 92.7% by the experiment. Cui Yaojun [19] et al mixed the modified nano-TiO_2 into the coating and made the experiment for the determination of formaldehyde degradation performance. The results showed that the formaldenhyde degradation of performance is high. Zhang Hao [20] et al invented the Cu doped nano TiO_2 particles by the sol-gel method and made it to be a coating film. From the experiments, it is found that the coating made the degradation rate of formaldehyde up to 99%. So the performance of formaldehyde degradation is excellent.

Zhao wen-chang [21] et al made a kind of photocataletic coating by using titanium dioxide. The determination of the degradation rate up to 90% through the experiment. STO •AG, Germany has successfully developed a photocatalyst coating, known as the Sto-cblor • clmason. The coating can be broken down into CO_2 and H2O under the visible light. So as to achieve the purpose of purifying the air. The U.S. patent described the preparation method of TiO_2 photocatalytic coating, and tested the ability of degrading toluene. Russian Yu.V.Kolen'ko et al. found the nano-TiO_2 particles with 75% of anatase, 25% of the rutile had a strong capacity for toluene degradation through the experiments. India M.Noorjahan et al. reported a new kind of photocatalyst TiO_2-HZSM-5, and tested on the degradation of phenol.

2.4 OTHER PHOTOCATALYST COATING

Japanese scientists found that TiO_2 has a strong reduction, so it was taken advantage of this feature to make rust-proof paint. TiO_2 and tungsten oxide or heteropoly acid are mixed together, and added to the coating. In the daytime, tungstic oxide and heteroacid could store electron energy, so, they can store the electron from TiO_2, and also release the electron in order to prevent the iron from rusting [22].

Coating binder polymer resin in the receipt of long-term ultraviolet radiation, the molecular chain is degraded; it has a serious impact on the physical properties of the coating. So it is enhanced the aging resistance of the film or coating by shielding ultraviolet rays in sunlight. Nano TiO_2 has both the function of the scattering ultraviolet and the function of absorbing ultraviolet [23]. So it is improved the weather resistance by adding titanium dioxide to paint or coating. For example, it is obviously improved the weather resistance of exterior paint by adding the nanometer material to the exterior paint, such as SiO_2, TiO_2 [24].

IV. PROSPECT

Now photocatalyst used in coating has become the focus of attention at home and abroad, it is a great achievement about coating industry development and the coating to a higher level of major power. Although many achievements obtained, but there are still some shortcomings and the insufficiency. For example, coating will cause shield to nanometer TiO_2, and affect the photocatalytic performance of the play of the titanium

dioxide. At the same time, when nanometer TiO_2 degrades contaminants on coating surface also makes the paint itself of the organic composition degraded or generated coating product will cause damage to itself and the human beings. We should establish the unity of the performance evaluation standard to make light catalyzing functional coatings applied to real life. Recently, Domestic of nanometer smooth accelerant coatings most is still in the laboratory level, we still need a lot of work to do about improving the coating performance, strengthen the theory and practical application of research is necessary to achieve industrialization. Therefore, we should do further study about nanometer coating and improve our coating industry level to promote the development and application of nanometer coatings.

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