Short Communication

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Durable Self-Cleaning Coatings for Hard Surfaces

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ABSTRACT

In this paper, an innovative approach for the development of self-cleaning coatings for hard surfaces is presented. The proposed scheme can yield enduring coatings which possess both anti-soiling and anti-static attributes that can be exploited in numerous industrial and commercial applications.

INTRODUCTION

Anti-soiling technologies for hard non-porous surfaces, based on easy-to-clean and self-cleaning coatings have received significant interest in research and commercial applications. For outdoor uses, such as solar systems, easy-to-clean hydrophobic coatings have perhaps bigger potential since the major portion of atmospheric pollution is inorganic. On the other hand, hydrophilic self-cleaning coating usually exhibits strong antistatic functions, although they seem to suffer from poor performance in real-field conditions. There is an increasing demand for cost effective coatings that combine the "best of the two worlds", i.e., the anti-soiling behavior of hydrophobic coatings with the anti-static attributes of hydrophilic coatings, within a single multifunctional approach for various substrates. Such configurations may be developed, for example, using common polymeric binders modified with organofunctional silane coupling agents. The resulting structures, however, have usually an increased thickness, which reduces transparency, and consequently applicability. Therefore, thin anti-soiling coatings are preferable.

The most common methods for fabricating hydrophobic coatings are, either the deposition of low surface energy materials, or substrate micro/nano-roughening which can be also accompanied by the deposition of low surface energy coatings. The second approach usually leads to the development of superhydrophobic coatings, the durability of which, however, is rather limited, due to low interfacial strength among the components embedded. In contrast, deposition of low surface energy materials directly on the substrate usually leads to highly adherent nano-layers, due to their chemisorption and covalent bonding with substrate active groups. Therefore, it is no surprise that many studies still focus on the development of hydrophobic coatings having water contact angles below 1200. Most of them primarily aims to the development of strong self-cleaning attributes to address the problem of outdoor pollution, such as industrial waste, exhaust/woodburning gases, acid rain, biological organisms and pollen as well as increased dust accumulation, such as desert dust storm. On solar systems especially, where unhindered light transmittivity is critical, the coating's anti-soiling attributes are often combined with anti-reflective properties. Unfortunately, the latter usually degrade abruptly, due to coating's abrasive wear during regular cleaning. Moreover, hydrophobicity losses result in poor anti-soiling performance. In other words, the combination of both anti-reflection and anti-soiling properties may sound attractive, but the direct benefits in actual transmission are rather questionable, especially when considering the possibility of soiling losses being higher than reflective losses, either due to non-uniform shading or due to location distinctiveness. Considering the above, durability of the coating is of primary importance, perhaps more important than any of its other attributes.

A vast number of techniques are available for the development of hydrophobic anti-soiling coatings for hard surfaces, such as chemical vapor deposition, plasma etching, self-assembly and layer-by layer methods, sol-gel, electrochemical deposition, electrospinning and wet chemical and hydrothermal routes. Most of them, however require strict processing conditions, expensive equipment and complicated chemical synthesis. Sol-gel is perhaps the most facile way for producing transparent hydrophobic coatings. The primary precursor materials used are alkoxysilanes. The latter can undergo hydrolysis and condensation reactions, thus creating covalently bonded hybrid networks with surface hydroxyl groups, resulting in their excellent adhesion to inorganic siliceous

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substrates, such as glass and metals. However, such formulations usually have limited durability on non-polar substrates, such as plastic substrates which lack hydroxyl groups.

An interesting perspective is the development of a durable hybrid coating comprising a quaternary ammonium silane (Si-QUAT) and an organic polysilazane (OPSZ). The two silanes should be preferably separately hydrolyzed before mixing. Subsequent aging of the mixture can yield a highly durable modified structure with enhanced self-cleaning ability. More specifically, Si-QUAT molecules consisting of up to three hydrolyzable alkoxy groups can promote strong crosslinked networks, enhance adhesion to various substrates and enable hydrophobic attributes. They can also provide enhanced anti-static functions due to the lubricity of their long aliphatic chain as well as to the surfactant capacity of N+R3 polar group, which allows interactions with moisture, thus increasing conductivity of the coating's surface and consequently, reducing its tendency to accumulate static electric charge. In addition, OPSZ are silicon-based materials with alternating silicon and nitrogen atoms, creating Si-N-Si structural frameworks. In comparison to common silanes and silicon compounds, they can be converted into organic/inorganic pre-ceramic materials.

Because of their structure and their reactivity in the presence of moisture, they are compatible with either siloxane or silicon-based materials having a reactive functional group, namely a silanol group. Hence, both Si-QUAT and OPSZ can undergo simultaneous hydrolysis and condensation reactions and transformed into a highly interconnected colloidal network. The latter consists of mutually crosslinked OPSZ and Si-QUAT nanostructures, which positively affect adhesion, hardness, uniformity and smoothness of the coating. Curing of the latter can be realized at ambient temperatures, thus creating hard, optically clear solid films. In such configurations, the polysilazane can provide a solid matrix able to adhere strongly on any surface, while additionally offering increased UV, abrasion, chemical and thermal resistance. At the same time, it can strongly bind to Si-QUAT molecules. The non-polar tail of the latter reduces the coating's surface energy, thus enabling pronounced anti-soiling attributes. Moreover, hydrophobicity can be enhanced due to co-condensation of OPSZ. As a result, a dense organic-inorganic Si-O-Si/Si-N-Si copolymer which can exhibit surface energies of the order of 30 mN/m is easily achieved.

The coating can be easily applied either by hand polishing or by HVLP. Curing takes place within 7 days under ambient conditions. Depending on the OPSZ concentration in the silane mixture the dry film thickness of the coating can be adjusted anywhere between 1-10μm. Increasing however the OPSZ concentration beyond a critical threshold, results in burying the Si-QUAT molecules into the OPSZ matrix, thus restricting their functionality. The above findings have been validated for varying OPSZ to Si-QUAT ratios and different smooth non-absorbent surfaces, either hydroxylated or not. Microstructure study and morphology analysis and their correlation to mechanical properties of the coating with the aid of analytical tools are currently underway. Besides anti-soiling attributes, other functionalities such as anti-adherent, anti-graffiti and anti-corrosion are also possible, due to the inherent barrier properties of OPSZ.

CONCLUSION

An innovative methodology for the development of self-cleaning coatings for all smooth, non-absorbent surfaces is hereby briefly described. This can be exploited in various applications offering long-lasting protection to various surfaces.

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