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Synthesis of pillared clays from metallic salts as pigments for thermosolar absorptive coatings

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ABSTRACT

A general procedure for developing stable solar absorptive coatings at both high temperature and a high solar radiation concentration is presented. In order to generally improve thermal efficiency, a coating with high solar absorptance is applied all over the surface of receiver tubes that is subjected to extreme working conditions. Consequently, a durable coating with high absorptivity for sunlight is needed. An alternative paint formulation research and development line to Pyromark-2500, the paint currently used in many commercial solar thermal power plants (CSP) is proposed. Pigment synthesis is developed by intercalating metallic salts into laminar or tubular clay structures. Metallic oxides, which provide paint with its color properties, are obtained by a calcination process. Addition of silane or surfactants during the pigment synthesis is also optimized. Once dried and ground to a precise size, pigments are mixed with a commercial binder and applied to a metallic substrate to study their properties. Thermal stability to high temperature is studied with different tests. The results showed that laminar structure was preferred to intercalate larger amounts of metallic salt into the clay structure, and no significant differences were found when using silane or surfactant modifiers. Although the highest absorptivity value was 85% after 24 h at 600 °C, samples presented very good adherence to the metallic substrate. Addition of a small quantity of commercial black pigment to the paint composition could improve the absorptivity and maintain the excellent adhesion shown. Furthermore, montmorillonite clay, modified with a surfactant before adding metallic salt, and without silane, resulted in a black pigment in a powder form. This pillared clay could be used in future paint formulations.

1. Introduction

In recent years, considerable efforts have been made to develop central receiver systems to harvest and convert sunlight into thermal energy and electricity. This energy source is enviro-friendly and reliable. The core component of a solar thermal power plant (CSP) is the receiver, which is coated with a highly absorptive coating. Searching for inexpensive optically efficient solar absorptive or selective coatings is a key factor in thermosolar energy applications.

This coating dramatically improves the energy collection yield of thermal solar collectors for thermal solar power plants. The coating is optimized to remain stable at high temperatures and to ensure long durability. By increasing both the energy collection yields of thermal solar power plants and the operating temperatures of power plants, it is possible to dramatically increase the efficiency of the solar to electric energy conversion rate (Lampert, 1987; Crnjak Orel, 1999; Smith et al., 2003; Gunde et al., 2003).

Black paints are common coating materials for solar absorbers but, in the course of time, they have been gradually driven out of use and replaced with coatings prepared by other more sophisticated deposition methods; e.g., reactive sputtering, vacuum evaporation, electrochemical deposition and spraying colloidal

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Abbreviations: CPS, solar thermal power plant; CPB, cetylpyridinum bromide; M, montmorillonite; L, laponite; HA, halloysite; SURF, surfactant; SIL, silane.

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solutions combined with post-treatment. Pyromark Series 2500 high temperature paint has been used on previous CSP central receivers and is considered a standard (Ho et al., 2014). Pyromark-2500 is a relatively inexpensive, easy-to-apply coating with a solar absorptance of (0.96), but with high thermal emissivity (0.94).

The main reason for research not being intense on paints is that they are not solar-selective and their thermal emittance at working temperatures is around 0.90–0.94, which corresponds to high thermal radiation loss. Such loss is suppressed because, with thin absorbing layers, they are deposited on a metal substrate obtained by one of the above-mentioned techniques (Orel et al., 2007).

Typically when formulating paints, lots of challenges are faced in the system and formulation design as many components are involved in compositions. Paint components can be classified as four groups: binders, solvents, pigments and additives. Their composition and quantities depend on the application method, the desired properties, the substrate to be coated, and on ecological and economic constraints.

The most important component of a paint formulation is binders. Binders essentially determine the application method, drying and hardening behavior, adhesion to the substrate, mechanical properties, chemical resistance, and resistance to weathering (Geng, 2012). Polyurethane/polyurea cross-linked binders confer the coating superior durability, mechanical strength and barrier properties (Levine et al., 2010). Fluoropolymers could be another option to obtain coatings with excellent exterior durability, chemical resistance, good flexibility, good adhesion, little dirt retention, and good moisture and fungus resistance (Wood, 2001; Iezzi et al., 2000; Motohashi and Miyazaki, 1987; Scheirs et al., 1995).

Pigments provide paint with color properties. One way of obtaining resistant pigments for extreme working conditions like high temperature, humidity, corrosion or thermal gradients is to use metal oxides as they present excellent chemical stability for the afore-mentioned conditions. Controlling oxide growth and disposition are key for controlling the optical properties of these natural pigments. One way of controlling oxide disposition is to use nanoclay as templates. Optical properties and color performance depend on nanoclay structures and the adsorption capacity of oxide precursors (metal salt solutions). Researchers have named composite materials (nanoclays and metal oxides) pillared clays. Laminar smectite clays (Montmorillonite or Laponite) or tubular-structured clays, such as halloysite, are used in ceramic industries as refractory materials, or as components when a thermal expansion risk is posed due to high temperatures as they present high thermal stability (Wu et al., 2005). The literature focuses mainly on pillared clays for catalysis use, but these materials can also be used as pigments for coating formulations (Li et al., 2010; Montes-Hernandez et al., 2006; Zhao et al., 2013).

It is possible to change the color appearance of any metal oxide by simply changing the intercalation conditions (Carbajal-Franco et al., 2013). Along these lines, our group is experienced in formulating hybrid composite-pigments based on organic dyes intercalated into laminar nanoclays to obtain a wide color gamut from the same organic dye (Seyama et al., 2008; Orel et al., 2005). Black pigments from mixing different color pigments, e.g., dark yellows and blues, can be obtained. The objective of this work was to confer innovation to the synthesis of metal oxide hybrid composite-pigments using different nanoclay structures to improve their stability under working conditions with high solar absorptance for CSP applications. For this purpose, a preliminary design of the experiments was performed to discover the relevance of metal salt hybrid composite-pigments synthesis factors. These factors were nanoclay structure (size and shape) and two structural modifiers: surfactant and silane.

2. Experimental

2.1. Materials

Three different nanoclays, two with laminar cationic exchange capacity, montmorillonite (M) and laponite (L) (Rockwood additives) and a tubular nanoclay, halloysite (HA) (Sigma Aldrich), were used. As the nanoclay structural modifiers, surfactant Cetylpyridinuim bromide hydrate (98%) (CPB) and silane (3-Aminopropyl)trimethoxy-silane (97%) were employed, and both were acquired from Sigma Aldrich. Three metallic salts were used, Manganese(II) chloride tetrahydrate (99%), Iron(III) chloride hexahydrate (>99%) and Cobalt(II) chloride hexahydrate (99%), which also came from Sigma Aldrich. To adjust pH during the synthesis process, the sodium hydroxide (NaOH) reagent agent (97%) was used.

2.2. Synthesis method

Clays were initially dispersed at 1500 rpm for 24 h in distilled water at different concentrations: 21.43 g/L for L and 30 g/L for M and HA. The concentration of metallic salt solutions depended on the nanoclay employed. For Cobalt and Iron salts, the concentration was $5.14 \cdot 10^{-03}$ M in distilled water when mixed with both M and HA, and $3.85 \cdot 10^{-02}$ M with L. For Manganese solutions, the concentration was $6.21 \cdot 10^{-02}$ M when using both M and HA, and $4.62 \cdot 10^{-02}$ M with L. Salt exchange was performed in two steps, first stirring at 1500 rpm at room temperature for 1 h, and second at 600 rpm for 24 h. Afterward, samples were centrifuged to remove the remaining solvent. The percentage of intercalated and adsorbed salt was calculated from the UV–VIS absorption spectra of the supernatant, measured in a spectrophotometer Jasco V650. At this point, the metallic salt intercalated into the clay presented a paste format as distilled water still remained in the structure. This paste was re-dispersed at 400 rpm for 30 min to remove any possible traces of salt that did not intercalate into the clay structure. The washing process was run 3 times. The paste-hybrid composite-pigment was dried in an oven at 90 °C for 24 h to obtain the pigment powder. Finally, metal oxides were obtained by a calcination process in a heating muffle at 800 °C for 3 h in an oxidant atmosphere (Fig. 1). The composite material that resulted from both the amorphous nanoclay structure and the generated metal oxides was finally called a hybrid composite-pigment. The final optical properties from the hybrid pigments could differ depending on synthesis conditions.

2.3. Design of experiments (DoE)

Taguchi's (L9) DoE was used to study the effect of four synthesis factors with three levels on the obtained pillared nanoclays. The synthesis factors were: nanoclay (CLAY) with levels: 1-M, 2-L, 3-HA, surfactant (SURF), and silane (SIL) addition with levels: 1-Before addition of salt, 2-After addition of salt and 3-with no addition. The last factor was the hybrid pigment form (FORMAT) with only two levels: 1-calcinated and 2-the paste format. The nine experiments that resulted from this design (Table 1) were replicated in three blocks, one for each metal salt (Co, Fe, and Mn). The synthesis process yield was calculated from the metal salt concentration in the nanoclay structure after removing the supernatant during the washing process. The best color performance was expected to be obtained for the maximum amount of metallic salt intercalated into the clay structure.