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Thermal barrier coatings based on alumina microparticles

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ABSTRACT

Buildings are large consumers of energy everywhere and a substantial share of energy goes to heat and cool buildings. This heating and air-conditioning load can be reduced through many means; a notable possibility is the proper design and selection of the building envelope. Therefore the use of thermal insulation in buildings contributes to reducing the annual energy cost. The objective of this paper is to present a new coating based on waterborne matrix, which is modified with gamma-alumina to form an inorganic–organic composite paint. Characterizations and performance, in terms of thermal conductivity, are presented. Due to both the high surface area of particles and the presence of interstitial cavities in the thin film, the product seems to be very interesting as insulation material.

1. Introduction

As the energy use in the building sector accounts for a significant part of the world's total energy use, there is a demand to improve the energy efficiency of buildings. Hence, in this respect, concepts like passive houses and zero emission buildings are being introduced.

The thermal insulation of buildings plays an important role to meet the demands of improved energy efficiency. To achieve the highest possible thermal insulation resistance, new insulation materials and solutions with low thermal conductivity values have been and are being developed, in addition to using the current traditional insulation materials with increasing thicknesses in the building envelopes. However, very thick building envelopes are not desirable for several reasons, e.g. considering space issues with respect to the economy, floor area, architectural restrictions and other limitations, material usage and existing building techniques [1].

The key property of a thermal building insulation material or solution is the thermal conductivity, where the normal strategy or goal is to achieve as low thermal conductivity as possible ($\lambda < 0.065$ W/(mK)). Low thermal conductivity enables the application of relatively thin building envelopes with a high thermal resistance R (m^2 K/W) and a low thermal transmittance U value (W/m^2 K) [1].

Many types of building thermal insulation are available which fall under the following basic materials and composites [2]:

a) Inorganic materials. (i) Fibrous materials such as glass, rock, and slag wool. Typical thermal conductivity values for mineral wool are between 30 and 40 mW/(mK). (ii) Cellular materials such as calcium silicate, bonded perlite, vermiculite, and ceramic products.
b) Organic materials. (i) Fibrous materials such as cellulose, cotton, wood, pulp, cane, or synthetic fibers. (ii) Cellular materials such as cork, foamed rubber, polystyrene, polyethylene, polyurethane, and other polymers. Typical thermal conductivity values for cork are between 40 and 50 mW/(mK). Typical thermal conductivity values for Expanded polystyrene (EPS) are between 30 and 40 mW/(mK); EPS has a partly open pore structure. Extruded polystyrene (XPS) has a closed pore structure; typical thermal conductivity values for XPS are between 30 and 40 mW/(mK). Typical thermal conductivity values for polyurethane are between 20 and 30 mW/(mK), i.e. considerably lower than mineral wool, polystyrene and cellulose products.
c) Metallic or metallized reflective membranes. These must face an air-filled, gas-filled, or evacuated space to be effective [1,3].

The thermal conductivities of other building materials, including the load-bearing ones, are normally considerably higher than the thermal conductivity values of the thermal building

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insulation materials, i.e. the very reason for the need and application of thermal building insulation materials. As a comparison, typical examples may be wood (0.1–0.2 W/(mK)), carbon steel (55 W/(mK)), stainless steel (17 W/(mK)), aluminum (220 W/(mK)), concrete (0.15–2.5 W/(mK)), plaster (0.9 W/(mK)), lightweight aggregate (0.1–0.7 W/(mK)), brick (0.4–1 W/(mK)), stone (1–2 W/(mK)) and glass (0.8 W/(mK)) [1].

Areogel is a possible solution, as thermal insulation material, and it may be the most promising option with the highest potential at the moment [4–7]. Commercially available aerogels have been reported to have thermal conductivities between 12 and 14 mW/(mK) at ambient pressure. However the production costs of aerogels are still very high. Aerogels have a relatively high compression strength, but are very fragile due to their very low tensile strength. A very interesting aspect with aerogels is that they can be produced as either opaque, translucent or transparent materials, thus enabling a wide range of possible building applications. In any case, costs have to be lowered substantially for aerogels, to become a widespread thermal insulation material for opaque applications [1].

When an insulation material is used, in order to lower the heat flow in the building, the materials with low thermal conductivity should have an optimal thickness to have an economic system. The insulation thickness will increase the investment cost, but the cost of energy will decrease up to the point where the thickness of the material is optimized and will contribute to the highest overall cost savings [8,9]; and therefore a superficial paint as a thermal barrier could be an interesting solution.

In the last twenty years, waterborne coatings have gained increasing importance due to strict environmental regulations on the emission of volatile organic compounds from solventborne coatings. To maintain constant product quality and to develop new products, structural characterization and measurement of barrier properties of these new coatings become crucial. Waterborne coatings usually contain different additives and an appropriate choice among various alternatives of these additives brings a challenge to both manufacturers and researchers. Several groups have reported the influence of particle morphology, surface treatment of inorganic pigments, corrosion inhibiting additives, fillers, dispersing agents and nature of the binder material on the performance of waterborne coatings [10–17].

Actually there are many applications where the barrier properties of paint coatings are key factors determining performance: for example, in protection against the corrosion of metals, carbonation of concrete and rotting of wood. The paint technologist therefore needs an understanding of the important parameters controlling properties in order to design an appropriate product [18].

For instance, adding additives and pigments not only improves the appearance of the coatings, but also helps to improve many properties of the coatings such as UV resistance, corrosion resistance, and mechanical properties like scratch and abrasion. In this study, an acrylic based waterborne coating was used as a base matrix, which was then modified with activated acid alumina to form a inorganic–organic composite coating [19].

The great chemical stability of Al_2O_3 at elevated temperatures makes it a particularly attractive material for wear resistant coatings. Furthermore, when compared with other materials [20], the relatively small thermal conductivity of Al_2O_3 at high temperatures will provide more effective thermal protection for the substrate [21,22]. Al_2O_3 exists in several crystalline polymorphs: the α phase based on an hcp oxygen sublattice; the γ, η, θ and δ phases based on an fcc oxygen structure; and the κ phase [21].

Gamma-Al_2O_3 is perhaps the most important nanomaterial used as a support for metal catalysts. It has been considered as one of the most promising advanced materials for a variety of applications due to its distinctive chemical, mechanical and thermal properties [23]. Usually γ-Al_2O_3 has high surface area in comparison for instance to the α one.

The paper presents the effect of the addition of high surface area Al_2O_3 as pigment on the performance of waterborne coatings, in particularly regarding the barrier properties and the thermal resistance.

In order to study the influence of alumina, paints are deliberately made without either titanium dioxide, the most expensive but indispensable component for any kind of paint due to its high refractive index and inertness, or calcite, used in paint recipes because it is cheaper than titanium dioxide [24].

The Al_2O_3 particles used were investigated by X-ray diffraction XRD, scanning electron microscope (SEM) for their shape and size, and the interaction of particles with base paint matrix was investigated by Infrared spectroscopy (FTIR) and SEM. Some properties of paint and dried coating were assessed, including the thermal conductivity.

2. Materials and methods

2.1. Materials and preparation of paints

The activated acid Al_2O_3 sample used throughout this study was from Sigma–Aldrich, with the following characteristic: density of 4.0 g/cm^3, surface area of 155 m^2/g, nominal pore size of 58 Å, pH in H_2O of 4.5 ± 0.5. The nominal mean diameter of the particles was 100 μm. The powder was sieved (<100 μm) in order to obtain a narrow particle size distribution

For the experiments, a typical wall paint water-based styrene-acrylic resin (with solid content 50%) was used. The dispersions were formulated by adding resin, Al_2O_3 (both sieved and not sieved), deionized water and additives (10% of the total) with adequate mechanical agitation by using a laboratory stirrer Dispermat, varying the speed between 300 and 1400 and 800 rpm for 30 min. To avoid foam, inadequate flow/viscosity, improper wetting, microbial growth, and to facilitate pigment dispergation and film formation, various additives were added, i.e. antifoam, associative thickener, surfactant, preservatives, coalescent. Moreover a neutralizing agent was added, during neutralization the pH of the resin solution was maintained between 8.0 and 8.5.

The ratio between water/resin/powder was 45/10/35 wt%.

The coating obtained in this way was applied with draw down on leneta charts and put in the oven at 20 °C for 24 h to control film forming conditions. The physical properties of the dispersions were characterized by measuring pH, density and viscosity. The dispersions were then kept at 40 °C for 2 months in order to evaluate the stability after 1 and 2 months, by measuring again pH, density and viscosity.

In order to study the interaction between alumina and resin, the activated alumina was mixed with two styrene-acrylic resins, with different solid content (50% and 30% respectively) without any other additives, each in two different ratios, namely resin/Al_2O_3 75/25 wt% and 50/50 wt% respectively.

2.2. Characterization techniques

Density was determined by pycnometer (volume of 100 ml) and viscosity profile by Brookfield digital viscometer Mod. RVDV-II+ (spindle n° 6, shear rate 1 s^{-1}) at 20 °C. Rheological measurements of paints were performed on a rotational rheometer Anton Paar MCR 301 (Germany) with coaxial cylinders geometry (Z3 DIN 25 mm), working in the controlled shear stress mode, equipped with PC and suitable software.

A small sample of powder was compressed in a suitable pan for the direct XRD analysis. The alumina was analyzed using a

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