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Masonry remediation and protection by aqueous silane/siloxane macroemulsions incorporating colloidal titanium dioxide and zinc oxide nanoparticulates: Mechanisms, performance and benefits

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HIGHLIGHTS

- Nanoparticulate titanium dioxide and zinc oxide were used to enhance silane facade treatments.
- Stability, rheology and post cured attributes were assessed and deemed enhanced.
- Morphology was assessed by nitrogen isothermal analysis and TEM.
- Negligible aesthetical compromise of the substrate.
- Commercially viable treatments produced.

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ABSTRACT

In this study the influence of metal oxide nanoparticulates on aqueous silane/siloxane pore lining facade remediation treatments is presented. Pre-treatment attributes including stability and rheological properties were investigated. Colloidal titanium dioxide and zinc oxide nanoparticulates were incorporated into the novel silane/siloxane o/w emulsions and characteristics of such systems were then assessed in terms of thermal stability and rheological modification. Post-treatment attributes including water repellence, sorptivity and aesthetical alteration were also assessed. Enhanced emulsion properties were found to be dependent upon the extent of aggregation which was attributed to the morphology and size of the particulates. Excess of colloidal medium did reduce viscosity, however a significant stabilization was achieved regardless. Post-treatment results showed that a improved water repellence could be achieved with negligible visible alteration to substrate aesthetics; a novel benefit of such treatments for retrofit and remediation products combined with zero VOC emissions, complying to new EU directives. Findings undoubtedly confirm the potential for nanoparticulates to be used as effective emulsifiers in similar emulsion systems while being commercially and practically viable for facade remediation due to the small concentrations required.

1. Introduction

Building facades are detrimentally affected by water ingress which has been observed to be the root cause of most facade degradation mechanisms; including organic and inorganic soiling, freeze–thaw spalling, and building envelope heat loss [1,2]. To prevent damage various water repellent solutions and emulsion systems are commonly employed to provide protection to dwellings from water ingress [3]. In general, water repellent treatments work though impregnation of the substrate and modifying the pore lining, creating a highly effective water repellent substrate. Coatings create a layer at the surface of the material but do not penetrate to any significant degree, although may still repel water at the surface. Polyurethane and acrylic coatings are used for different purposes such as anti-graffiti coatings and aesthetical alteration of the substrate. Coatings unlike treatments are prone to cracks and chips which reduces barrier efficacy while altering the aesthetics of the substrate. Of these, pore liners are preferable for above ground applications as they reduce internal humidity due to their ability to allow water vapour to permeate while stopping liquid water ingress. In addition, they do not generally alter the aesthetics

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of substrates which is of prime importance for retrofit and heritage remediation schemes to reduce carbon dioxide emissions while increasing thermal envelope efficiency in line with EU targets [4,5].

Aqueous macroemulsions eliminate problems commonly associated with volatile organic compound (VOC) emissions from solvent base emulsions [6]. Fig. 1 shows how these emulsions may appear before application, with a variety of viscosities and rheological traits achievable depending upon requirement. Low viscosity concentrates are predominantly used for spray application, whereas partially gelled emulsions are useful for brush/roller applications as it minimises waste from splatter. Water may also be used as a catalyst for curing in such systems eliminating the need for harmful peroxides. Organosilicone emulsions in general may therefore be considered greener and safer to use than their conventional solvent based counterparts.

Typically organosilicone emulsions comprise of silane and siloxane constituents which are collectively used to increase a building's thermal envelope efficiency without extensively compromising its aesthetics or functionality [4,7]. Silanes are used to modify the internal capillary surfaces making them hydrophobic while allowing water vapour to still permeate due to their small size. Siloxanes however are larger and used to more effectively alter the interfacial energy at the surface of the substrate due to reduced functional sites for charge interaction, although to reduce pore blocking concentration needs to be optimised. A highly stable 3D interpenetrating network between silane molecules and the substrate and with themselves may be achieved through hydrolysis of tri-alkoxy groups (ethoxy/methoxy functionalities) with water present within the continuous phase of the treatment, this is followed by a condensation reaction [3,8,9]. Architectural paints, agricultural biocides and cosmetics all typically use branched nonionic surfactants to reduce the concentration required for stabilization [10,11]. These types of surfactants conventionally have branched polar head groups which bond with local continuous phase molecules to reduce micelle hydrodynamic interactions [12]. Fig. 2 shows a typical composition of such surfactants.

In the specific case of silane/siloxane emulsions previous studies have shown that either solely particulate-stabilized or surfactant-stabilized emulsions are not stable for long; even at high concentrations they typically separate within two days [11]. The amphiphilic nature of the oil phase allows for a degree of aqueous solubility, making segregation of phases difficult and thus causing irreversible micelle rupture and coalescence. However, it has been reported that stabilization of these types of emulsions by various surfactant and particulate co-emulsifier systems was achievable by using silica or metal oxide particulates and a polyoxyethylene based surfactant [11,13,14].

Fig. 1. Aqueous silane/siloxane nanoparticulate enhanced emulsion on a cube of mortar (developed by authors).

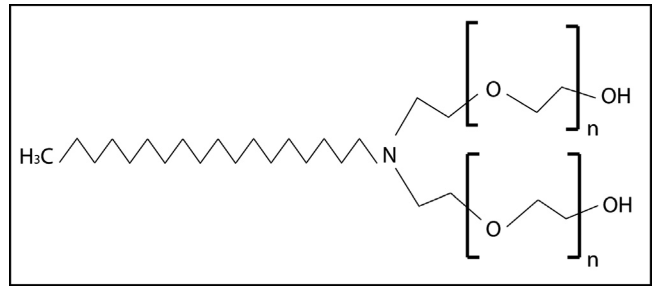

Fig. 2. Polyoxyethylene stearyl amine exhibiting a conventional functionality arrangement.

Ramsden [15] was the first to observe particulate stabilized emulsions, which were then evaluated extensively by Pickering [16] nanoparticulates can improve micelle shape compliance, provide greater surface area for networking and are less influenced by sedimentation [10]. Recently a variety of nanoparticulates have been studied in numerous emulsion systems and their effect on overall stability, oil droplet size, tendency to coalesce, and rheological properties have been investigated [17–19]. If the amount of surfactant in a system is below critical aggregate concentration (CAC) it has been found that particulates first stabilize the micelles by filling gaps, after which micelles are aggregate with excess monomeric or oligomeric particulates achieving greater stability. If there is too little surfactant absorbed on the outer layer of aggregated particulates bridging may not be achieved, which in turn increases flocculation. In addition to this, smaller surfactant molecules produce larger micelles and bridging is also hindered due to smaller surface area available for interaction between micelles, which reduces stability. Conversely, if the surfactant concentration is too high the surfactant may cover particulates achieving an isotropic surface tension, causing irreversible particle-micelle separation and thus destabilizing the emulsion [11]. In addition, higher concentrations of surfactant tends to reduce the efficacy of treatments and coatings to protect the interface they are applied to while also being a costly as an emulsifier. Thus the larger surface area to weight ratio that nanoparticulates provide could help reduce detrimental build-up of excess surfactants for relatively low quantities making such products possibly more economically viable.

Currently self-sanitising coatings only come in white due to high quantities of metal oxide incorporation detrimentally altering substrate aesthetics. Nanostructured coatings usually rely on controlling surface roughness and interfacial energy to repel water effectively, however producing an effective controlled surface topography can be difficult or expensive to achieve. In addition, harmful solvents and costly processing methods are usually required, while effectiveness can diminish with environmental exposure over very short periods of time. Treatments unlike coatings allow a structure to 'breathe', reducing internal humidity problems while not being affected by chipping problems mitigating structural protection [20]. However although post curing of these treatments have been investigated by authors, it is unclear how these particulates altered the properties of the emulsions before and after application and the imparted performance. It is hoped that the work presented here will help the further development of this new field leading to enhanced organosiloxane emulsions; providing enhanced water repellence, better thermal insulation for structures, reduced bioreceptivity through photo-induced sanitisation, and negligible impact to aesthetical alteration of the substrate due to the relatively low concentrations required. Through these