Proceedings of the 2nd International Conference on Functional Materials and Civil Engineering
DOI: 10.54254/2755-2721/98/20241114

Innovations and Insights in Superhydrophobicity: Learning from Nature to Surpass It

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Abstract. Superhydrophobic surfaces, inspired by natural examples, have emerged as a promising area of research due to their unique properties. This paper reviews the characteristics and challenges of creating surfaces that can exceed the capabilities of natural counterparts. Key aspects include surface tension, contact angle, and morphology, with a focus on natural models such as lotus leaves and gecko feet. The paper highlights knowledge gaps in durability and manufacturing, and discusses design challenges in achieving roughness, hierarchy, and balance between hydrophobicity and durability. Methods for enhancing durability, such as chemical and roughness restoration, are explored, alongside the potential of AI in optimizing material and design choices. The paper concludes with recommendations for future research directions in the field.

Keywords: nature superhydrophobicity, multifunction application, self-healing, artificial intelligence.

1. Introduction

Biomimetics, coined by Otto Schmitt, emulates nature's strategies to solve human problems, spurring innovations in materials and devices. This interdisciplinary field, including bionics and biognosis, collaborates across biology, physics, and engineering, to mimic biological functions and principles. Notably, natural phenomena like the lotus leaf's self-cleaning and spider silk's strength [1-6] have inspired advancements in robotics and materials science, demonstrating biomimetics' potential for sustainable and efficient solutions.

1.1. Overview of Superhydrophobic Surfaces

Superhydrophobic surfaces, with water contact angles exceeding 150 degrees and sliding angles below 10 degrees, exhibit strong water-repellency due to their micro/nanostructured surfaces and low surface energy. These surfaces, inspired by the lotus effect, are promising for self-cleaning and anti-fouling applications, including ice prevention in automotive and aerospace industries, biofouling reduction in maritime settings, and hydrodynamic drag decrease, prompting extensive research on their fabrication and commercial scaling.

1.2. Knowledge gaps

Self-healing hydrophobic materials can autonomously repair surface damage to preserve superhydrophobicity, crucial in liquid-exposed environments. This is achieved through complex chemical and physical interactions, such as microcapsule-encased healing agents or reversible bond mechanisms that enable material rejuvenation.

Superhydrophobic surfaces, despite offering self-cleaning and anti-fouling benefits, face durability challenges due to their low surface energy and micro/nanostructured porosity, which make them prone to mechanical and environmental degradation. Researchers are developing strategies to enhance their mechanical and chemical robustness, including cross-linking agents and nanoparticle integration. Balancing manufacturing techniques with cost-effectiveness and safety is crucial, with toxicity assessments and biocompatibility research needed to address safety concerns for widespread application.

1.3. Scope and Objectives

This review comprehensively analyzes the principles, characteristics, and fabrication methods of natural superhydrophobic surfaces, highlighting their biological features that guide artificial material design. It critically assesses current limitations and identifies knowledge gaps, proposing potential research directions for superhydrophobic technology advancement.

2. Characterization of Superhydrophobic Surfaces

Because equations such as the Young-style equation used to characterize surface energies have been explored in depth in other articles, this article focuses on other aspects of superhydrophobic characterization.

2.1. Surface Tension, Surface Energy, Contact Angle, and Contact Angle Hysteresis

Surface energy and surface tension are crucial factors that influence the wettability of materials. Surface energy refers to the work required to increase the surface area of a liquid, and it is correlated with the liquid's surface tension, which is the force acting on the surface of a liquid to minimize its area. In the context of superhydrophobic surfaces, having low surface energy is essential as it promotes non-wetting behavior. This is achieved by utilizing materials with low surface energy and creating micro- and nanostructured surfaces that trap air, thereby reducing the contact area between the liquid and the solid surface [7]. The contact angle is a measure of how a solid surface is wetted by a liquid and is defined as the angle formed at the three-phase contact line where the solid, liquid, and vapor phases meet. A contact angle greater than 90° indicates hydrophobicity, while a contact angle greater than 150° is typically associated with superhydrophobic surfaces. Contact angle hysteresis, which is the difference between the advancing and receding contact angles, is a measure of the surface's resistance to wetting and dewetting. It is a significant parameter for characterizing the dynamic behavior of superhydrophobic surfaces [8].

2.2. The Role of Surface Texture and Chemistry in Natural Superhydrophobic Surfaces

The surface morphology of superhydrophobic surfaces, analyzed using techniques such as scanning electron microscopy (SEM) and atomic force microscopy (AFM) [9], is critical in determining their wetting behavior. The micro- and nanostructured features on these surfaces can create a Cassie-Baxter state, where the liquid is suspended on top of the surface, supported by trapped air pockets. This leads to high contact angles and low contact angle hysteresis, defining the superhydrophobic behavior. Furthermore, breakthrough pressure [10], the minimum pressure required for a liquid to penetrate a surface and breach the air barrier, is an important parameter for evaluating the performance of these surfaces in applications such as self-cleaning and anti-icing. Furthermore, the critical contact angle is the threshold angle at which a surface transitions from hydrophobic to superhydrophobic behavior and

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plays a crucial role in designing and characterizing superhydrophobic surfaces with tailored wetting properties.

Natural superhydrophobic surfaces, such as lotus leaves and butterfly wings, have inspired the design of artificial superhydrophobic surfaces. The surface texture and chemistry of these natural surfaces play a crucial role in their superhydrophobic behavior. The combination of micro- and nanostructured surfaces with low surface energy coatings replicates the non-wetting properties observed in nature. By studying these natural surfaces, researchers can gain insights into the design principles for creating durable and effective superhydrophobic surfaces.

3. Natural Superhydrophobic Surfaces

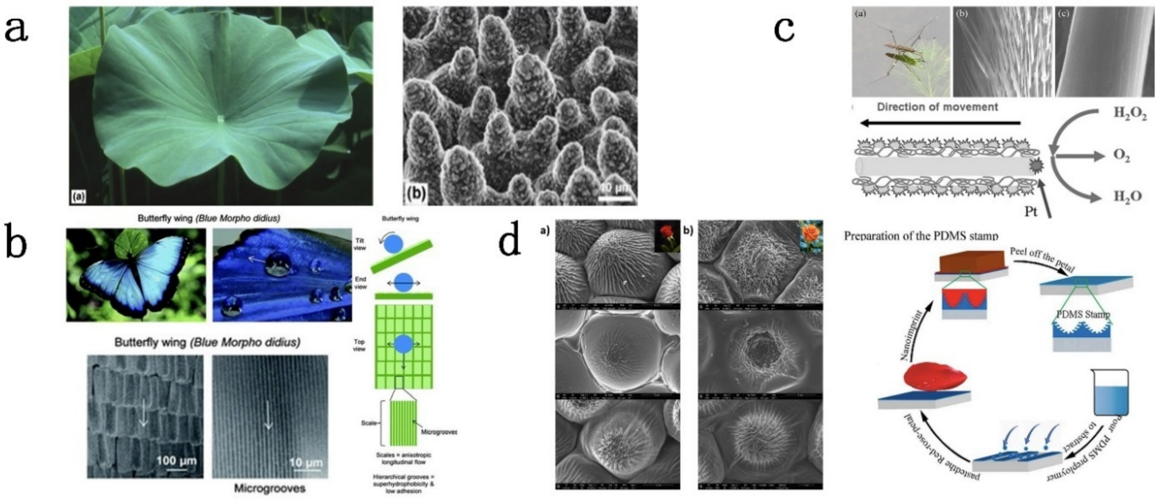


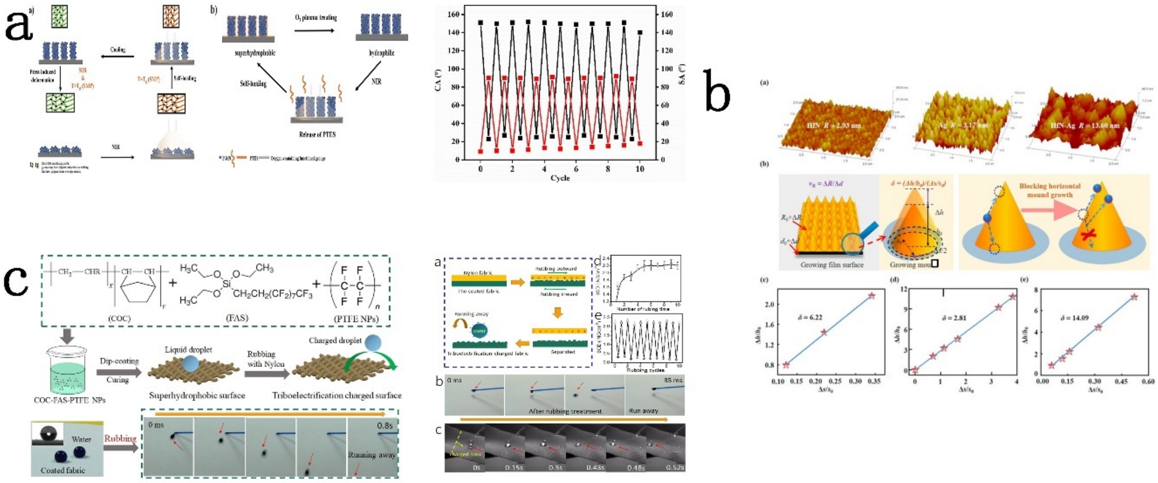
Figure 1. Examples from nature and their microstructure. a. [11] b. [12] c. [13] d. [14]

3.1. Nature examples

In the realm of nature, superhydrophobic surfaces distinctively demonstrate self-cleansing and water-repelling capabilities, attributes that stem from their intricately designed micro-nano architectures. The lotus leaf (**Figure 1.a**), for instance, features a dual-scale micro/nano structure, further complemented by a waxy film, which confers a contact angle greater than 150 degrees. This natural wonder serves as a bio-inspiration for creating innovative materials suitable for self-cleaning glass and anti-fouling fabrics. Butterfly wings (**Figure 1.b**), a fusion of structural color and superhydrophobicity, act as natural photonic crystals, holding potential for a spectrum of applications, from self-cleaning surfaces to advanced waterproof materials and microfluidic systems. Water striders (**Figure 1.c**) adeptly navigate aquatic environments with their legs coated in superhydrophobic hierarchical micro/nano structures, balancing on the water's surface by harnessing curvature forces over buoyancy. These coatings generate an air pocket capable of supporting weights beyond mere flotation, enabling sophisticated adjustments to buoyancy for prey capture, influenced by body size and hair traits.

By emulating these natural models, scientists and engineers are capable of synthesizing materials that mirror these functionalities, thus enhancing human convenience. Additionally, the superhydrophobic properties of rose petals, resulting from their intricate hierarchical microstructures, give rise to high contact angles and adaptable adhesion, widely recognized as the "petal effect." Comparative analysis of Freedom Rose and Mariyo Rose **(Figure 1.d)** varieties has elucidated diverse wetting behaviors, which can be successfully replicated through soft-lithography utilizing polydimethylsiloxane (PDMS). The variations observed in cellular structures also impact hysteresis characteristics. Furthermore, ice adhesion experiments and environmental scanning electron microscopy (ESEM) analysis of micro-condensation have uncovered sophisticated interactions between surface topography and the behavior of water and ice, revealing dual condensation mechanisms and mixed wettability. These insights offer valuable bio-inspiration for water management strategies. By integrating this knowledge, our comprehension of the multifaceted expressions of superhydrophobicity in nature is expanded, as is the potential for their application across various domains.

3.2. Conclusion



a. 【16】Schematic illustration of both surface structural(left) and surface chemistry(right) recovery of the PTES@MS@SMP – CS surface
b. 【18】(a) Surface topography image of pure HfN, pure Ag and Ag-doped HfN film with thickness of about 1.5 μm. (b) The microcosmic growth process of surface mounds during film growth. (c, d, e) The effective mound growth coefficients of Ag, HfN and Ag doped samples, respectively.

Figure 2. Surface self-healing process and its mechanism

Analyzing the highlighted examples, the defining features of biological superhydrophobic structures can be ascribed primarily to key facets. Foremost is the microtopography of these surfaces, characterized by pronounced roughness, which facilitates the emergence of significantly higher contact angles on the microscale. This enhanced contact angle effectively minimizes the interaction surface between water molecules and the material, substantially bolstering the hydrophobic response. Furthermore, these structures are frequently coated with materials of low surface energy, such as waxes or oils, naturally occurring or synthetically applied, which markedly strengthen their hydrophobic traits. Finally, biological superhydrophobic surfaces capitalize on their intricate microstructure to produce a distinctive cushioning mechanism that efficiently impedes water penetration, inherently reinforcing their hydrophobic characteristics. It is the synergistic combination of these attributes that endows biological superhydrophobic surfaces with their unparalleled waterproofing abilities

4. Developing Durable Superhydrophobic Surfaces

Surface roughness plays a pivotal role in determining superhydrophobicity, where the arrangement of topography, rather than its absolute scale, predominantly governs wettability, as substantiated by impedance spectroscopy. The presence of multiscale roughness hierarchies is indispensable for maintaining stability and durability, effectively forestalling non-hierarchical phase transitions. Micro/nanoscopic air pockets significantly augment superhydrophobicity, a phenomenon demonstrated by both microscopic observations and insulin pen titration.

Any commercial application of superhydrophobic surfaces requires the produced coatings to be extremely durable. One approach to enable such a development is through self-healing surfaces. The significance of self-healing superhydrophobic surface technology is pronounced, primarily due to its ability to rapidly revert to its original superhydrophobic state post-damage, substantially enhancing material durability and reliability. For instance, researchers such as Qin [15] have successfully developed an ultra-fast self-healing superhydrophobic surface, which can recover its macrostructure, microtextures, mechanical strength, and hydrophobic properties within an extremely brief period, even

DOI: 10.54254/2755-2721/98/20241114

after severe damage. Such self-healing capability is crucial for the practical application of artificial superhydrophobic surfaces, playing an indispensable role, especially in sectors such as self-cleaning, anti-icing, and corrosion resistance.

4.1. Restoration of Surface Chemical Composition and Surface Roughness

Self-healing superhydrophobic surfaces, which can be categorized into two types, are engineered by constructing microscale structures and applying low-energy coatings. These surfaces are designed to repair themselves using external stimuli such as heat and light. For instance, Hou (**Figure 2.a**) et al.'s research focused on rejuvenating the surface chemistry through the use of near-infrared (NIR)-activated microcapsules that release polydimethylsiloxane (PDMS) for chemical restoration and shape memory polymers (SMPs) for structural recovery. Additionally, Zhou [17] et al. developed a robust, self-healing coating that harnesses static electricity to enhance superhydrophobicity, thereby promoting self-cleaning and liquid repellency (**Figure 2.c**). The restoration of surface roughness is another critical aspect of self-healing mechanisms. The Wang (**Figure2.b**) group innovatively achieved ultra-hydrophobicity in rigid inorganic films with exceptional durability by employing a surface ultra-roughening strategy. This strategy involved creating silver-doped hafnium nitride films with a vertically aligned growth structure, where the inherent non-wettability and chemical inactivity of silver atoms played a crucial role in stimulating the upright formation of surface asperities. This unique attribute allowed for precise control over the roughening process, thereby enhancing the film's superhydrophobic efficacy and longevity. The interplay between surface roughness and wettability is also a key factor, as roughness can increase the effective contact area for liquid-solid interactions, potentially enhancing wettability. However, excessive roughness can lead to a decrease in wettability by creating air pockets and reducing the effective contact area. Therefore, striking the right balance between roughness and wettability is essential for optimizing performance in various applications.

4.2. Versatile Integration

To achieve the restoration of superhydrophobic surfaces, researchers have developed dual restoration systems that address both the chemical composition and the microstructure of the surfaces. Fu's [19] group fabricated self-healing foams using a combination of PDMS-PUa, multiwalled carbon nanotubes (MCNTs), and salt. These foams are capable of repairing both chemical and mechanical damage, making them suitable for oil-water separation applications. Liu's [20] elite team, on the other hand, established a superhydrophobic film composed of vinyl terminated polydimethylsiloxane (V-PDMS), vinyl triethoxychlorosilane (VTES), and silica particles (28SiO2) This film demonstrates durability by reproducing its surface roughness, allowing it to withstand 75% damage to the circulation system and opening the water pattern design.

Zhang [21] et al. further developed a durable superhydrophobic surface with hierarchical roughness, which is efficient for water collection. This surface shows chemical stability and holds potential for addressing water scarcity issues. These advancements in the integration of superhydrophobic surfaces with various functionalities and properties demonstrate the versatility and potential of these surfaces in various applications.

4.3. The Durability of Self-Healing Superhydrophobic Surfaces and Practical Application Challenges

Self-healing superhydrophobic surfaces show promise in repairing physical damage but struggle with chemical challenges like corrosion. The need for external triggers limits spontaneity, and performance in aquatic environments is poor. Understanding of repair mechanisms is incomplete, and despite years of research, practical applications are limited. Concerns about durability and high costs hinder widespread use, calling for more research to improve performance and reduce costs for real-world deployment.

5. Material Considerations

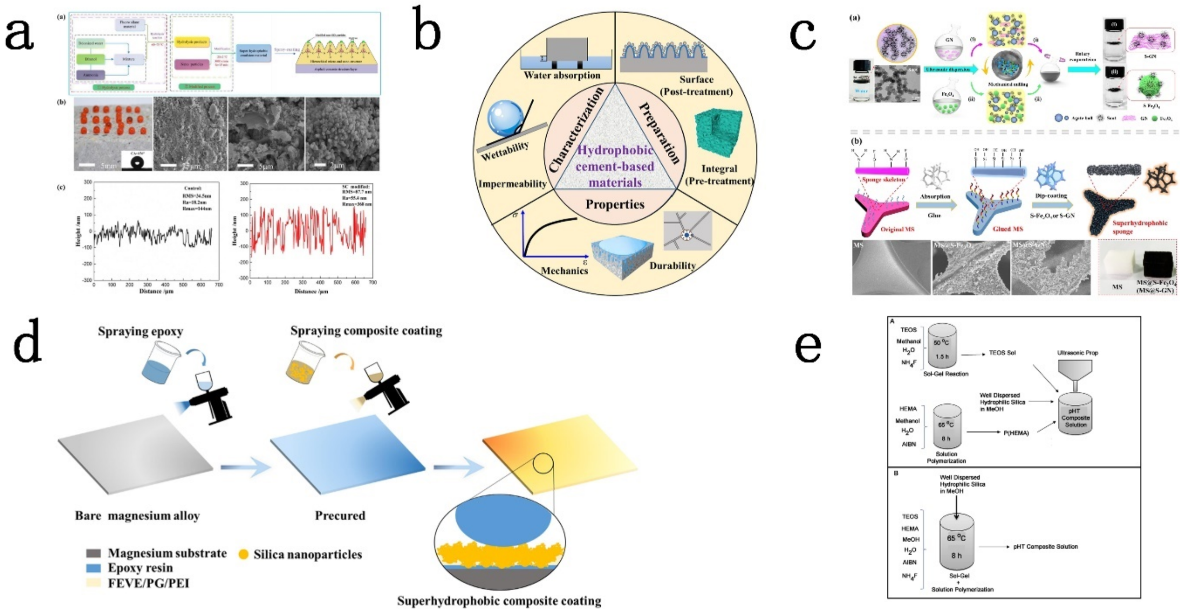


Figure 3. Surface spraying mechanism demonstration. a. [22] b. [23] c. [25] d. [24] e. [26]

5.1. Selection of Base Materials

In the domain of hydrophobic material substrates, a careful evaluation of various candidates such as polydimethylsiloxane (PDMS), epoxy acrylate (EPA), silica particles (SiO2), and carbon nanotubes is essential, with the final selection dependent on the specific requirements of the intended application. For example, the synergistic use of PDMS and EPA has proven highly effective in creating three-dimensional hydrophobic composites with superior mechanical properties and self-healing capabilities.

Similarly, the strategic combination of carbon nanotubes with SiO2 aerogel has significantly improved the anticorrosive properties of coatings on Q235 steel. The choice of substrate is critical, as demonstrated by Wu et al. (**Figure 3.a**), who showed that while hydrophobic modification of concrete enhances waterproofing, it may compromise mechanical integrity. Ongoing research investigates how substrate characteristics like pore structure and topography affect hydrophobic coating effectiveness and the impact of different modification techniques on hydrophobicity. The selection of hydrophobic substrates greatly influences functional performance, with a focus on materials such as concrete, polymers, and metals. Material properties and modification strategies, including both surface and bulk applications, are vital, as highlighted by Yao (**Figure 3.b**) et al., to enhance durability and properties without sacrifice mechanical strength. Future research should concentrate on maintaining hydrophobicity over time and understanding the underlying mechanisms. The analysis should concentrate on the influence of substrate properties like pore structure and surface texture on hydrophobic coating functionality, the effects of various modification methods on outcomes, and the relationship between substrate/modification choices and performance indicators such as water contact and roll-off angles, as well as durability.

An in-depth examination of these issues will clarify the fundamental relationships between the performance of hydrophobic substrates, structural dynamics, and modification procedures, providing theoretical direction for the synthesis and refinement of hydrophobic materials. The cornerstone of this research is to pinpoint the optimal substrates and modification methods to achieve superior hydrophobic performance and longevity. Concurrently, due attention must be allocated to the influence of substrate modification on other material characteristics to ensure the material's viability for a wide spectrum of applications. Ultimately, the objective is to refine the performance of hydrophobic materials through

DOI: 10.54254/2755-2721/98/20241114

strategic substrate selection and modification tactics while maintaining their long-term stability and applicability.

5.2. Coating Techniques

The preparation techniques of coating materials and their intrinsic properties play a decisive role in achieving superhydrophobic characteristics. The application of diverse methods such as spraying, deposition, and sol-gel processes not only shapes the microtopography of the coating surfaces but also profoundly influences their mechanical and chemical properties. These techniques facilitate the fabrication of everything from basic binary coatings to complex composite coatings with multilevel micro-nano structures. The following section elaborates on these three methods.

Cui et al. (**Figure 3.d**) devised a robust superhydrophobic coating with enhanced mechanical stability and resistance to thermal and chemical agents, suitable for self-cleaning and anti-icing uses due to its cost-effective production. Similarly, Xu's (**Figure 3.c**) team produced superhydrophobic particles from waste materials for applications in oil-water separation, while Kaya's (**Figure 3.e**) one-step sol-gel approach created transparent, superhydrophilic, and anti-fog surfaces with optimal properties at 20 wt% silica content, ideal for industrial products.

6. Future Directions, Innovations and Conclusion

6.1. Recommendations for Future Research

Future research on superhydrophobic surfaces should prioritize the development of micro-nanostructured architectures, advanced chemical tailoring, and self-healing abilities, aiming to integrate multifunctional coatings for enhanced durability and applicability. By drawing inspiration from biomimicry and biological integration, researchers can address critical challenges such as instability, susceptibility to degradation, and the need for multifunctionalization without compromising hydrophobicity. The fabrication process should be optimized for industrial-scale production, with a strong emphasis on environmental sustainability. Innovative theoretical and experimental approaches are necessary to unravel the fundamental principles of these materials, enabling advancements in self-healing and multifunctionality. This research will not only drive the widespread use of superhydrophobic surfaces in applications such as water treatment, environmental remediation, and smart devices but also foster sustainable and economic growth.

6.2. Final Thoughts :Identify the trade-offs in superhydrophobic surfaces, what can AI help with?

Artificial intelligence (AI) has unleashed its tremendous potential within the realm of materials science, significantly expediting the discovery process and accurately predicting material properties, thereby demonstrating unparalleled efficacy. Machine learning algorithms have achieved significant milestones by discerning intricate patterns and trends within the vast materials landscape, effectively steering the synthesis of innovative materials. These algorithms excel in processing complex, high-dimensional datasets and incorporate knowledge from physics and chemistry to enhance predictive precision. In the context of structural materials research (27, 28), AI adeptly elucidates the complex correlations between microstructure and macroscopic properties, thereby facilitating optimal material design.

In the field of material treatment and manufacturing, AI's integration is crucial. When combined with machine learning and high -throughput experiments, researchers can quickly screen and determine the best material combination, transition from traditional tests and error methods to data -driven paradigms.AI auxiliary simulation and design may greatly reduce experimental costs and speed up the timetable, and equipped with strong new tools for material scientists.

The potential of AI's in the super hydrophobic surface has not been developed to a large extent, providing time -saving solutions for the structure optimization of material adjustment and bionic design. Its powerful data processing capabilities can enhance theoretical models and can broaden biology analysis.

DOI: 10.54254/2755-2721/98/20241114

Author contributions

Yuhan Zhang conducted this paper with the assistance of Zhengzhong Huang, Daniel Tianrui Li and Peilin Li.

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