Research Progress and Application Status of Thermal Insulation Coatings

Yue Pan\textsuperscript{1,a}

\textsuperscript{1} Department of Chemistry and Material, Naval University of Engineering, 430000, Wuhan, HuBei Province, China

\textsuperscript{a}Corresponding author: Yue Pan 379368571@qq.com

Abstract. In this paper, the thermal insulation mechanism of thermal insulation coatings was outlined. The research progress of barrier, reflective, radiant and composite thermal insulation coatings was introduced at home and abroad. And the future research direction of thermal insulation coatings was prospected.

1. Introduction

In recent years, with the rapid development of modern industry, the number of energy consumption is staggering, and the problem of lack of energy has become increasingly prominent. Energy conservation and consumption reduction have gradually attracted everyone's attention, so energy-saving and consumption-reducing materials with excellent performance have become a research hotspot.

Now, the use of thermal insulation coatings is an effective way to save energy and reduce consumption. Thermal insulation coatings improve the working environment and save energy by reducing the heat accumulation inside the coated objects. They are widely used in exterior walls, vehicle housings, tank housings and aerospace\cite{1}. Because of its high economy, convenient construction and good heat insulation effect, it is gradually favored by people and has broad development prospects. This paper reviews the main types of thermal insulation coatings at this stage and their development, briefly introduces the mechanism of thermal insulation, and forecasts the development trend of new thermal insulation coatings in view of the existing problems of thermal insulation coatings.

2. Thermal insulation coating

Coating is a type of liquid or solid material that is applied to the surface of an object to form a film under certain conditions to provide protection, decoration or other functions\cite{2}. It is usually composed of film-forming substances, pigments, fillers, additives and solvents. Thermal insulation coating is one of the functional coatings, which has the functions of thermal insulation and heat preservation.

Where there is a temperature difference in nature, there is spontaneous transmission of heat. According to the heat transfer mechanism, there are three heat transfer modes: heat conduction, heat convection, and heat radiation\cite{3}. According to the above three heat transfer mechanisms, the thermal insulation coatings can be classified in three ways: the barrier, the reflective and the radiation\cite{4}. These three coatings with different thermal insulation mechanisms have different applications and thermal insulation effects.
2.1 The barrier thermal insulation coating

The barrier thermal insulation coating refers to a coating that achieves passive cooling by blocking heat transfer[5]. Usually, film-forming substances with a low thermal conductivity (λ) are selected or functional fillers with a low λ are added to the matrix to reduce the heat conduction of the coating in order to achieve the purpose of heat insulation, so that the λ of each component in the coating is critical to the thermal insulation performance.

In the 1980s, the development and application of barrier thermal insulation coatings began in China. At that time, inorganic silicate materials represented by natural mineral fiber materials were used as main raw materials, and mixed with fillers, binders, additives to form silicate composite heat insulation materials[6]. It is mainly used in equipment with high working temperature, such as vehicle engines and casting molds. However, due to its some disadvantages like long drying time, large shrinkage, and poor shock resistance, its practical applications have been limited[7]. In the 1990s, based on the original research results, scholars developed new thermal insulation materials based on organic materials such as synthetic resin emulsions, and tried to use organic substances as fillers. Wu[8] tried to use waste polystyrene particles as insulation fillers, which not only reduced the cost of the product, but also improved the thermal insulation properties of the coating.

With the development of production technology, some functional fillers with better thermal insulation performance have appeared since the 21st century, such as hollow glass microspheres (HGB), expanded perlite, etc. Since the λ of air is only 0.023 W/(m∙K)[9], which is much lower than that of other solids, hollow materials that introduce a non-convective air to provide a heat insulating effect are currently attracting attention. Wang[10] added the hydrophobic modified perlites to the polyvinyl alcohol resin. The results showed that the incorporation of perlite significantly reduced the thermal conductivity of the matrix. It was also determined that when the blending amount was 90wt.%, the thermal conductivity of the polyvinyl alcohol composite material reached the lowest value of 0.043W/(m∙K). Shinkareva[11] incorporated nickel-plated HGB into polyacrylic acid at 30wt.%. The λ of resulting coating was reduced from 0.48 W/(m∙K) to 0.12 W/(m∙K), which had good thermal insulation properties and lower surface resistivity. Zhang[12] prepared the paint by mixing powder coal ash glass beads into silicone-acrylic emulsion and styrene-acrylic emulsion, and applied it to the steel plate for exposure experiment. The results showed that the backside equilibrium temperature of the paint test plate with the addition amount of 40 wt.% of the beads was reduced by 8 °C compared with the blank test plate without microbeads in the coating. Xing[13] added HGB to the pure acrylic emulsion to obtain the thermal insulation coating. The backside equilibrium temperature of the paint test plate with HGB was reduced by 15 °C compared with the blank test plate without HGB in the coating. Yu[14] compared the thermal insulation performance of HGB, barite powder, silicon micropowder, mica powder and diatomite. The results showed that the HGB insulation effect was better than the other four fillers. At the same time, the smaller the density, the larger the particle size, the better the HGB thermal insulation performance. Because the larger the particle size, the more air was contained, and the stronger the heat insulation capacity of the continuous cavity structure was.

Barrier thermal insulation coatings are generally available in raw materials, low in cost, simple in preparation process and equipment, and can be applied to elbows, spherical devices and the like. It is mainly used in industrial heat insulation fields such as high temperature boilers and pipelines. However, due to the introduction of a large amount of air, there are usually many pores inside the coating, and the structure is loose, resulting in a high water absorption rate. The λ of water is much higher than that of air. Once it absorbs water, the thermal insulation capacity of the coating is significantly reduced. Therefore, it is necessary to provide a waterproof layer and an outer protective layer outside the thermal barrier coating, which increases the difficulty of construction. In addition, due to the thick coating, the drying cycle is long and susceptible to external weather. At the same time, there are also shortcomings such as low impact strength and large drying shrinkage[15].
2.2 The reflective thermal insulation coating

The reflective thermal insulation coating, also known as solar thermal reflective coating, is developed on the basis of aluminum-based reflective coatings. Originally designed for military and aerospace applications, it was widely used in the petroleum and petrochemical industry due to its significant reduction in solar radiation[16].

When sunlight is incident on the surface of the object, it will reflect, transmit and absorb. Since the coating is usually opaque, no transmission occurs. The reflective heat-insulating coating reduces the absorption of sunlight by the coated object by reflecting visible light and infrared light, and achieves the purpose of heat insulation and cooling[17]. The solar radiant energy is mainly concentrated in the visible light region and the near-infrared light region, that is, in the wavelength range of 400 to 1800 nm, accounting for more than 95% of the total solar energy[18]. The higher the reflectivity of the coating in this range, the better the thermal insulation effect. Therefore, the high reflectivity of the resin and pigment in this band become the key to determining the thermal insulation effect of the coating.

As early as the 1950s, foreign researchers have successfully developed reflective insulation coatings and industrialized production. Ogawa[19] made a ceramic filler with titanium dioxide, zinc oxide, magnesium oxide and other raw materials. Its particle size was below 1μm, which had the characteristics of low thermal conductivity and high reflectivity. It could be mixed with topcoat resin with good heat dissipation to produce a smooth surface reflective coating. Doulos[20] prepared zirconia ceramic beads coated with potassium silicate on the surface. It had a high light reflectivity and a higher short wave reflectance than long wave. At the same time, it was also found that the thinner the thickness of the coating layer, the smaller the particle diameter of the ceramic microbead, the higher the reflectance to light, the better the heat insulation effect. Neil[21] used a dibutyl maleate-vinyl acetate copolymer as film-forming substance, and adopted the method of adding Ceramic Sil32 pearlescent heat insulator to obtain a water-based paint with good heat insulation performance. It is both heat-insulated and environmentally friendly. Naofusa[22] used a variety of pigments to create various reflective heat-insulating coatings that broke the limitation of traditional reflective insulating coatings that used only light-colored coatings.

In recent years, domestic researchers have also done a lot of research work on resin modification of reflective insulation coatings and selection and proportioning of pigments and fillers.

The rutile titanium dioxide has a refractive index of 2.8, and has a reflectivity of 80% for ultraviolet, visible, and near-infrared light regions, and has good hiding power and reflective heat insulation ability[23]. Zhang[24] incorporated rutile titanium dioxide into acrylic resin to produce a reflective thermal insulation coating. The results of the exposure test showed that the equilibrium temperature on the back of the coated test plate decreased by 12.2 °C compared with the blank test plate, and the front balance temperature decreased by 13 °C. Chen[25] investigated the effect of particle size distribution and size of TiO\textsubscript{2} on the thermal insulation properties of coatings. The experimental results showed that the larger the refractive index of TiO\textsubscript{2}, the more uniform the particle size and the higher the reflectivity of the coating. At the same time, the TiO\textsubscript{2} content had an optimum value of 30 wt.%. Yu[26] used fluorocarbon resin and acrylic resin as the base material, and rutile TiO\textsubscript{2}, silica and ceramic hollow microspheres as reflective functional fillers to prepare thermosetting reflective thermal insulation coatings. Compared with the blank template, the inner side of the sample coated with the reflective thermal insulation coating had a lower equilibrium temperature of 9.5°C, and the thermal insulation performance was good. Ma[27] hydrolyzed TiCl\textsubscript{4} on the surface of HGB to form a functional filler with high reflectivity, and made a reflective heat-insulating coating based on polyacrylate emulsion. The dry coating thickness was 0.3–0.8mm, and the total reflectance to sunlight was over 90%.

In order to meet the needs of the use of glass windows, transparent heat-insulating coatings have been developed to ensure the glass lighting while ensuring the heat insulation effect. Takeda[28] incorporated nanoparticles such as ATO, ITO and LaB\textsubscript{6} into a resin matrix to produce a transparent heat-insulating coating. Transparent insulation function was achieved by using three materials to
selectively block different wavelengths light. Li[29] combined nano-ATO and nano-TiO₂ modified by silane coupling agent into waterborne polyurethane to produce transparent heat-insulating coating, which had good reflective property for infrared light regions and high permeability for visible light regions. The thermal insulation temperature difference of the coating film under the illumination of infrared light was up to 6.23 °C.

Reflective thermal insulation coatings have higher reflectivity and better reflective heat insulation performance than barrier thermal insulation coatings. However, due to the thin coating of the actual construction, the insulation effect is not obvious when used alone, so it needs to be used together with the external insulation system, which increases the construction cost. In addition, the nanofillers are mostly inorganic materials, and there are problems of poor dispersibility and stability. At the same time, the problems of poor weather resistance and easy foaming of the coating also limit its wide application[30].

2.3 The radiant thermal insulation coating
The radiant thermal insulation coating emits solar energy absorbed by objects into the atmosphere at a certain wavelength by means of heat radiation to achieve the purpose of heat insulation and cooling, and it is an active heat-insulating and cooling coating[31]. Since the water vapor and CO₂ in the atmosphere are very weak in light absorption in the 8~13.5 μm wavelength region, the atmosphere has a high transmittance for infrared radiation in this band. This band is also called the "atmospheric window”[32]. Therefore, in order for the radiant heat-insulating coating to have a higher emissivity in this band, fillers having a peak absorption value in the band should be incorporated, thereby converting the absorbed solar energy into heat energy, and directly radiating to the absolute zero zone of outer layer of atmosphere through the window by infrared radiation[33]. Li[34] doped Fe₂O₃, MnO₂, CuO, Co₂O₃ and cordierite, and obtained ceramic infrared radiation powder by high temperature solid phase sintering. The result of XRD showed that it was an inverse spinel phase with high infrared activity. And at 26 ℃, the radiance in the 8 ~ 13.5 μm band was greater than 94%. The infrared powder was mixed into a fluorocarbon emulsion to prepare a radiant heat insulating coating, and the radiance was greater than 74% in the atmospheric window band. Wo[35] removed iron and metal scraps, mineral raw materials and oxide raw materials from iron and impurities, and mixed them with Al₂O₃, TiO₂ and mica powder after high temperature sintering to obtain infrared emission powder. And it was mixed with acrylic resin to produce radiant heat-insulating coating. The test showed that its full emissivity (5~15μm) is more than 85%, and other indicators met the requirements of GB/T 4653-1984. Xu[36] prepared Fe₂O₃-MnO₂-Co₃O₄-CuO transition metal oxide ceramics by solid phase sintering, and its infrared radiance reached 0.93. It was also determined that the formation of inverse spinel and mixed spinel structure was the intrinsic cause of high infrared radiant of ceramics, and the sintering temperature had no effect on infrared radiance. In addition, some foreign companies have also introduced high-infrared radiation coating products, such as Envelt CC-100 coatings in the United States, the thermal conductivity is only 0.11 W/(m·K), the emissivity is 0.88, and does not contain VOC; British CRC company launched ET-4 infrared radiation coating and Japan's HRC infrared radiation coating.

Compared with the first two kinds of thermal insulation coatings, the radiant thermal insulation coating can actively radiate the heat absorbed by the coating in the form of heat radiation to achieve the purpose of cooling. However, due to the complicated selection and sintering process of infrared radiation powder raw materials, the cost is high, and the product emissivity cannot be well controlled, so the preparation technology needs further research and optimization.

2.4 The composite thermal insulation coating
Barrier, reflective and radiant thermal insulation coatings each have their own advantages and disadvantages, and they can be compounded and used with complementary advantages and synergistic cooperation. We should use a variety of thermal insulation mechanisms to develop composite thermal
insulation coatings that prevent heat transfer, fully synergistic spectral features, and active outward radiation.

At present, relevant research work has begun in China. Ye[37] studied the effects of diatomite, HGB and nano-ATO on the thermal insulation effect of polyvinylidene fluoride coating, determined reasonable amount of each filler, and prepared the composite thermal insulation coating with synergistic thermal insulation effect. The test showed that the thermal insulation performance of the coating was good, and the thermal insulation temperature difference of the coating could reach 16.9 °C. Cao[38] prepared composite heat insulation by using fluorocarbon emulsion and silk fibroin emulsion as the base material, and incorporating appropriate amount of aluminum silicate fiber, expanded perlite, HGB, titanium dioxide, sepiolite powder and various additives. Tests have shown that the coating has a reflectance of 78% in the visible region and a thermal conductivity of 0.054 to 0.074 W/(m∙K), while providing excellent water resistance. Cheng[39] prepared a composite thermal insulation filler coated with diatomite-transition metal oxide-silica-titania layer by mixed method and chemical method, and incorporated into water-based acrylic emulsion to obtain heat-insulating coating. Its reflection ratio reaches 86.1%. The exposure test showed that the lower surface temperature of the coated test plate was lowered by 20 °C compared with the blank plate, and the heat insulation effect was good. Compared with a single thermal insulation coating, the composite thermal insulation coating combines three thermal insulation mechanisms to provide superior thermal insulation. However, at present, the research on this aspect is not as mature as the single insulation mechanism coating, and the development space is large.

3. Conclusion
At present, barrier thermal insulation coatings are still the most technically mature and the most widely used domestically. Reflective, radiant and composite insulation coatings still need to be developed deeply. The development of thermal insulation coatings should take into account both anti-corrosion and weather-resistant properties, thereby extending their service life and reducing the cost of use. In addition, environmental friendliness should also be considered when focusing on thermal insulation performance. Waterborne, solvent-free, high solid content should be the mainstream trend in coatings development.

References
[1] Q. Jiang, J.H. Li, X.Q. Lu. Infrared Technology 20, 39–41 (1998)
[2] L. Cang. Coatings Technology (Chemical Industry Press, Beijing, 2009)
[3] S.M. Yang, W.Q. Tao. Heat Transfer (Higher Education Press, Beijing, 2006)
[4] F. Xu, X.B. Zhu, L. Wang. Functional Architectural Coating (Chemical Industry Press, Beijing, 2009)
[5] X.X. Sun. Cogeneration Power Technology, 8, 26 (2008)
[6] S.H. Ye. New Building Materials 12, 27 (1994)
[7] X.L. Ren, D.L. Xie, X.Y. Zhang. Modern Chemical Industry 5, 35-38 (2014)
[8] F. Wu, X.J. Xu. Paint and Coatings Industry 33, 10 (2003)
[9] F. Xu. Environmentally Friendly Inorganic Coatings (Chemical Industry Press, Beijing, 2004)
[10] C. Wang, Z.J. Shu, Y. Wang. E-Polymers 18, 13-17 (2018)
[11] E.V. Shinkareva, A.M. Safonova. Glass and Ceramics 63, 32-33 (2006)
[12] Z.Q. Zhang, L. Hu, H. Zhan. Journal of Chongqing Jianzhu University 30, 132-134 (2008)
[13] J. Xing, Q.W. Lin, H. Chen. Water-borne Coatings and Application 24, 37-40 (2009)
[14] X. Yu, C.H. Xu. Paint and Coatings Industry 44, 1-5 (2014)
[15] S.X. Luo, Y.Q. Yang, Z.L. Zheng. New Buildings Materials 10, 33 (1999)
[16] Y.P. Ma, F. Yang. Materials Reports 29, 300-304 (2015)
[17] O.R. Van Buskirk. US, 4310596 (1982)
[18] G.J. Liu. Architectural Coatings And Application 26, 21-25 (2011)
[19] N. Ogawa, T. Hayakawa, M. JP, 262072A (2001)
[20] L. Doulos, M. Santamouris, I. Livada. Solar Energy 77, 231 (2004)
[21] R. Neil. US, 5445754 (1995)
[22] Y. Naofusa, I. Hatsuo. US, 5540998 (1996)
[23] M.J. Sun. Research on the solar reflective and insulation coating. http://kns.cnki.net/KCMS/detail/detail.aspx?dbcode=CMFD&dbname=CMFD2011&filename=2010170107.nh&v=MTgzNDRSTE9mWk9kb0ZDdmxVYnpBVjEyNkhySy91dERNcUpFYlBJUjhWDFMdXhZUzdNMUZyQ1UcldNMUZyQ1U= (2010)
[24] Y.J. Zhang, L.P. Zhang, Q.B. Zhang. Modern Paint and Finishing 03, 9-10 (2006)
[25] Chen, X. Academic Conference on Ship Materials and Engineering Applications. (2012)
[26] Y. Yu, J.N. Yu, Z.J. Li. Technology And Development of Chemical Industry 41, 11-13 (2012)
[27] C.Y. Ma, Y.S. Li. Materials Reports 04, 27-29 (2004)
[28] H. Takeda, K. Yabuki, K. Adachi. US, 6319613 (2001)
[29] X.B. Li, X.M. Fu, G.Y. Yu. Journal of Materials Protection 47, 19-21 (2014)
[30] R.Z. Zhang, W. Zheng, F. He. Paint and Coatings Industry 44, 75-79 (2014)
[31] L. Luo, P. Wang, J. Wang, New Chemical Materials 45, 33-36 (2017)
[32] Z.H. Chen, J. Jiang, G.J. Zhang. Acta Energiae Solaris Sinica 29, 257-262 (2008)
[33] X.S. Ge. Chinese Journal of Nature 08, 593-596 (1981)
[34] Li, J.T., Cai, H.W. Paint and Coatings Industry 42, 39-43 (2012)
[35] Q.M. Wo. Material Research 04, 11-12 (1998)
[36] Q. Xu, W. Chen, J.X. Zheng. Journal of Ceramics 21, 18-22 (2000)
[37] X.F. Ye, D.C. Chen, Q.H Liang. Modern Chemical Industry 34, 90-92 (2014)
[38] X.C. Cao. http://kns.cnki.net/KCMS/detail/detail.aspx?dbcode=CMFD&dbname=CMFD2012&filename=1011300146.nh&v=MTIyMTdyejk1WRI2SEdDEh0RE1xWkViUElSOGVYMYUx1eF1N0RoeMVQzcVRyV00xRnJDVJMT2T2RuRmlEbVU= (2011)
[39] Y.G. Cheng, L.J. Wang, X.L. Xie. New Building Materials 38, 7-11 (2011)