Research status of photocatalysis and Thermal insulation building coatings

Teng Dong1,2,*, Yunfa Huang1,2, Xiaopeng Song1,2, Hongrui Lv1,2

1High performance special concrete key laboratory of Hunan Province, University of South China, Hengyang, China
2School of Civil Engineering, University of South China, Hengyang, China

*Corresponding author e-mail: uscdongt@163.com

Abstract: The research status of photocatalytic and thermal insulation coatings at home and abroad was summarized. The different types of photocatalytic coatings were summarized. The factors influencing the photocatalytic coatings, such as the activity of photocatalytic coatings, the load of photocatalytic coatings, and the dispersion process, were expounded. The type and property of insulation coatings and the effects of fillers on the properties of insulation coatings were summarized. At present, the primary problem of photocatalysis and heat preservation and heat insulation building coatings in China is lack of research and development of dispersants and composite materials. The evaluation system of photocatalysis, heat preservation and heat insulation need to be improved. It is of significance for the multi-functional coatings with the performance of luminescent catalytic insulation.

1. Introduction

With the improvement technology, the Building coatings can increase the aesthetics and has the function of heat insulation and photocatalysis. The multifunctional coating is a new type of coatings with many excellent functions, such as solar energy absorption, high-temperature resistance, the absorption and decomposition of toxic substances and heat preservation, etc. At present, the emission of automobiles has become a new topic of global environmental governance in recent years due to some environmental pollutants such as carbon monoxide, nitrogen oxide, and sulfide. They can have a very large greenhouse effect on the earth, destroy the ozone layer and result in acid rain, etc., the effect to the human health is also very large, so there are some reports about catalyzing the photolysis of automobile exhaust paint. Nowadays, "Energy conservation and emission reduction" is the general trend of today’s society. Thermal insulation coating can effectively reduce building energy consumption, and photocatalytic coating can effectively decompose automobile exhaust. This kind of building coating with both functions is significant to "Energy conservation and emission reduction". In this paper, the current researches on photocatalytic thermal insulation building coatings at home and abroad are reviewed and the existing problems are summarized.

2. The Research status of photocatalytic coatings

The Photocatalytic coatings can catalyze reactions in the presence of sunlight and other light rays of a particular kind of light wave. They absorb ultraviolet light to oxidize and decompose harmful substances. In addition to the above functions, photocatalytic coatings have antibacterial and organic degradation functions and even self-cleaning functions.
2.1 The types and properties of photocatalytic coatings

Researchers often divided according to the composition of the enzyme in light catalytic properties of the coating types, as in the early years have the properties of the material so far has rarely been civil because they are extremely unstable, and CdS and ZnO are representative of the two kinds of materials, that is, they will be at the same time of catalytic ion leaching poison, but a few areas still using them. At present, the nano TiO$_2$, WO$_3$, Fe$_2$O$_3$, SnO$_2$, the photocatalytic activity of ZnS is administered the main material, most of other material, most other materials photocatalytic activity for prone to corrosion and not appropriate for or single as the raw material of clean air, but nano TiO$_2$ because of no pollution, good catalytic performance, cost-effective, acid and alkali resistance, and is widely applied and attention, in the field of building photocatalytic coating is highly scientific significance.

2.1.1 Pure titanium dioxide photocatalyst. TiO$_2$ is a semiconductor material with three crystal structures, among which only two crystal structures have the photocatalytic effect, namely anatase and rutile[1]. Foreign researchers have proposed that adding an appropriate amount of TiO$_2$ particles which have been processed to the nanometer level into the paint used for building painting can make it absorb light and have a catalytic effect[2]. Zhang Wengang[3] proposed that the combination of TiO$_2$ photocatalytic coating agent and asphalt material has a good decomposition effect on automobile exhaust, so he also established a series of catalytic performance technical indicators and technical systems. Huang Anna[4] et al. found that adding TiO$_2$ into the coating could effectively flight bacteria through controlled tests, and provided the condition when the antibacterial rate reached the maximum, under which the antibacterial rate could reach 99.9%.

2.1.2 Doped metal titanium dioxide photocatalyst. TiO$_2$ is a kind of forbidden broadband material, which has low effective absorption of sunlight and can only absorb a small number of ultraviolet rays. In order to improve its photocatalytic efficiency, most people choose to dope some other substances to improve their utilization rate of light. Zhang Hao[5] et al. added Ce ion into the coating, and the analysis results showed that the size and shape structure of the photocatalytic particles were not significantly different from that of pure TiO$_2$. Under the excitation of sunlight, impurity-free TiO$_2$ had no obvious catalytic reaction on the substance, while the coating with Ce ion had a significant effect on the formaldehyde solution with toxicity, and its degradation efficiency was as high as 80.7%. Wang Haitao[6] added chromium ion to the photocatalytic coating for the experiment, and the photocatalytic efficiency measured under visible light source was 82.9%. Liu[7] added tin ions in the experiment, and the degradation efficiency was 76.94% after the 12th of light irradiation. Chen Changbing et al.[8] added lanthanum ion to paint to degrade formaldehyde. Under optimal conditions, the degradation efficiency was 71.2%. Bismuth ion can also improve titanium dioxide’s response to visible light, but part of it will be oxidized when formaldehyde is degraded in paint[9]. Wang Jiaheng[10] et al. compared the effects of single and co-doped metal substances on the catalytic efficiency of TiO$_2$, and found that the photocatalytic effect of multiple ions mixed was much better than that of a single ion added.

2.1.3 Composite titanium dioxide photocatalyst. In order to realize the goal of widely using photocatalyst TiO$_2$ in the industrial field, a new supporting TiO$_2$ composite material was used in building coatings, which was prepared by some researchers trying to use nano TiO$_2$ on the suitable TiO$_2$ on the material of appropriate carrier, and diatomite was the suitable TiO$_2$ carrier of this new material. Zheng Shuilin et al.[11] used the rate of color fading of rhodamine solution to indicate the degree of solution catalysis under light, they found that the degradation rate of the toxic solution with a new photocatalytic material prepared by TiO$_2$ diatomite was over 90%. The degradation rate was significantly higher in the same test environment than in the catalyst group alone. Qin Qian[12] found that titanium dioxide had stable catalytic activity and the degradation rate of formaldehyde reached the highest 93.3% after the composite reaction of titanium dioxide and tourmaline for 2h. Wang Xuming[13] repeated the use of catalyst TiO$_2$ mixed with diatomite for many times in the experiment and found that the catalytic effect of TiO$_2$ under light was mostly unchanged, and the catalytic degree of methylene blue solution reached over 95%. Cheng Yan[14] found that titanium dioxide and sulfur...
dioxide were made into a composite gel, which could improve the thermal stability of titanium dioxide while maintaining a high degradation rate, and the catalytic rate could reach 95% under the light. Liu Shiju\cite{15} compounded carbon nanotubes with TiO$_2$ to improve the dispersion of TiO$_2$, which solved the problems of poor dispersion of titanium dioxide, the small contact area with air, unsatisfactory photocatalytic effect, and increased the degradation efficiency of formaldehyde by 2% compared with pure titanium dioxide. Thus, it can be seen that this new type of composite catalytic material can increase its surface area in contact with the air, accelerate its dispersion rate, and thus enhance the catalysis, which is the main way to realize the industrial application of photocatalyst containing TiO$_2$.

2.2 The influence of the amount of photocatalyst added on the catalysis

The content of the catalyst in the coating is one of the factors of the degradation efficiency of the photocatalytic coating. It has been reported\cite{16} that with the constant increase of the amount of photocatalyst, the photocatalytic efficiency of the coating decreases after being significantly increased. When the amount of photocatalyst is 3%, the catalytic efficiency reaches the peak. This curve change is due to the excessive dose, which leads to the significant weakening of the catalytic effect. Cha Zhenlin et al.\cite{17} also obtained through comparative tests that the degradation efficiency of photocatalysts with different loads gradually decreased with the increase of concentration and time, and the photocatalysts with a load of 2.5% had a good catalytic effect on coatings. The experimental result of Sun Lulu et al.\cite{18} was also 2.5%. Through the controlled test, it was found that the degradation efficiency of the photocatalytic coating with the best load was 2.5 times higher than that without the addition of photocatalyst. Some experiments\cite{19} showed that the optimal degradation rate was the best when the load of titanium dioxide was 7%. Based on the above research, we can know that the content of photocatalyst should not be increased blindly, but the appropriate load should be selected.

2.3 Influence of catalyst dispersion on the photocatalytic performance of coatings

The dispersibility of the catalytic materials directly affects the catalytic performance of the coatings under sunlight. In the reaction system, the more dispersed the catalytic material is, the more the area in contact with the reactants can be increased, and the reaction rate will be faster. Therefore, it is important to select the catalytic materials with good dispersibility and suitable dispersing technology to improve its catalytic performance. The dispersion methods of catalysts are mainly electric, ultrasonic, and ball grinding. Wang Dongying\cite{20} showed in the experiment that OP-10 has good spatial barrier property, which can prevent the reunion of nano-molecules, thus increasing the chance of reactants and photocatalyst meeting in the reaction system, to improve its catalytic efficiency. Chen Xi\cite{21} showed in the experiment of dispersion mode that the high-speed shear agitation method could not eliminate the adsorption attraction between nanoparticles, and the ultrasonic oscillation law could cause emulsification, while the dispersion effect was very good when the two were combined. By comparing the influences of different dispersants on ceramic slurry, Liu Yunfei\cite{22} found that the thickening ratio of ionic dispersants in the sodium polyacrylate group was relatively small and the dispersing effect was poor. However, when several dispersants were mixed in a certain proportion, the effect was much better than that of dispersants alone.

2.4 Effects of temperature and humidity on the photocatalytic performance of coatings

As an external factor, the environmental temperature and humidity are less extensive than the above two factors, but the experiment shows that they have a certain influence on the photocatalytic efficiency. The research results of Cheng Jin et al.\cite{23} showed that with the increase of temperature, the molecular motion rate would increase, which greatly improved the chance of contact between photocatalyst and formaldehyde, so the degradation efficiency increased significantly. When the temperature reaches 25°C, the improvement curve of photocatalytic efficiency reaches a gentle level, proving that the improvement of temperature on efficiency is limited. In the change curve with humidity as the horizontal axis and formaldehyde solution degradation rate as the vertical axis, the graph fluctuates up and down with the increase of the X-axis value. The results show that when the X-axis value is 50%, the graph reaches the highest point. Also, Li Hong\cite{24} experiment show that
temperature rise will make the catalyst efficiency, but the catalytic efficiency and the relationship is not monotone increasing humidity, but the performance of the water molecules can stop the photocatalytic reaction, so the humidity 50% is the best, and money Fu Ping [25], etc. The test shows that this simple monotone increasing relation is established in a certain scope. Therefore, a good dispersion method can give play to the role of each nano-molecule as much as possible, to improve the efficiency of the photocatalytic reaction. In this respect, we are not involved deeply, and the dispersing method and dispersant with better effect still need further study.

3. Research status of thermal insulation coatings

Good insulation technology and coating applied to industry, construction industry, and other industries, can effectively achieve the purpose of energy conservation and emission reduction. In recent years, thermal insulation coatings with high thermal resistance, low thermal conductivity, and high thermal reflectivity have become a hot topic in the field of building materials research. This coating not only has a good cooling effect on the overall appearance and inside temperature, but also can alleviate the surface temperature of the floor and the house and reduce the radiation heat transfer and conduction heat transfer, and finally plays the role of heat insulation. Slurry thermal insulation material has a fixed type and dry type two, it is a kind of sepiolite, mineral fiber, silicate as the main material by composite and into light thermal insulation material.

3.1 The types and properties of thermal insulation coatings

3.1.1 Barrier type thermal insulation paint. Barrier type insulation coatings with low thermal conductivity and high thermal resistance have the advantages of low density and small and fine cavities, so it is not conducive to the external conduction and diffusion of indoor temperature [26]. This kind of material is a kind of paste flocculent thermal insulation coating that can be produced by using Stone decay, sepiolite, and perlite powder as the main raw materials and other additives through a specific technical process [27]. Yang Qi [28] et al. added 20% diatomite powder into the coating to make a thin layer barrier type of external thermal insulation coating. After testing, the temperature difference between the two sides of the board can reach 12℃. Ye [29] et al. modified LHPM with nano TiO2 (hollow polymer microspheres) to obtain TiO2/LHPM composite particles, which were mixed with building coatings, which made the whole system characterized by lightweight and high stability, and its thermal conductivity was 0.1687W/(m·K). Yang Xiaohong [30] et al. developed a coating with light film quality, good interior void, heat preservation, and heat resistance effect, and various performance indexes of this coating reached the corresponding production standards.

3.1.2 Reflective thermal insulation paint. By controlling the amount of base material, pigments, and fillers, reflective heat insulation coatings with high reflectivity can be prepared. This coating not only has the function of anti-corrosion and decoration but also has the function of heat insulation and cooling after the surface is reflected by sunlight. Wang shu [31] is put forward, such as by changing the houses and, etc in heating and heat flux on the surface of the floor to strengthen the effect of heat preservation and heat insulation, and both inside and outside the building and floor surface coated with insulation, thermal insulation coatings can achieve this effect, and also calculate the equivalent thermal resistance were 0.78 at this time (m2), K/W and 0.88 (m2), K/W, Lu Hongbin [32] et al. used titanium sulfate as the titanium source material and prepared a heat insulation coating with a specific technology, and found that the thermal reflection ratio of the coating was up to 97.76%. Zhang [33] et al. prepared a reflective thermal insulation coating and found that the content of TiO2 and insulating glass microbeads would affect the reflectivity of the coating. When the content of the two were respectively 12% and 6%, the reflectivity of the coating was as high as 90% and the thermal insulation temperature difference was 24℃. Xu Feng [34] found that transparent reflective and thermal insulation coating has high permeability and high reflection on the light area of sunlight, which makes the film formed by it weaken the heat transfer and exchange, thus achieving the effect of heat resistance and insulation. The experiments conducted by Sun Shunjie [35] et al. showed that compared with the housing durability, pollution resistance, and thermal insulation performance of painting general coatings, the reflective
thermal insulation coatings with different color series and different lightness points L* have better performance.

3.1.3 Radiant heat insulation paint. A kind of radiant heat insulation coating that actively reduces the surface temperature of the building floor and blocks the heat transfer has also been widely concerned and studied in the field of coatings. Li Jiantao[36] showed that the emissivity of ceramic infrared radiation powder was greater than 94%, and the rate of a kind of exterior wall energy-saving coating made of ceramic infrared radiation powder as a functional filler was greater than 78%. Shad[37] et al. used heat treatment to prepare SiB_{2} coating with a dense structure on the ZrO_{2} substrate. At room temperature, when the coating thickness was 0.3~2.5 μm, the emissivity could reach 90%. Feng Chunxia[38] et al. prepared a radiant heat insulation coating with a reflectivity up to 73.2%, which was made by Fe_{2}O_{3} and MnO_{2} as the main components and mixed with NiO, Co_{2}O_{2}, and CuO.

3.1.4 Other thermal insulation materials. Reflective, barrier, and radiant heat preservation and insulation coatings have different advantage, so, how to fuse the advantages of the above three heat preservation and insulation coatings on a coating is a new target for researchers. Cai Peng[39] et al. used the glass beads, ceramic microbeads, and reflective powder in the above three coatings as functional fillers to prepare an elastic coating with thermal resistance temperature difference, hemispheric emissivity, sunlight reflection ratio of 5.3℃, 0.88, 0.84 and reflectivity and insulation. Liu[40] et al. prepared a kind of thermal insulation coating for external walls within the range of 250~2500nm suitable for sunlight wavelength, with the solar reflection ratio, the hemispheric emissivity of 0.85 and 0.87 respectively, and the thermal insulation temperature difference of 13℃.

Experimental studies have shown that the high efficiency and high-temperature aluminum silicate fiber composite insulation material with a thickness of 8~10mm can achieve a significant cooling effect, from 800℃ to 200℃[41]. The United States has developed a water-based ultra-thin thermal insulation coating that can block 95%~98% of the external heat outside the matrix by brushing 0.33mm on the surface of the matrix. The thermal insulation effect of this material is similar to that of R20 grade foam insulation material with a thickness of 10cm[42]. Better thermal insulation coatings can be prepared by using acrylic resin or pure acrylic emulsion as the film-forming substrate and glass beads as the functional filler[43,44]. Tong Xiaomei[45] et al. prepared a paraffin/PMMA phase change heat storage microcapsule. Its phase change temperature, phase change latent heat, and heat storage density were 60℃, 64.2J/g, and 168.2J/g, respectively.

To sum up, heat preservation and heat insulation coating have become a hot spot in people's research due to its characteristics of heat insulation, high efficiency, convenient application, energy-saving and environmental protection, and good economic effect. By adding different functional fillers and using different film-forming materials and additives, the researchers have made the building coatings with various properties such as heat insulation and heat protection. The composite multi-functional coating with better performance can be developed by integrating the good performance of various heat preservation and heat insulation coatings. In the context of energy conservation and emission reduction, with the deepening of research, the development of composite multi-functional thermal insulation coatings has become a major direction.

3.2 Effect of functional fillers on the performance of thermal insulation coatings

Some researchers have conducted a series of studies on the important effects of functional coatings on thermal insulation. Through experimental research and analysis, Hu Jun[46] concluded that the amount of functional fillers, such as sepiolite, had a relatively large impact on the thermal conductivity of the coating, while the coating thickness and the size of the substrate particles had a relatively small impact on the coefficient, so the coating was conducive to use at different temperatures. Zhang Xiaozhen[47] pointed out that functional fillers have a great impact on the thermal insulation performance of such coatings, which are integrated with protective warmth and heat insulation, and their thermal insulation performance is mainly affected by "refractive index, thermal conductivity, and
particle size”. Peng Hong showed that 15% of the coating content was the best content of functional diatomite.

3.3 Effect of pigment filler on the performance of thermal insulation coatings

With the development and progress of The Times, the vast majority of buildings have moved towards the aesthetic color diversity types, and most of the current thermal reflection and thermal insulation coatings are light or white, so the study of color fillers to enrich the types of thermal reflection and thermal insulation coatings has important significance. Liu Lili pointed out that the pigment filler has a certain influence on the heat preservation and heat insulation of building coatings, and also pointed out that it plays a major role, and its optimal blending amount is within the range of 20wt%–30wt%. The test of Xiang Bo shows that the type, volume concentration, particle size, and other factors of fillers will have a certain effect on the thermal insulation performance of the coating. Among them, when the volume concentration of pigment packing > emulsion paint critical pigment packing volume concentration, the heat insulation effect increases with the increase of pigment packing volume concentration, on the contrary, when the volume concentration < critical concentration, the volume concentration has little effect on its heat insulation. Li Chanjuan showed that the heat resistance of thermal insulation coating was the best when 400 mesh pearlite mica powder (2%):150 mesh drift beads (12%) and 325 mesh infrared ceramic powder (4%) were mixed into the coating in sequence. Tian Jing developed a thermal insulation coating with a temperature difference of 14.9℃ through optimal design and introduced a new CICP pigment filler to obtain a more reflective coating.

To sum up, in addition to the aesthetic feeling of ordinary architectural coating, color thermal reflection coating has excellent thermal reflection performance and thermal insulation performance. Moreover, it is an efficient method to optimize the thermal insulation performance of the coating by adjusting the content of film-forming substances, functional fillers, and additives.

4. Problems existing in photocatalytic heat preservation and heat insulation coatings

At present, there are many kinds of photocatalytic heat preservation and insulation materials that have been researched and developed, but the properties of these materials differ greatly. Besides, compared with foreign countries, China's photocatalytic heat preservation materials start late, so there is still a lot of confusion in the study of this material, which needs to be further discussed.

4.1 Dispersion process to be improved

The catalytic effect can be effectively enhanced by increasing the area of the reaction, and the catalytic effect can be even enhanced by using some dispersants and photocatalysts together. Zhang Jie showed that the four dispersants were added to the composite TiO2/SnO2 photocatalyst respectively, and it was found that the surface of SnO2 with acetone dispersant was smoother and not easy to aggregate, thus increasing the specific surface area and increasing the catalytic rate of the composite TiO2/SnO2 photocatalyst. At the same time, for today's rapidly developing nano thermal insulation coatings, the dispersion of nano pigment fillers will directly affect the coating performance. However, due to the limitations of current technologies, the dispersion of dispersants and storage stability still needs to be further studied, and there is still a long way to go for their wide application in the industrial field.

4.2 Insufficient research and development of composite photocatalyst materials

At the same time, composite photocatalyst materials with the properties of photocatalysis, heat preservation, and heat insulation have become the research trend of today's researchers, but there are not many reports about multifunctional composite photocatalyst materials. Many factors such as film-forming material and filler restrict the development of this new material. For coatings with photocatalytic function, the adsorption of substances on the surface of the catalyst and the consumption of hydroxyl radicals may lead to the inactivation of the catalyst and the loss of the coating function. Although the use of pickling and water washing can make the photocatalytic coating to restore the approximate activity, and timing to restore its activity in large-scale construction
projects will not only slow down the progress of the project but also will waste a lot of money, so it is not appropriate to use. Besides, there is no clear research on increasing the photocatalytic activity in China, which brings some difficulties to the popularization of photocatalytic coatings. Because all aspects of the research are not mature enough, to realize the industrialization of photocatalyst coatings, we need to solve the problem as soon as possible, improve all aspects of performance, focus on the development of composite photocatalyst materials.

4.3 Evaluation standards of photocatalytic heat preservation and insulation coatings need to be improved

"Energy conservation and emission reduction" and "green environmental protection" have become the hot topics of the current era, so most of the traditional photocatalytic thermal insulation coatings in the construction process of solvent volatilization and pollution of the environment and harm to the public health problems need to be solved urgently. Up to now, there are no relevant standards for evaluating the performance of photocatalytic coatings and thermal insulation coatings in China, and the performance characterization indexes are not strict enough. Therefore, a lot of work is still needed to improve and improve the basic performance of coatings.

5. Conclusion and prospect

The current researches on building coatings with catalytic effect under light mainly focus on the activity of photocatalysts, the quantity of additions, and the process of the increasing reaction area, while the types, properties, and fillers of coatings are the main research elements of building coatings with mild and thermal insulation effect. In the new era of "Energy conservation and emission reduction" and "Green environmental protection", new composite thermal insulation coatings have become a new research direction for scholars. At present, the main problems of photocatalysis and thermal insulation building coatings in China are the lack of research and development of dispersants and composite photocatalyst materials and the improvement of the evaluation system of photocatalysis and thermal insulation.

China's urban construction volume is increasing year by year, but most of the current external wall insulation performance of the building is poor, building energy consumption is high, so energy-saving renovation is important. Additionally, people mostly choose to use oil and diesel vehicles in the daily travel, most of the gas released by such vehicles will worsen the environment and harm the human body. The exterior surface of the building has been in contact with air for a long time. If the exterior wall is endowed with a certain performance, it can not only purify the air but also have thermal insulation performance, which will effectively solve the above problems. Based on this, the research and development of a building coating that can purify the air through photocatalysis and has the characteristic of heat preservation are of great significance for "Energy conservation and emission reduction".

6. Acknowledgments

The authors gratefully acknowledge the Chinese National Students’ Platform for Innovation and Entrepreneurship Training Program (Grant No. 201810555001, 201910555059) and the Natural Science Foundation of Hunan Province, China (Grant No. 2020JJ6053)

References:
[1] Tang Y C, Li W, Hu C, et al. Studies on Morphological Structure and Photoactivity of TiO2 Heterogeneous Photocatalysts[J], Chemical Progress. 15 (2003) 05 379-384.
[2] Nakatani H, Motokucho S, Miyazaki K, Difference in polystyrene o xo -biodegradation behavior between copper phthalocyanine modified TiO2 and ZnO paint photocatalyst systems[J], Polymer Degradation and Stability. 120 (2015) 1-9.
[3] Zhang W G, Study on TiO2 Catalytic Decomposition of Asphalt Pavement Materials from Automobile Exhaust[D], Xi’an: Chang'an University. 2014.
[4] Huang A N, Su H J, Study on antibacterial property of nano-titanium dioxide photocatalytic
coating under visible-light irradiation[J], Journal of Environmental Engineering. 5 (2011) 02 477-480.

[5] Zhang H, Huang K, Huang X J, Study on Degradation Effect of Ce-TiO2 Photocatalyst Coating on Formaldehyde Solution and Its Prediction Model[J], Rare Earth. 35 (2014) 04 18-24.

[6] Wang H T, Degradation effect of Ce-TiO2 photocatalytic coating on indoor formaldehyde gas and accuracy of prediction model[J], Materials Protection. 46 (2016) 05 17-19+2.

[7] Liu H, Research on tin doped Nano TiO2 functional Coatings [D], Zhengzhou: Henan University of Technology. 2010.

[8] Chen C B, Chen Y, Liu X W, et al. Preparation and Formaldehyde Degradation Performance of La-TiO2-Based Photocatalytic Coatings[J], Paint Industry. 46 (2016) 05 24-27+32.

[9] Wang D, Zeng P L, Visible Photocatalytic Degradation of Formaldehyde by Bi-doped TiO2 in Water-borne Coatings[J]. Guangzhou Chemical Industry, 46 (2018) 07 51-53+59.

[10] Wang J H, Gong C W, Fu X K, et al. Research progress on modification and application of TiO2 photocatalyst[J], Chemical New Materials. 44 (2016) 01 15-18.

[11] Zheng S l, Wang X B, Sun Z M, Performance Characteristics and Application of Nano-TiO2/Diatomite Composite Photo-catalytic Material[J], China Coatings. 30 (2015) 07 63-66+76.

[12] Qin Q, Preparation of TiO2 / tourmaline composite photocatalyst and its photocatalytic performance study[D], Wuhan: Wuhan university of technology. 2013.

[13] Wang X M, Mechanical force chemical preparation of nanometer TiO2 / diatomite composites and photocatalytic performance study[D], Beijing: China University of Geosciences. 2012.

[14] Cheng Y, Using fly ash to mention aluninate slag SiO2 aerogel preparation and TiO2 / SiO2 composite photocatalytic materials[D], Changchun: Jilin University. 2017.

[15] Liu S J, Preparation and characterization of titanium dioxide/carbon nanotubes composite photocatalyst[D], Shenyang: Shenyang Institute of Aeronautical Technology. 2009.

[16] Zhao M, Study on Monitoring and Effect Evaluation of NOx Degradation by TiO2 on Asphalt Pavement[D], Harbin: Northeast Forestry University. 2013.

[17] Cha Z L, Xu S H, Fang J M, et al. Factors Influencing the Photocatalytic Effect of Paint[J], Coatings Industry. 50 (2008) 03 9-12.

[18] Sun L L, Preparation and Properties of photocatalytic coatings[D], Daqing: Northeast Petroleum University. 2013.

[19] Xu S H, Study on photocatalytic active building coatings[D], Wuhan: Wuhan University of Technology. 2006.

[20] Wang D Y, TiO2 and ZSM - 5 / TiO2 composite catalyst preparation and physicochemical properties of research[D], Qinhuangdao: Yanshan University. 2016.

[21] Chen X, Nano TiO2 of asphalt concrete road use performance and performance of automobile tail gas degradation research[D], Changsha: Central South University. 2014.

[22] Liu Y F, Architectural ceramics with the preparation of compound dispersants and performance study[D], Tianjin: Tianjin University. 2012.

[23] Cheng J, Li Z W, Li Q, et al. Preparation of Nano-TiO2 Photocatalytic Coatings and Its Function of Formaldehyde Degradation[J], Paint Industry. 44 (2014) 11 41-45.

[24] Li H, Preparation of TiO2 photocatalytic coatings and its degradation of formaldehyde[D], Beijing: Beijing University of Chemical Technology. 2009.

[25] Qian F P, Zhang H, Preparation of Cu-TiO2 Photocatalytic Coatings and Its Effect on Formaldehyde Degradation[J], Paint Industry. 41 (2011) 05 46-48+56.

[26] Luo L, Wang S, Wang J, et al. Research progress of architectural coating for thermal insulation[J], Chemical New Materials. 45 (2017) 11 33-36.

[27] Wang S P, Research and Development of Thermal Insulating Coatings for Building[J], Shanghai Coatings. 44 (2005) 03 13-15.

[28] Yang Q, Peng H. Functional Material Choosing and Content Optimization of Thin Layer Heat-insulating Thermal Insulation Coating[J], Coal Technology. 32 (2013) 11 163-164.

[29] Ye , Wen X F , Lan J L , et al. Surface modification of light hollow polymer microspheres and its
application in external wall thermal insulation coatings[J], Pigment & Resin Technology. 45 (2016) 1 45-51.

[30] Yang X H, Study on the hollow glass-bead coating with heat-preservation[J], Journal of Wuhan Institute of Technology. 22 (2003) 02 75-76.

[31] Wang S, Wang J, Tang X P, et al. A Research on Insulation Effect of Thermal Insulation Coating[J], China Construction Science and Technology. 17 (2018) 16 105-109.

[32] Lu H B, Feng C X, Li W D, et al. Preparation and characterization of heat-insulted coatings containing TiO₂ modified hollow glass beads[J], Chemical New Materials. 38 (2010) 08 81-83+96.

[33] Zhang Z T, Wang K T, Mo B H, et al. Preparation and characterization of a reflective and heat insulation coating based on geopolymers[J], Energy and Buildings. 87 (2015) 11 220-225.

[34] Xu F, The Application and Development of Architectural Reflective Thermal Insulation Coatings in China[J], Shanghai Coatings. 55 (2017) 05 25-29.

[35] Sun S J, Yang W Y, Feng X J, et al. Preparation and Performance of Color Solar Reflective Thermal Insulation Coatings[J], Paint Industry. 43 (2013) 04 17-22.

[36] Li J T, Cai H W, Development and Characteristics of Energy Saving High Emissivity Infrared Radiation Coatings for Exterior Wall[J], Paint Industry. 42 (2012) 02 39-43.

[37] Shao G F, Wu X D, Kong Y, et al. Microstructure, radiative property and thermal shock behavior of Ta₂Si₂-SiO₂-borosilicate glass coating for fibrous ZrO₂ ceramic insulation[J], Journal of Alloys and Compounds. 663 (2016) 10 360-370.

[38] Feng C X, Chen Jianhua, Hu Xu, et al. Study on Radiation Heat-insulated Paint [J], Journal of Changshu Institute of Technology. 20 (2007) 04 75-79.

[39] Cai P, Ying X D, Wan C L, et al. Preparation and Performance Research of Reflective Insulation Architectural Coatings[J], Paint Technology and Abstract. 33 (2012) 07 14-16+42.

[40] Liu L, Yue Y, Cao J X, Study of xonotlite architectural coatings for exterior wall insulation mechanism[J], Materials Science Forum. 890-810 (2014) 12 672-675.

[41] Zhang N, Zhang Y J, The Study of the Thermal Insulations Made of the Alumina-silica Fiber[J], Ceramics. 36 (2009) 05 48-52.

[42] Zhao J B, Development focus of world coatings and development process of water-based thermal insulation and moisturizing coatings[J], Shanghai Coatings. 46 (2007) 03 45-46.

[43] Yu X, Xu C H, Influence of High-Performance Hollow Glass Microsphere on Thermal Insulation of Coatings[J], Coatings Industry. 44 (2014) 04 1-5.

[44] Pan Q Z, Wei J H, Cheng W, et al. Development of Nanocomposite Thermal Insulation Exterior Coating[J], Modern Coatings and Fittings. 20 (2017) 04 27-28+41.

[45] Tong X M, Yan Z Y, Han Y, Study on the preparation and the properties of P(MMA-co-AA)/paraffin phase change thermal storage microcapsules modified by graphite and nano-SiO₂[J], New Building Materials. 42 (2015) 11 58-61.

[46] Hu J, Study on a new silicate thermal insulation coating[D], Xi'an: Northwest University. 2008.

[47] Zhang X Z, Preparation and Properties of Water-based thermal insulation coatings[D], Dalian: Dalian Maritime University.2011.

[48] Peng H, Preparation and performance of high efficiency exterior wall insulation coatings[D], Chongqing: Chongqing University.2009.

[49] Liu L L, Characteristics of Fillers and their influence on the performance of heat-insulating coatings[D], Wuhan: Wuhan University of Science and Technology.2015.

[50] Xiang B, Study on environmental protection Water-based Building Thermal insulation Coatings[D], Guangzhou: South China University of Technology.2012.

[51] Li C J, Characteristics of functional fillers and their influence on the performance of building insulation coatings[D], Chongqing: Chongqing University.2009.

[52] Tian Jing, Preparation and properties of polychromatic heat-reflecting thermal insulation coatings[D], Shenyang: Shenyang Jianzhu University. 2012.

[53] Zhang J, Preparation and characterization of nano-SnO₂ and composite TiO₂/SnO₂ photocatalysts[D], Hangzhou: Zhejiang University of Technology. 2012.

[54] Li C Z, Liu X G, Nano-ATO Particles Dispersed Technology in the Preparation of Water-based Transparent and Heat Insulating Coatings[J], Surface Technology. 42 (2013) 04 119-121.

[55] Xiao J, Fan H T, Zhou H D, Effect of Dispersing Technique of Fillers and Paints on the Properties
of Epoxy Thermo-protective Coating[J], Surface Technology. 43 (2013) 02 150-155.

[56] Yang X Y, Preparation of nano-TiO2 photocatalyst supported on glass fiber cloth and study on its photocatalytic performance[D], Hefei: Hefei University of Technology.2007.