

Research Progress on Thermal Barrier Insulation Coatings

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Abstract. Thermal barrier insulation coatings can effectively improve the energy efficiency of devices and pipes and reduce energy losses. It has promising applications in the chemical and geothermal energy industries, but its thermal insulation performance needs to be further improved, and there is still some room to expand the application scenarios. In this paper, the principles of thermal barrier insulation coatings, the current state of application, the main component materials, and the methods to improve the thermal insulation performance are systematically presented. In the face of the demand for carbon peak and carbon neutrality, future research directions and application extensions of thermal barrier insulating coatings are in prospect.

Keywords: Waterborne Coatings; Barrier Insulation; Coating Components; Current Status of Research; Thermal Insulation Properties.

1. Introduction

In recent years, with the rapid development of modern industry, the energy crisis and the deteriorating ecological problems pose a serious threat to the sustainable development of mankind[1-3]. Since the publication of the 14th Five-Year Plan for Energy Conservation and Emission Reduction, energy-saving and green technologies have become the focus of scientific research, among which energy-saving and consumption-reducing materials with excellent performance have attracted much attention[4, 5].

Thermal barrier insulation coatings prevent the heat exchange between the external environment and the internal object, reducing the heat loss of the material inside the coating, thus achieving the purpose of energy saving and reducing consumption and improving the working environment. Insulation insulation coating is mainly divided into barrier type, reflection type and radiation type three kinds, of which the thermal barrier insulation coating is widely used in chemical industry, oil pipeline insulation and other fields[6].

So far, experts and scholars from home and abroad have conducted in-depth studies on the thermal insulation properties of barrier coatings and proposed the main components of barrier coatings, which are usually composed of film-forming substrates with cementing effects, insulation fillings, additives, solvents, etc.[7, 8], and the thermal insulation performance of thermal barrier insulation coatings is gradually improved by studying the thermal insulation effect of different components and ratios.

2. The Principle of Action and the Current State of Application of Barrier-Type Thermal Barrier Insulation Coatings

2.1 The Principle of Action of Barrier Insulation Coatings

Heat can be transferred by heat conduction, heat radiation and heat convection[9] in 3 ways. The heat insulation principle of thermal barrier insulation coatings is through the addition of elevated porosity fillings or the introduction of air into the coating. The key is to prevent heat transfer between the surface of the substrate and the environment through heat conduction, so as to achieve the effect of heat insulation, its principle of action as shown in Figure 1[10]. According to the Quinson effect, when the pore size of the extremely porous filler is less than 50nm, within the average free range of the air molecules, the gas in the pores cannot flow freely and the collision between the gas molecules will be considerably reduced, effectively reducing the convective heat exchange between the

gases[11]. At the same time, as the air molecules in the pores are unable to flow like normal static air, the pores inside the coating are in a near vacuum, which further prevents heat transfer, and the thermal conductivity of the filler can be lower than the thermal conductivity of conventional air at $0.0267\text{W}/(\text{m}\cdot\text{K})$ [12]. In addition, experimental studies have shown that the introduction of air as a component of the thermal insulation inside the coating increases the porosity of the coating and increases the water absorption, which leads to a decrease in the mechanical properties and thermal insulation properties of the coating[13]. Therefore, the incorporation of suitable high-porosity thermal fillers into the coating has become the focus of research on thermal barrier insulation coatings.

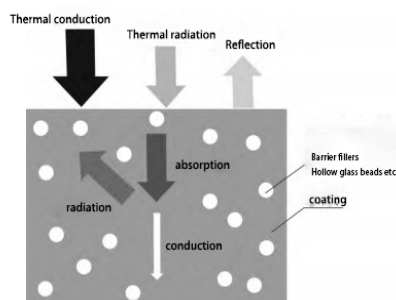


Figure 1. Schematic diagram of the mechanism of barrier-type thermal barrier insulation coatings

2.2 Status of Application of Barrier Insulation Coatings

Since 1980, China has started the development and application of thermal barrier insulation coatings, mainly inorganic silicate materials represented by natural mineral fibre materials as the main raw material, mixed with fillers, adhesives, additives to make silicate composite insulation materials, mainly used for elevated temperature work equipment insulation[14]. However, due to its steep moisture absorption rate, lengthy drying time and short service life, it has limited its wide application[15].

In the early 1990s, researchers developed a new type of insulation material based on organic materials such as synthetic resin emulsions and experimented with organic substances as fillers, mainly for thermal insulation of internal walls[16]. With the rapid development of building energy efficiency, the building insulation system has changed from internal walls to external walls and Yin[17] has developed A new composite silicate thermal insulation and heat preservation coating using waste polystyrene particles as insulation filler, which not only reduces the cost of the product, but also is environmentally friendly and has excellent heat preservation performance, and is mainly applied to the thermal insulation and heat preservation of the external walls of buildings.

In the 21st century, with the advancement of production technology, scholars have discovered fillers such as hollow glass beads (HGB), SiO_2 aerogels with excellent properties such as low density, high porosity, low water absorption and low thermal conductivity[18]. However, the above materials still have certain drawbacks, such as the poor compatibility of common hollow glass beads and the poor mechanical properties of common SiO_2 aerogel, which can lead to the degradation of the prepared materials when used directly. In order to address the above issues, scholars have modified the two materials separately, and the combined performance of the modified materials has been nicely improved. To date, barrier-type thermal insulation coatings have been applied in a variety of fields, such as housing and construction, aerospace, military industry, and current energy vehicles.

3. Current Status of Research into the Components of Barrier Insulation Coatings

Thermal barrier insulation coatings generally consist of four main components: base material, solvent, filler and additives[19]. The main function of the substrate, also known as the adhesive, is to bond the other components of the coating into a whole. Therefore, that when the coating hardens, it

can adhere to the surface of the coated base to form a uniform continuous and firm film[20]. The main function of the solvent is to dissolve the polymer and the filler to make it evenly dispersed[21]. The main function of the filler is to fill in the internal structure of the paint and prevent heat transfer. The additives are very tiny in the paint, accounting for about 2% of the total paint, but they play an essential role in the dispersion, stability, hardening and levelling of the paint [22].

3.1 Current Status of Research on Base Materials

The base material can be divided into solvent, emulsion (water-based), reactive and hot melt type, and the base material for thermal barrier insulation coatings is mainly solvent and emulsion (water-based).

The main components of solvent-based base materials are organic solvents dissolved resin solutions, weather resistance, acid and alkali resistance, water resistance, adhesion is its key indicators. EP has excellent reactivity, good bonding function, high mechanical properties, good stability, etc. It is widely used in machinery, industry, aviation, ships and other fields. PU is characterized by strong abrasion resistance, excellent adhesion, good acid and alkali resistance, low temperature resistance, wide range of soft and hard adjustment, etc., so it is often used in the fields of waterproof, anti-corrosion, decoration, etc. in the construction industry. Acrylic resins are characterised by high gloss, high transparency, good resistance to water penetration, good adhesion and low thermal conductivity, and are often used in the automotive, electrical and thermal insulation fields. Silicone resins are characterised by high temperature resistance, good weather resistance, strong adhesion, hydrophobicity and good corrosion resistance, and are mainly used for thermal protection, high temperature equipment or chemical pipeline insulation. These resins are extremely commonly used materials in the field of thermal insulation. By analyzing the technical difficulties in the application, the problem faced in the application can be effectively solved by choosing the most suitable substrate material to prepare the coating.

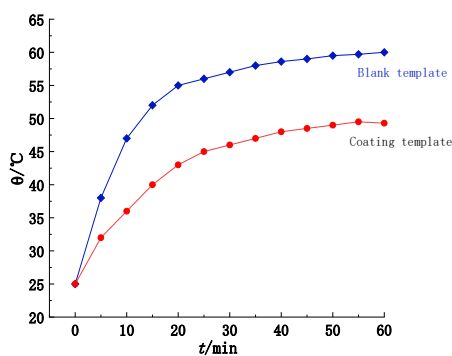


Figure 2. Comparison of thermal insulation temperature difference between blank and coated panels [26]

The solvent-based binder will emit a large amount of volatile organic compounds (VOC) during the hardening and film forming process, which is highly unfriendly to the environment. In response to national policies for energy conservation and emission reduction and carbon neutrality, the proportion of solvent-based substrates is becoming smaller and water-based substrates are being replaced[23]. With the advantages of simple process, low energy consumption, low emissions, safety and non-pollution, waterborne bases are promising for a wide range of applications. Research on aqueous bases has been carried out by scholars from home and abroad. Zhu[24] et al. used fluorinated acrylic emulsions and aqueous silicone emulsions as film-forming substances and added carbon black and SiO₂ nanoparticles to successfully prepare thermal insulation and antifouling coatings, with a temperature difference and reflectivity of 30°C and 68%, respectively, compared with the blank group. Wang[25] et al. prepared silicone acrylic emulsion coatings containing different doses of ATO microspheres by introducing ATO hollow microspheres as the film-forming substance, and the results showed that the thermal conductivity was as low as 0.128 W/(m·K) and the infrared emissivity was

as high as to 97.4%. Li[26] Using silicone acrylic emulsion as the film-forming substance, SiO₂ aerogel and hollow glass beads were selected as the thermal insulation filler. The results showed that the thermal conductivity of the thermal barrier insulation coating could reach 0.065 W/(m·K), the reflectivity reached 91.0% and the thermal insulation temperature difference was 15.8°C with 1% of SiO₂ aerogel and 9% of hollow glass beads, and the thermal insulation characteristics of the coating were measured (as shown in Figure 2).

Chen [27] et al. prepared a barrier-type waterborne thermal barrier insulation coating using waterborne benzene propylene emulsion as the film-forming base and silica aerogel as the thermal insulation filler. When the thickness of the coating was 2 mm, the thermal conductivity was 0.061 W/(m·K), with excellent overall performance. Pan[28] et al. used waterborne polyurethane as the film-forming material, added hollow glass beads, titanium dioxide, SiO₂ and aluminium oxide to prepare the thermal insulation coating. The results showed that the reflectivity of the coating was as high as 95%, the thermal conductivity was as low as 0.048 W/(m·K), and the thermal insulation temperature difference was 20.1 °C. Sun[29] et al. used aqueous polyurethane as the film-forming material and silica aerogel as the main thermal insulation filler to prepare coatings with thermal conductivity up to 0.05 W/(m·K) or fewer, and the coating surface did not crack, with excellent overall performance.

3.2 Current Status of Research on Solvents

A solvent is a liquid that dissolves or disperses a base material and is volatile, and is divided into three main classes of solvents. Of these, hydrocarbon solvents mainly include products such as aliphatic hydrocarbons, aromatic hydrocarbons, chlorinated hydrocarbons, and terpene hydrocarbons, oxygenated solvents mainly include products such as alcohols, ketones, and alcohol ethers, and another type of solvent is water, which is mainly used in waterborne coatings[30].

During the drying process of solvent-based coatings, the volatility of organic solvents largely affects the drying rate, structure and appearance of the coating film, and in addition to the viscosity, surface tension and chemical properties of organic solvents, they also affect the coating performance. Considering that there are many influences on solvent selection, and that most organic solvents are volatile and harmful substances that are not environmentally friendly, waterborne coatings prepared by using water as a solvent are more promising and valuable for research.

3.3 Current Status of Research on Thermal Insulation Fillers

Thermal Barrier thermal insulation coatings are coatings that achieve a thermal insulating effect through their own high thermal resistance. By adding some thermal insulation fillers to the coating, the thermal conductivity can be reduced to prevent heat transfer[10]. most common fillers are hollow beads, silica aerogel, expanded perlite, vermiculite and seafoam[31, 32]. basic properties of these fillers are shown in Table 1[33, 34] .

Table 1. Basic properties of common insulation fillers

Thermal insulation fillers	Density (kg/m ³)	Grain size (um)	Thermal conductivity [W/(m·K)]
Hollow glass beads	125~200	30~120	0.030~0.070
SiO ₂ aerogel	3~200	20~100	0.015~0.030
Expanded perlite	60 to 80	150 to 2500	0.048~0.052
Vermiculite	140~200	300~5000	0.069~0.077
Seafoam	120~185	150 to 2500	0.042~0.058

Due to the elevated water absorption rate of expanded perlite, vermiculite and seafoam, the heat insulation and thermal insulation effect of the coating is considerably reduced, so at present, the thermal insulation filler of the thermal barrier insulation coating at home and abroad is mainly for SiO₂ aerogel, hollow micro-beads two kinds of further research.

3.3.1 Status of Research on SiO₂ Aerogel Fillers

SiO₂ aerogel is a extremely porous three-dimensional network structure formed by the hydrolysis and condensation of amorphous nano silica particles (see Figure 3 for typical structure model), and it is a greatly dispersed solid material filled with gas dispersion in the pores[35, 36]. Because of its unique nanoporous network structure, it has low density, high specific surface area, high porosity, good chemical stability and low thermal conductivity etc., and it has broad application prospects in aerospace, thermal and acoustic insulation, biomedicine, building energy saving and other neighbouring fields[37-40].

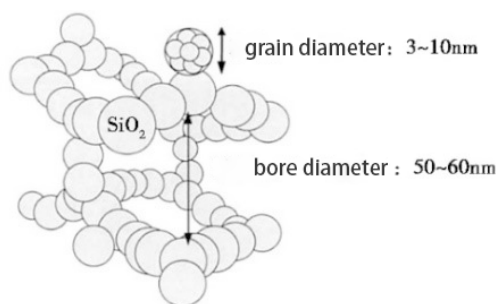


Figure 3. Model diagram of a typical aerogel structure

Foreign research on SiO₂ aerogel thermal insulation has started earlier, Schmidt et al.[41] prepared a thermal barrier insulation coating by adding SiO₂ aerogel particles to ethylene vinyl acetate copolymer (EVA), which has a low thermal conductivity of 0.02 W/(m·K) and a excellent thermal and acoustic insulation effect. Chang[42] found that the thermal conductivity of silica aerogel prepared by the precursor method was lower than that of the solvent exchange method, and then it was blended with polyurethane to prepare an aerogel polyurethane composite coating with a thermal conductivity of only 0.13 W/(m·K) and also excellent water corrosion resistance. Sun[29] developed a flexible SiO₂ aerogel thermal insulation coating with SiO₂ aerogel as the main thermal insulation filler, and explored the influence of the amount of SiO₂ aerogel on the coating performance (as shown in Table 2). The results show that when the amount of SiO₂ aerogel is 13%~16%, the thermal conductivity of the coating can reach below 0.05 W/(m·K). He[43] et al. prepared silica aerogel thermal barrier insulation coatings by co-blending silica aerogel and acrylic emulsion, and studied the effect of different densities of silica aerogel particles on the thermal conductivity of the coatings (as shown in Figure 4).

Table 2. Effect of SiO₂ aerogel addition on coating film properties [29]

SiO ₂ Aerogel doping/wt%	Coating appearance	Water resistance (48h)	Thermal conductivity/(W/(m·K))
8.0	level	No change	0.059
10.0	level	No change	0.050
13.0	level	No change	0.047
16.0	Less smooth	No change	0.042
20.0	Cracked	Blistering	0.037

Although SiO₂ aerogel is a lightweight nanosolid material with excellent thermal insulation properties, it is prone to structural instability in practice due to its porous structure, which results in brittleness and poor mechanical properties[44]. Based on this, experts have used organically modified silica precursors to enhance the structure of SiO₂ aerogels or doped with fibrous materials[45, 46]. Maleki et al.[47] used flexible organic polymers to modify SiO₂ aerogels, thus improving the mechanical properties of SiO₂ aerogels. Li[48] et al. successfully prepared aramid fibre-reinforced silica aerogel composites. The microstructure showed that the aramid fibres were embedded in the

aerogel matrix as a supporting skeleton, which improved the flexibility of the material, and in addition, the thermal conductivity was maintained between 0.0221~0.0235 W/(m·K). Shi[49] et al. prepared hydrophobic SiO₂ aerogel composite thermal insulation by incorporating thin layers of fluff-treated glass fibres and investigated the effect of adding different contents of fibres on the thermal conductivity (as shown in Figure 5). The results showed that the amount of glass fibre added was inversely proportional to the thermal insulation function of the composites, but positively proportional to their mechanical properties.

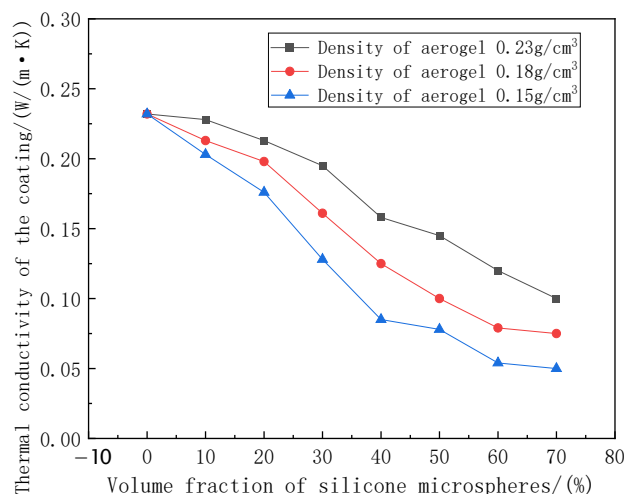


Figure 4. Thermal conductivity of silica gel microsphere coatings of different densities[43]

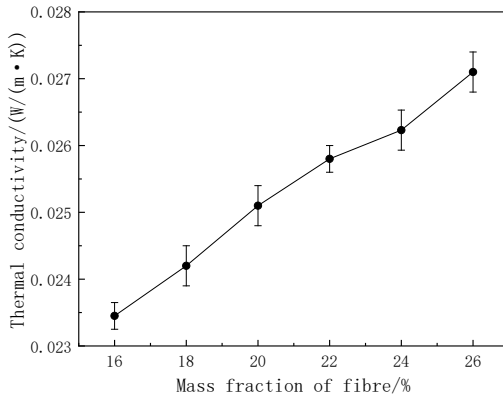


Figure 5. Effect of fibre content on the thermal conductivity of SiO₂ aerogel composites[49]

Hung[50] et al. prepared glass fibre (GF)/carbon fibre (CF)/SiO₂ aerogel composites using the sol-gel method and APD, which exhibited better flexural strength and very low thermal conductivity (0.031 W/(m·K)) compared to pure aerogel. Yu[51] et al. prepared quartz fibre/nanorod/ aerogel composites using in situ grown TiO₂ nanorods, showing a compressive strength of 0.37 Mpa at 10% strain, a thermal conductivity of 0.071 W/(m·K) at high temperature and a reflectivity of >95% at the optimum ratio. Yi[52] et al. prepared a multi-scale aluminosilicate fibre/mullite whisker structure using an impregnation-drying process and heat treatment to successfully synthesise silica aerogel composites. The results showed that they had ultra-high compressive stress and modulus of 6.45 Mpa and 69.74 Mpa at 50% strain with ultra-low thermal conductivity of 0.0275 W/(m·K) at the same time under optimal ratios. Wang Huanhuan et al. Wang[53] prepared SiO₂ aerogel thermal insulation coating with long diameter glass fiber and short diameter zirconium containing ceramic fiber as phase reinforced filler. When the optimum ratio was used, the thermal conductivity was as low as 0.0539 W/(m·K) and the adhesion strength was 294 kPa, and it also had good corrosion resistance.

3.3.2 Current Status of Research on Hollow Glass Bead Fillers

Hollow glass beads (HGB) are tiny spherical powders with a hollow structure and an inert gas (N_2) inside, which have excellent properties such as light weight, high strength, good fluidity and low thermal conductivity (shown in Table 3) [54]. It is widely used in aerospace, petrochemical, deep-sea and other fields. Foreign research on hollow microbeads began in the 1950s and 1960s, but Chinese research on them began later.[55].

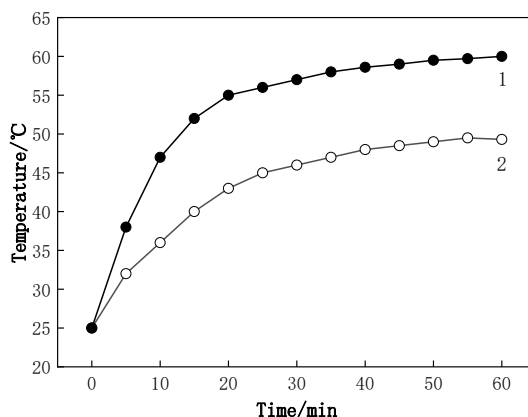
Table 3. Physico-chemical properties of hollow glass beads

Projects	Performance
Appearance	A white powder with good flowability
Thermal conductivity (20°C) W/(m·K)	0.0512~0.0934
Bulk density/ (g·cm ⁻³)	0.017~0.42
Particle size range/um	2~125
True density/ (g·cm ⁻³)	0.25~0.60
Compressive strength/MPa	5~82
pH	7~8

Wang[56] prepared EVA/HGB thermal insulation composite coating by extrusion blending method, and the study showed that the thermal conductivity of the composite filled with hollow glass beads of 40um particle size decreased by 22.5% to as low as 0.2199W/(m·K) compared with unfilled HGB, and its tensile strength reached 32.26Mpa, which has excellent thermal insulation performance and mechanical properties. Meng[57] prepared a heat insulation and reflective composite coating by mixing appropriate amounts of hollow microbeads and rutile titanium dioxide, and then adding binder, curing agent and solvent. The results showed that the coating reached a heat insulation temperature of 12-15°C and a reflectivity of 95%, and also had excellent insulating properties and corrosion resistance. Zhong[58] used $ZnSO_4 \cdot 7H_2O$ and NH_4HCO_3 and hollow glass beads as raw materials to prepare a zinc oxide coated hollow glass bead coating by the chemical packing method, and it was shown that the equilibrium temperature of the back side of the base plate coated with zinc oxide coated hollow glass bead coating was 61.4°C, which was 9.3% lower than that of the hollow glass bead coating, and had excellent thermal insulation properties. Chen et al.[59] prepared a new thermal insulation and heat preservation coating with 8% tourmaline and 4% hollow glass beads as the main functional fillers. The structure of hollow glass beads produced scattering and multiple reflections of solar radiation on the surface of the coating, while the oxide of tourmaline particles and hollow beads radiated the absorbed heat from the coating back to the atmosphere, and the results showed that the integral mean value of the thermal insulation effect was increased by 6.66%. Wang et al.[60] used nano TiO_2 encapsulated HGMs as the main thermal insulation and heat preservation filler and added nano fillers to prepare a nano thermal insulation and heat preservation coating with excellent performance, and tested the thermal insulation characteristics of the coating (as shown in Figure 6), which has a low thermal conductivity of 0.1698 W/(m·K) and a high reflection ratio of 0.8231, and the coating adhesion, alkali and acid resistance have met the national standards. Numerous studies have shown that modified HGMs can exhibit better insulation and other integrated properties.

Chen[61] used zinc phosphate as the coating material to modify the hollow glass beads to prepare a zinc phosphate modified hollow glass bead coating. The results showed that the thermal conductivity of the coating was reduced to 0.157 W/(m·K), while it had good anti-corrosion properties and effectively improved the service life of the coating.

In addition, some experts and scholars have doped various materials as thermal insulation fillers. Wang[62] et al. prepared thermal insulation composites using seafoam and hollow glass microspheres as binary fillers, which had very high stability and thermal insulation properties in the face of thermal environments up to 500°C. Li et al.[63] prepared high-performance thermal insulation composites using an alkali-activated binder as the matrix and adding hollow glass microspheres and aerogel, with thermal conductivity as low as 0.0434 W/(m·K) when the optimum ratio was used.



1 - Blank glass; 2 - Coated glass

Figure 6. Variation of internal temperature of blank and coated glass with time [60]

3.4 Current Status of Research on Auxiliaries

Compared with traditional solvent-based coatings, the overall composition of waterborne coatings is relatively simple, but the additives are essential materials, which can not only make the application of waterborne coatings in the application of better performance advantages, but also to achieve the construction process and product quality improvement[64]. Common additives used in waterborne coatings are: dispersants, wetting agents, defoliant, leveling agents, film-forming agents, etc. Although the number of additives in waterborne coatings is small, they have a key role in the final performance of waterborne coatings [65].

The effect of the dispersant and the wetting agent is considerably the same, the main effect being to reduce the surface energy between the solid and the liquid, and the packing aggregates as far as possible to disperse into primary particles. Waterborne coatings in the commonly used dispersant for polyethylene oxide[66]. The common wetting agent is acetylene diol wetting agent, because it has less foam, excellent wetting effect and other characteristics[67].

The main function of defoamer is to inhibit and eliminate foam in the production process of waterborne coatings, as waterborne coatings are more likely to produce bubbles than solvent-based coatings[68]. These bubbles can cause porosity within the coating and affect the thermal insulation performance, so defoamers are very important additives. Common defoamer is divided into mineral oil, silicone, polyether, The type of defoamer commonly used in waterborne coatings is silicone modified polysiloxane defoamer[69].

The main function of the levelling agent is to effectively regulate the efficiency of water loss during the film formation process of a waterborne coating, thus ensuring that a smooth and flat coating can be formed. Commonly used levelling agents include acrylic copolymers, silicones and fluorocarbon surfactants[70]. At present, the common levelling agents for waterborne coatings are polyether modified, polyester modified or alkyl modified silicone levelling agents[71].

The main function of film-forming additives is to bond polymer particles by lowering the glass transition temperature of the film-forming substance (T_g) to create plastic flow through swelling[72]. Film-forming agents can be classified according to their chemical composition into hydrocarbons, diols, water-soluble alcohols and ethers, esters and alcohol esters, and the most common film-forming agents used in water-based coating formulations are dodecanol ester[73].

4. Conclusion and Outlook

4.1 Concluding Remarks

(1) Thermal barrier insulation coating is a kind of coating that directly stops the heat conduction on the surface of the object, according to the site conditions and construction technology requirements, choose the suitable base material, filler, solvent, additives to formulate the best performance of

thermal barrier insulation coating, so as to meet the thermal insulation requirements of industrial facilities, waterborne coatings have additional market prospects and research value.

(2) Currently, SiO₂ aerogel and hollow glass beads are commonly used as insulation fillers in both domestic and foreign markets for the exploration and development of barrier-type insulation and barrier insulation coatings, which have great potential for development in the construction, petrochemicals, aerospace and other sectors. While improving the insulation and thermal insulation properties of coatings, improving the mechanical properties, adhesion and service life of coatings as well as other performance indicators are also the focus of research.

4.2 Outlook

(1) To date, the overall performance of barrier insulation coatings still has certain shortcomings, such as insufficient corrosion resistance and thermal insulation properties and poor adhesion of barrier insulation coatings. The future of barrier coatings is therefore to be guided by the need to improve their overall performance on the basis of their good thermal insulation properties. Nowadays, water-based composite thermal barrier insulation coatings with a variety of thermal insulation mechanisms are attracting attention, as they have a multiple of thermal insulation mechanisms, which can play a synergistic role in maximising the thermal insulation effect.

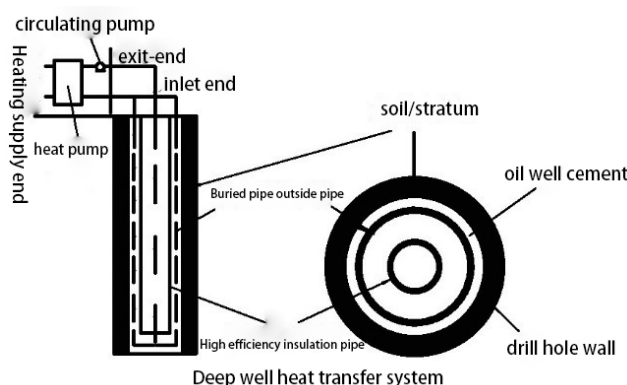


Figure 7. Coaxial casing heat exchanger

(2) Geothermal energy exploitation presents an unprecedented opportunity for development in the face of national carbon neutrality and carbon peak targets. The current geothermal energy development method is used as shown in Figure 7[74], however, the industry is now using steel and polyurethane pipes as geothermal energy transportation pipes, resulting in heat loss and greatly reduced heat extraction efficiency. The author's team considered preparing a thermal insulation and heat preservation coating suitable for the underground heat extraction environment and coating it on the surface of the steel pipe, thus reducing the heat loss and achieving a good thermal insulation and heat preservation effect in response to the national energy saving and consumption reduction policy.

Acknowledgments

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