Greener Solutions to PFAS in Aftermarket Carpet Treatments

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Final Report

December 18, 2020

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Acknowledgements

We would like to thank Dr. Simona Balan, Senior Environmental Scientist at the California Department of Toxic Substances Control for welcoming us and guiding our team throughout the semester. We would also like to thank Dr. Megan Schwarzman, Dr. Thomas McKeag, Dr. Billy Hart-Cooper, and Kimberly Hazard for creating an uplifting and creative space for us to delve into the adoption of more sustainable chemistry. Thank you to all five for their continued dedication, time, and support to this year's cohort of the *Greener Solutions* course.

Executive Summary

Per- and polyfluoroalkyl substances (PFAS) have been used for hydrophobic and oleophobic applications since the 1950s when 3M developed PFAS-containing products, including TEFLON and Scotchgard.[1] Since then, PFAS have frequently been used as a durable stain and water repellent to protect fabric, furniture, and carpets from stains.[1] However, concern over the use of PFAS has grown over the past several decades as its environmental persistence and toxicity and a wide range of serious health effects have been identified. While the response to these concerns has often been to replace existing PFAS with other PFAS chemical analogues, these analogues often have similar or in some cases worse hazards than the original compounds.

The California Department of Toxic Substances Control (DTSC) recently identified PFAS in aftermarket treatments as a potential priority product. There is an urgent need for the chemical production of PFAS to be phased out; however, there is currently a lack of knowledge of feasible alternatives to PFAS that provide the same water and oil repellency. This report aims to identify current and potential materials that serve the same functions as PFAS without the associated risks. We explored the formulations of currently available aftermarket treatments, as well as conducted a literature search of water- and oil-resistant treatments for fabrics and other materials such as paper and electronics. We determined performance and health benchmarks and used these to compare alternatives from a broad range of applications and sources.

We have identified several alternatives to PFAS with lower hazard and similar performance. These are broken into three categories: Waxes and Oils, Biopolymers, and Silicon-Based Materials. Waxes and oils currently used for hydrophobic treatments include paraffin waxes, beeswax, and mink oil. While these provide high water-resistant performance, their oleophobic performance is limited, and there are concerns over their sustainability due to their sourcing from oil-based sources or animals. These strategies served as launch points for exploring more sustainable strategies.

The biopolymers studied include chitosan and cellulose. Chitosan is a naturally abundant polymer with strong antimicrobial properties and biodegradability. Acute aquatic toxicity and skin and eye irritation ratings imply that chitosan does present some drawbacks as a potential strategy, so it should be used with some caution. While it can also impart hydrophobicity onto carpet fibers, chitosan may be most beneficial acting as a cleaning agent in a solution containing other hydrophobic and oleophobic instilling compounds. Another innovative chemical we examined was cellulose nanocrystals (CNCs). Although CNCs face more data gaps in the health and technical criteria than our other alternative solutions, its unique structure allows for potential modifications that, given time and proper lab experiments, could improve its shortcomings.

The final category was silicon-based materials, including silicon dioxide nanoparticles (SiNPs) and silicones. SiNPs and silicones are already ubiquitous in many household materials, including fabric treatments. Because silicon dioxide is an earth-abundant inorganic material, this is an economically feasible and sustainable solution. This category was the only PFAS alternative that exhibited oleophobic performance in addition to hydrophobic performance. However, concerns remain regarding nanoparticle- and polymer- specific human and environmental toxicity, and the durability of these solutions must be explored further.

Our final recommendation combines chitosan with SiNPs to achieve not only protection against water- and oil-based stains, but exceed the utility of PFAS-based treatments by introducing antimicrobial activity as well. While this combination has not been used before to our knowledge, we believe it is a promising area for further exploration. With additional research, this novel solution will be an improvement to the human and environmental health hazards associated with PFAS.

Introduction

The Department of Toxic Substances Control's (DTSC) mission is broadly to "protect California's people and environment from harmful effects of toxic substances" via a variety of methods, including "encouraging the manufacture of chemically safer products."[2] Late last year, the DTSC published a report identifying textile and leather treatments containing perfluoroalkyl or polyfluoroalkyl substances (PFAS) as a potential priority product.[3] This classification would impose regulations on the priority product due to potential human and environmental exposure and adverse effects and encourage the identification and development of alternatives.

We aim to assist the DTSC in encouraging safer chemical manufacture by providing a comparative analysis of the technical, health, and environmental performance of current aftermarket carpet protector formulations as well as chemicals in development. Carpets are commonly made of nylon fibers which can readily absorb water or oil-based compounds.[4] Therefore, PFAS have been used in aftermarket treatments to impart stain/soil/grease resistance. PFAS-containing treatments can be applied to carpets anytime between the manufacturing of individual carpet fibers up until the moment that the carpet is in someone's home. During the 1950's, 3M developed Scotchgard, the first PFAS-based stain and soil-repellent designed for textiles.[5] Scotchgard will be used as our baseline comparison product due to its PFAS containing composition and its widespread consumer name recognition.[6]

PFAS chemicals have garnered notoriety due to their adverse environmental and health effects. To the best of our knowledge, the predominantly used PFAS in the aftermarket treatment industry consist of fluorinated polymers such as fluorochemical urethane.[7] While these polymers have little known bioaccumulation or toxicity, the small molecule monomers used to synthesize these polymers have many potential hazards. These monomers may escape into the environment during production, be present as impurities in the finished product, or result from degradation of the polymer during use or disposal of the product.[7] One ubiquitous degradation product of these fluoropolymers is fluorobutane sulfonate, which exhibits developmental, endocrinal, neurodevelopmental, and reproductive toxicity, among others.[8] Small molecule PFAS are also extremely resistant to degradation and bioaccumulation in the environment, causing concern both for their toxicity to aquatic life and, for some PFAS, global warming potential.[9] Their ability to transfer through lactation or transplacentally put infants and fetuses at special risk.[7] Short- and long-chain PFAS are often recognized for their persistence in the environment and bioaccumulation. However, intermediate degradation products, which may be short-lived relative to the ultimate degradation product, also exhibit concerning health effects.

The PFAS used as a comparison point for our strategies were perfluorobutanesulfonic acid (PFBS) and 6:2 fluorotelomer alcohol (6:2 FTOH) due to their role as stain repellents and synthetic components in current PFAS-containing aftermarket treatments. Although no clear evidence showed that these two PFAS chemicals have potential carcinogenic effects, other toxicities to humans and the environment still exist. For example, PFBS is the most frequent PFAS chemical found in the seawater and its developmental toxicity to fish has been identified.[7] 6:2 FTOH, a common building block of polyfluorinated polymers, has relatively low bioaccumulation and persistence, yet it can metabolize to several smaller PFAS upon ingestion or inhalation and subsequent metabolism. These metabolites, including 5:3 fluorotelomer carboxylic acid, perfluorohexanoic acid, and perfluoroheptanoic acid, persist within organisms longer than 6:2 FTOH itself and have toxic effects.[10,11] This demonstrates the necessity of understanding not only the toxicity profiles of building blocks of fluoropolymers and their environmental degradation pathways, but also their metabolic products. PFBS and 6:2 FTOH also present high hazards for developmental/reproductive toxicity, skin/eye irritation, and endocrine activity according to data from the European Chemicals Agency (ECHA) and The Endocrine Disruption Exchange, or TEDX (Table 1).

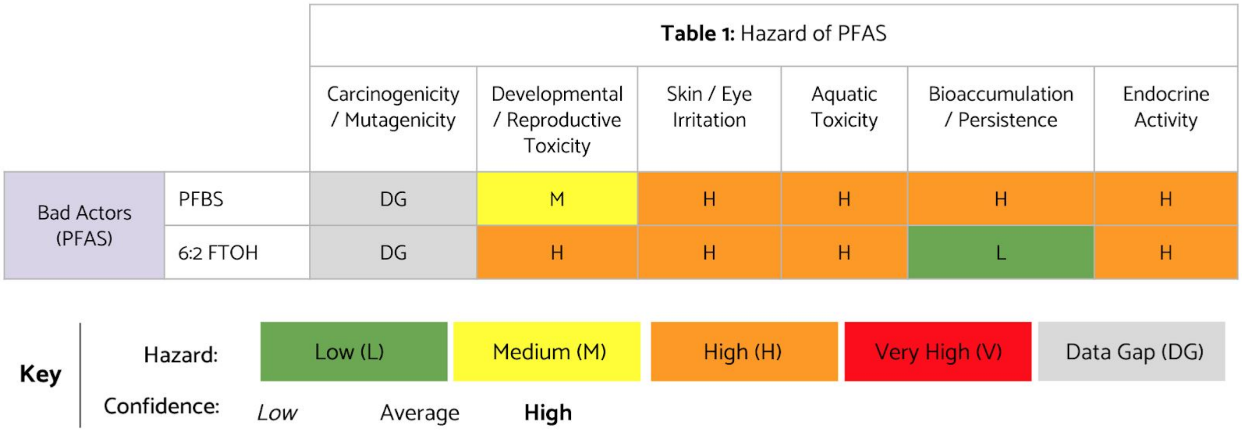

Table 1: Hazard of PFAS

		Carcinogenicity / Mutagenicity	Developmental / Reproductive Toxicity	Skin / Eye Irritation	Aquatic Toxicity	Bioaccumulation / Persistence	Endocrine Activity
Bad Actors (PFAS)	PFBS	DG	M	H	H	H	H
	6:2 FTOH	DG	H	H	H	L	H

Key

Hazard: Low (L) | Medium (M) | High (H) | Very High (V) | Data Gap (DG)

Confidence: *Low* | Average | **High**

The other components of aftermarket treatments used in conjunction with PFAS, like organic solvents which may be necessary to dissolve PFAS, must also be considered for both their separate and synergistic health effects. These solvents include isopropanol, xylenes, and acetone, all of which pose physical hazards due to their low flash points.[12] These chemicals are also volatile, exposing product users via inhalation upon use of the product. Exposure to these solvents produces numerous potential adverse health effects including organ damage upon multiple exposure, developmental toxicity, eye corrosivity, and acute aquatic toxicity, among others. The fabric protection industry, encompassing upholstery and apparel protection, was valued at $1.11 billion in 2018; this does not include the large industry of carpet and leather protectors.[13] There are many unknowns about this industry that our group aims to address: notably, the demographic information about users of these treatments, where they are most used, and the average frequency of use. Scotchgard is among the most popular and best-recognized fabric protectors, though there are numerous alternatives. These include products such as Teflon EcoElite, Trinova and Vectra, which do not publish information about their formulations but claim that fluorine is not present in their products. The consumer demand for alternatives to Scotchgard and other PFAS-based textile protectors is fairly high due to negative publicity about

PFAS and its health effects. Governmental regulation of PFAS in general is challenging since PFAS comprise a multitude of structures; while progress is being made toward regulating this class of chemicals, preventing regrettable substitutions is a significant challenge.

Approach

The main goal of the project is to determine alternative water and oil repellent strategies to confer stain resistance in carpets. The desired product is a liquid solution that can be directly applied onto the carpet, either through a spray formulation or an aerosol mechanism. Once the liquid solution dries, water and or oil repellency will be imparted on the carpet in a similar manner to the Scotchgard application, but with less hazardous effects. This project focused on at-home carpet treatments because information was more fruitful compared to the industrial carpet sector. Additionally, we are concerned with understanding the risks consumers face when they have carpets in their homes, so strategies have been developed with the consumer as the intended applicator. We focused on carpet protection as opposed to spot cleaning with the hope that meaningful protection-based strategies mitigate the need to use spot cleaners. Preventing stains from occurring in the first place drives our research, not cleaning them up once stains infiltrate the carpet. One of our proposed strategies presents antimicrobial, or cleaning, properties as well, which is an added bonus to the project. Finally, hydrophobicity is prioritized over oleophobicity because most stains, like beverage spills and pet accidents, are hydrophobic in nature. Hydrophobic data was more available compared to oleophobic data, but both hydrophobic and oleophobic alternatives are proposed to address water-based and oil-based stains, respectively.

Three primary categories of criteria were used to evaluate potential alternatives to PFAS-containing carpet protectors: health effects, protective performance, and manufacturing feasibility. The nature of this challenge requires that our proposed solution be applied to carpets, which are found in homes and regularly come into contact with skin. These treatments may be applied by either workers or consumers in an aerosol form, making respiratory irritation a significant concern. Therefore, avoiding skin and respiratory irritation is a strong priority for carpet and rug treatments. Additionally, potential alternatives should avoid the major health detriments of PFAS-containing treatments,[7] including carcinogenicity,[14] reproductive toxicity,[15] and endocrine disruption.[16] A notable characteristic of PFAS is their persistence in the environment;[9] our proposed solutions will ideally be easily biodegradable and lack aquatic toxicity. We also wish to avoid regrettable substitutions, in which new hazards not found in PFAS-containing treatments are introduced with the alternative strategy.

The health and environmental hazard scorecard used to evaluate each aftermarket treatment alternative is shown in Table 2. Health and environmental hazards were evaluated based on the Globally Harmonized System (GHS) hazard classification whenever this data was available for the specific chemicals and strategies evaluated. When considering human health specifically, substances with the highest level of hazard, indicating that the substances have demonstrated irreversible detrimental effects in humans, receive a classification of 1 or 1A. Those with strong evidence of detrimental effects, including those demonstrated in animal models, receive a classification of 1B, 1C, or 2A. Suspected health hazards receive a score of 2 or 2B, and chemicals with benign or mild and reversible effects receive a score of 3. Environmental toxicity is based on both the environmental persistence and toxicity to terrestrial or aquatic life. Persistence is measured in the number of days needed for a released substance to degrade in the environment, while aquatic toxicity is based on the tendency of the substance to accumulate in tissue and the dose at which it is lethal. Specific benchmarks for these values are given in the table below.

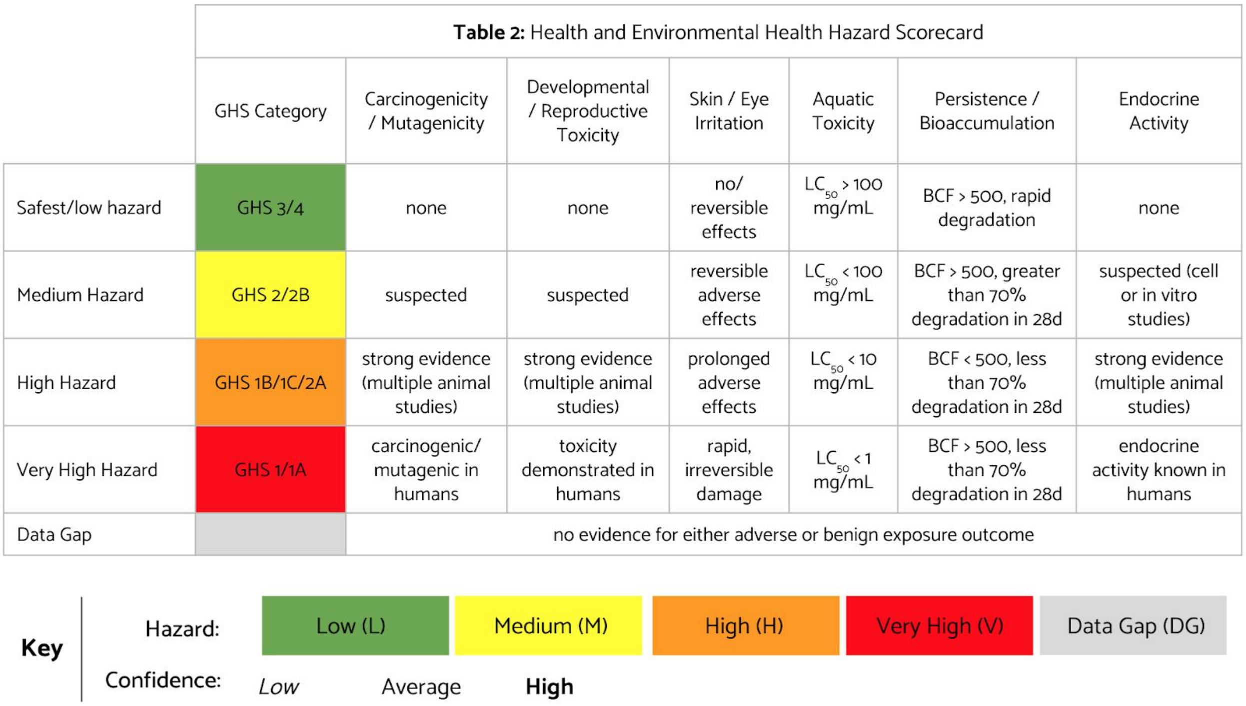

Table 2: Health and Environmental Health Hazard Scorecard

	GHS Category	Carcinogenicity / Mutagenicity	Developmental / Reproductive Toxicity	Skin / Eye Irritation	Aquatic Toxicity	Persistence / Bioaccumulation	Endocrine Activity
Safest/low hazard	🟩 GHS 3/4	none	none	no/ reversible effects	$LC_{50} > 100$ mg/mL	BCF > 500, rapid degradation	none
Medium Hazard	🟨 GHS 2/2B	suspected	suspected	reversible adverse effects	$LC_{50} < 100$ mg/mL	BCF > 500, greater than 70% degradation in 28d	suspected (cell or in vitro studies)
High Hazard	🟧 GHS 1B/1C/2A	strong evidence (multiple animal studies)	strong evidence (multiple animal studies)	prolonged adverse effects	$LC_{50} < 10$ mg/mL	BCF < 500, less than 70% degradation in 28d	strong evidence (multiple animal studies)
Very High Hazard	🟥 GHS 1/1A	carcinogenic/ mutagenic in humans	toxicity demonstrated in humans	rapid, irreversible damage	$LC_{50} < 1$ mg/mL	BCF > 500, less than 70% degradation in 28d	endocrine activity known in humans
Data Gap	⬜	no evidence for either adverse or benign exposure outcome					

Key

Hazard: 🟩 Low (L) 🟨 Medium (M) 🟧 High (H) 🟥 Very High (V) ⬜ Data Gap (DG)

Confidence: *Low* Average **High**

GHS data for potential aftermarket treatments was gathered from authoritative lists including GHS Japan, GHS New Zealand, and others. For chemicals and materials for which GHS data was unavailable, primary, peer-reviewed literature was consulted. When possible, data gathered from primary literature was converted to a GHS classification using quantitative cut-offs. In cases where this was not possible, the substance was added to a category based on the descriptions shown for each health or environmental endpoint illustrated in Table 2. In some cases, no data was available on an endpoint for several of our evaluated solutions; this is indicated with a gray color. In future tables throughout this report, both coloring and the symbols L for low, M for medium, H for high, V for very high, and DG for data gap will be used. Confidence will be indicated via formatting; a bold formatting (example: **L**) will be used for endpoints present with a GHS category and on one or more authoritative lists; a neutral formatting (example: L) will be used for endpoints which may not be present on an authoritative list but which are validated via multiple reviewed journal articles; and an italicized formatting (example: *L*) will be used for endpoints found in only a single study, or studies in which the results were inconclusive or unclear.

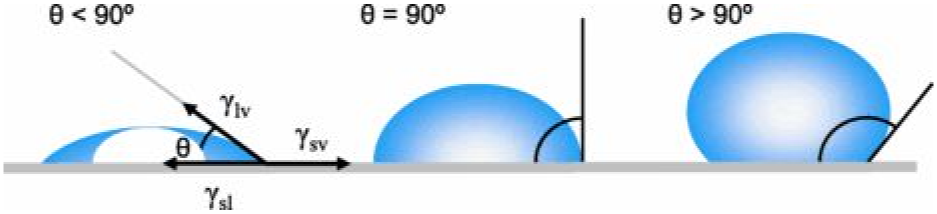

Figure 1. Contact angle illustration. Substances with a contact angle with water <90° are considered hydrophilic, while contact angles >90° are considered hydrophobic. Substances with contact angles >150° are considered superhydrophobic.[17]

While avoiding hazard, it is also important to meet the expectations of businesses and consumers regarding stain-resistant and economic performance of alternatives. Achieving the stain resistant performance of PFAS is challenging due to the uniquely powerful hydrophobicity and oleophobicity of this chemical class.[18] With this in mind, the performance of our alternatives are defined primarily by both hydrophobicity and oleophobicity, as well as secondary considerations of durability, washability, and manufacturing feasibility of the finished product. Contact angle with water or oil is an important measure of hydrophobicity and oleophobicity, respectively. This is defined by the angle of beading of water or oil when dropped on a surface spread with the substance of interest, as illustrated in Figure 1. Traditionally, a substance is considered hydrophobic or oleophobic with a contact angle of >90°, with higher contact angles indicating greater water or oil repellency and a contact angle >150° being considered superhydrophobic or superoleophobic.[17,19] Our alternatives will be evaluated for hydrophobicity based on this metric as well as oleophobicity based on similar logic. The ideal solutions have contact angles with water and oil >150° and adequate solutions having contact angles >90° (Table 3). For many in-home applications, medium performing stain resistance is likely adequate to achieve repellency for occasional and light spills.

In addition to stain resistance, our solutions are evaluated for their wash resistance and sustainability. Wash resistance is defined as the number of laundry wash cycles that a product can undergo without compromising stain resistant performance. This avoids the need for frequent re-application of the product. Our best solutions will be able to undergo greater than 20 wash cycles, with medium performers being amenable to greater than 5 wash cycles (Table 3).[20] Finally, the manufacturing feasibility and sustainability of the alternative will be addressed. A solution will be most likely embraced by a company if it can be synthesized using established protocols and infrastructure already part of the company; cost is also a significant factor for both companies and consumers. Ideal solutions will be derived from earth-abundant inorganic or easily farmed plant material, with less ideal solutions being animal-derived. Alternative materials derived from petroleum or involving lengthy synthetic routes will not be considered due to both environmental and economic concerns (Table 3). For several of the alternatives proposed, there may be data suggesting the product's protective characteristics without numerical values, or some data on performance may be missing. Confidence will be designated using the same formatting as aforementioned for the hazard scorecard, and alternatives for which there is currently not any information will be designated with a gray color and the term "data gap".

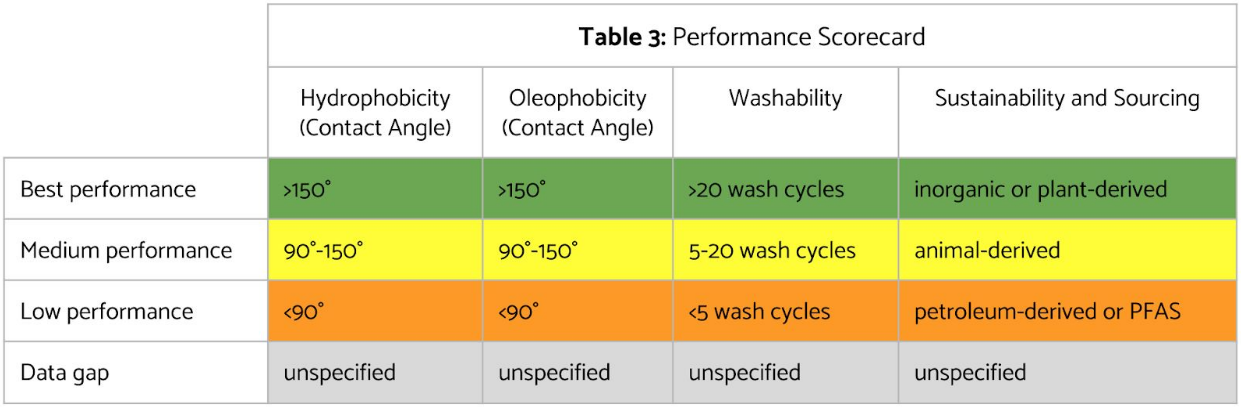

Table 3: Performance Scorecard

	Hydrophobicity (Contact Angle)	Oleophobicity (Contact Angle)	Washability	Sustainability and Sourcing
Best performance	>150°	>150°	>20 wash cycles	inorganic or plant-derived
Medium performance	90°-150°	90°-150°	5-20 wash cycles	animal-derived
Low performance	<90°	<90°	<5 wash cycles	petroleum-derived or PFAS
Data gap	unspecified	unspecified	unspecified	unspecified

Overview of Alternative Recommendations

We introduce three alternative recommendations: *Waxes and Oils*, *Biopolymers,* and *Silicon-Based Materials*.

We have labeled Waxes and Oils as *Inspiration* as a result of early identification of major limitations among the 3 strategies. Therefore, the *Waxes and Oils section* of the report does not provide as much detail as the *Biopolymers* and *Silicon-Based Materials* sections. Instead, we used them as inspiration for moving forward with the remaining alternative recommendations.

Alternative Recommendation: Waxes and Oils (Inspiration)

Strategy A: Paraffin Wax

Figure 2. Paraffin wax beads [21]

Background:

Paraffin waxes are utilized in numerous industrial applications including cosmetics, candle wax, and fabric finishing, among others.[22] Sourced from petroleum by dewaxing light lubricating oil stocks, there is some potential for use in aftermarket treatment solutions.[23]

Inspiration:

The use of paraffin waxes for carpet protection was biologically inspired by a natural product, beeswax. Beeswax is produced by honey bees of the genus Apis, and mainly consists of esters, fatty acids, and various long-chain alcohols. Beeswax is used as a waterproofing agent for many products, including shoes or clothes. Paraffin wax has a similar function as beeswax. Either of them alone can be used as consumer impregnation products for waterproofing outdoor clothing. Paraffins are long-chain hydrocarbons with the general formula, C_NH_{2N+2}, and they are widely used in industrial products, such as lubricant, fuel, and mineral oil. It is also one of the earliest technologies used in water repellency.[24]

Paraffins are hydrophobic in nature because of their long fatty acid chains that repel water. This water-repelling property occurs because of stronger intermolecular forces (hydrogen bonding and dipole-dipole interactions) between water molecules than between water molecules and fatty acid chains (only capable of Van der Waals interactions). Paraffins are bound to textiles via emulsions of paraffins containing metal salts of fatty acids, usually stearic acid. A paraffin chain cross section of fiber is shown in Figure 3. The metal ion, e.g. Zr_2, provides fixation onto the fiber and ensures that the water repellent groups have the right orientation on the fiber surfaces.[24] In this way, water droplets and mud run off easily and are much less likely to adhere to the fiber.[25]

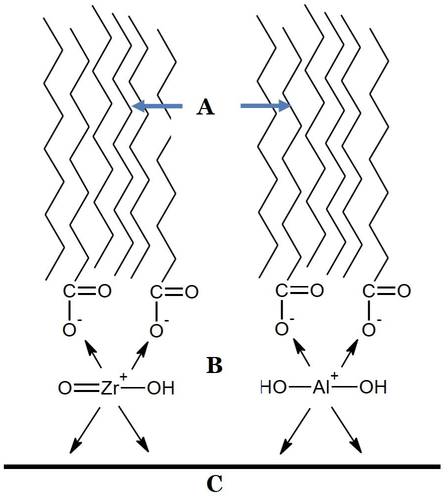

Figure 3. The metal ions, Zr^+ and Al^+, attach to the fiber (C) and ensure that the water repellent chains (A) are properly oriented.[24]

Technical Performance:

Technical performance of paraffin waxes and all other proposed strategies will be measured by contact angles, durability, and number of wash cycles. This data, when available, will be compared to the baseline chemical Scotchgard in the hopes that the alternative solutions will perform similarly or better than the current fluorinated chemicals used today.

In order to determine the most practical way to convert the paraffin wax into a sprayable form, it is necessary to understand how pH can affect nylon carpets and paraffins. One study found that for nylon and wool, paraffin chain anions absorb better in acidic solutions, and paraffin chain cations absorb better in basic solutions.[26] The zeta potential for nylon, which measures the interface charge between the solid and its liquid medium, fluctuated with change in pH; at a pH of 3 the adsorption was higher for anions and at pH 11, cations had a higher adsorption ability.[8] This is important to note because the Zirconium acetate paraffin wax utilizes the Zirconium cation to adhere to the nylon fabric; including it in a basic solution would likely increase the adsorption ability between the paraffin wax and nylon, thereby creating a stronger barrier between the carpet and incoming stains.

Several textile protecting products, such as Ecorepel, already incorporate paraffin waxes into their formulations. Another commercially produced paraffin-based product, a paraffin wax-polyolefin thermoplastic blend, has demonstrated potential for waterproofing of electronics.[27] The commercial production of paraffins is a strong indicator of waterproofing performance and feasibility, as strategies incorporating this technology are already on the market. Several measures of hydrophobicity and durability have been recorded. The contact angle with water and paraffin wax, at 109°,[28] nearly achieves the same performance as PFAS-containing TEFLON, at 111°.[29] While paraffin waxes do not exhibit inherent oleophobicity, additives may improve oil-repellent performance. The application of paraffin wax along with polydimethylsiloxane to textile fibers, for example, resulted in improved oleophobic performance.[30] Additionally, polymerization of long-chain stearic acid with citric acid applied to cotton textiles resulted in increased oil repellency while maintaining water repellency.[25]

Human and Environmental Health Hazards:

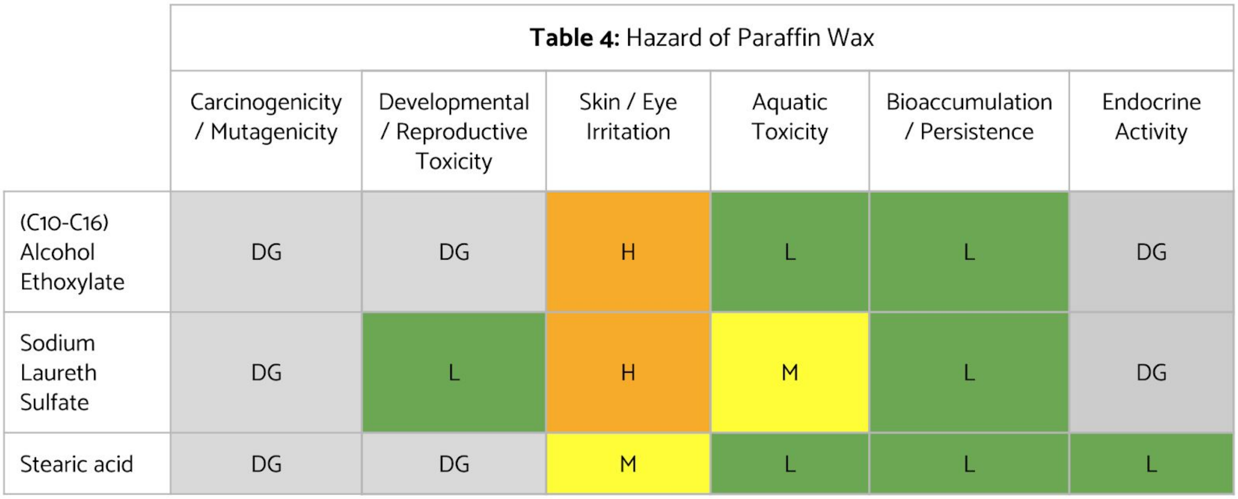

Table 4: Hazard of Paraffin Wax

	Carcinogenicity / Mutagenicity	Developmental / Reproductive Toxicity	Skin / Eye Irritation	Aquatic Toxicity	Bioaccumulation / Persistence	Endocrine Activity
(C10-C16) Alcohol Ethoxylate	DG	DG	H	L	L	DG
Sodium Laureth Sulfate	DG	L	H	M	L	DG
Stearic acid	DG	DG	M	L	L	L

The paraffins we identified are: (C_{10}-C_{16}) alcohol ethoxylate, sodium laureth sulfate, and stearic acid (Table 4).

Paraffins do not exhibit carcinogenicity and mutagenicity when data is available. According to the Australian Government Department of Health, sodium laureth sulfate is unlikely to cause skin tumors.[31] Additionally, stearic acid showed no mutagenicity in bacteria.[32] However, data gaps remain pertaining to the health effects on humans. Unfortunately, paraffin skin and eye irritation have similar hazard ratings compared to PFAS. For skin corrosion/irritation alone, stearic acid has the worst GHS classification: 1. Stearic acid, (C_{10}-C_{16}) alcohol ethoxylate, and sodium laureth sulfate were all classified as GHS 2/2A, thereby presenting moderate hazards for eye damage/irritation. Sodium Laureth Sulfate is the only paraffin with data corresponding to developmental and reproductive toxicity, and it has a low hazard rating (Table 4).

Paraffin wax is one of the three types of petroleum waxes. Since paraffin wax is derived from petroleum, it is important to acknowledge that petroleum is widely accepted among the scientific community as a highly unsustainable and non-renewable resource. Overall, paraffin waxes are an already-in-use waterproofing treatment with fewer human and environmental hazards than PFAS. Additives such as silicones may improve their oleophobic performance in addition to their hydrophobic performance. Serious concerns for this solution include its sourcing from petroleum, potential for causing skin and eye irritation, and hazards of additives that may be needed to confer oleophobicity.

Conclusion:

Ultimately, we decided to exclude this group of chemicals from our final list of suggestions due to its highly unsustainable sourcing methods and extremely high eye and skin irritation. However, this set of chemicals helped us establish our criteria, technical performance, and inspiration for our other strategies.

Alternative Recommendation: Waxes and Oils (Inspiration)

Strategy B: Beeswax

Figure 4. Beeswax.[33]

Background:

Beeswax is a sturdy wax secreted from bees' special glands that is used to form the structure of their hive. A mixture of several chemical compounds combine to form beeswax's general formula, $C_{15}H_{31}COOC_{30}H_6$. Beeswax is insoluble in water, slightly soluble in cold alcohol and completely soluble in fixed or volatile oils, chloroform, ether, benzene and carbon disulfide. Additionally, this wax has been used as a waterproofing agent for hundreds of years, and now is also widely used as barriers in food wrap and cosmetics.[12]

Technical Performance:

Beeswax shows high hydrophobicity, with a water contact angle of about 153° and moderate durability with 15 cycles.[34] Rubbing beeswax onto a surface like leather or canvas and then heating it allows the wax to seep into the materials' fibers and block water from passing through. So far, evidence has not indicated beeswax can act as an oil repellent material.

Health and Environmental Health Hazards:

Beeswax is a natural product with low hazard ratings overall. No significant acute animal toxicity, ocular irritation, skin irritation, or skin sensitization were observed. Additionally, beeswax is not a long term hazard, as it is not listed as carcinogenic. According to GHS, Beeswax is not classified for physical or health hazards either (Table 5). However, environmental toxicity data is not listed for beeswax, so more information and testing are needed to determine the environmental impacts.[35]

Conclusion:

In conclusion, beeswax has not yet been used in aftermarket carpet treatments, so there are multiple data gaps that need to be addressed, specifically concerning the feasibility of putting beeswax in a sprayable form. However, its high cost-efficiency, accessibility, low hazard, and strong hydrophobicity should be considered as inspiration for PFAS alternatives.

Alternative Recommendation: Waxes and Oils (Inspiration)
Strategy C: Mink Oil

Figure 5. Mink oil used in a leather waterproofing polish.[36]

Background:
Mink oil is a pale yellow liquid, obtained from the fatty tissues of minks.[37] Mink oil is a mixture of the mink's natural glycerides, mainly triglycerides, of 14 to 20 carbon chain fatty acids.[37] Given its chemical properties, mink oil is reportedly used in over 100 products, including leather boot care, hair conditioner, lipstick, and moisturizers.[37] While mink oil is popularly known as a waterproofing agent in the form of a shoe polish, it has been used in products that may be found in sprays or aerosols.[37]

Technical Performance:
Mink oil is insoluble in water, resulting in strong hydrophobicity and poor oleophobicity.[37] There was no available information regarding mink oil's contact angle; given the oil-based nature, it was assigned as having high performance. Similarly for washability, there was no available information regarding the number of wash cycles; our low rating was based on the suggestion that mink oil polish be applied about every 2 weeks on leather items.[38]

Human and Environmental Health Hazards:
All health and environmental performance data came from a single article published in 2005 on the Safety Assessment of Mink Oil.[37] Confidence was categorized as low for these ratings (Table 5). There was only available information for carcinogenicity/mutagenicity and skin/eye irritation.[37] This information is predominantly based on safety test data for glycerides, as the panel involved in this safety assessment agreed it was relevant to mink oil.[37] According to this article, research suggests that carcinogenicity/mutagenicity and skin/eye irritation are both of low hazard for mink oil.[37]

Conclusion:

While mink oil has relatively low carcinogenicity/mutagenicity and skin/eye irritation, has applications as a waterproofing agent, and is widely used in commercial products, its animal based-sourcing makes it unlikely to be widely accepted as a possible solution. Therefore, along with Beeswax, we did not move forward with further detailed investigations.

The human and environmental hazard of wax and oil showed in Table 5. Overall, we will not include any of them as alternative strategies. They serve as inspirations due to the immature technical performance of beeswax and milk oil and high aquatic toxicity and concerning sourcing of paraffins.

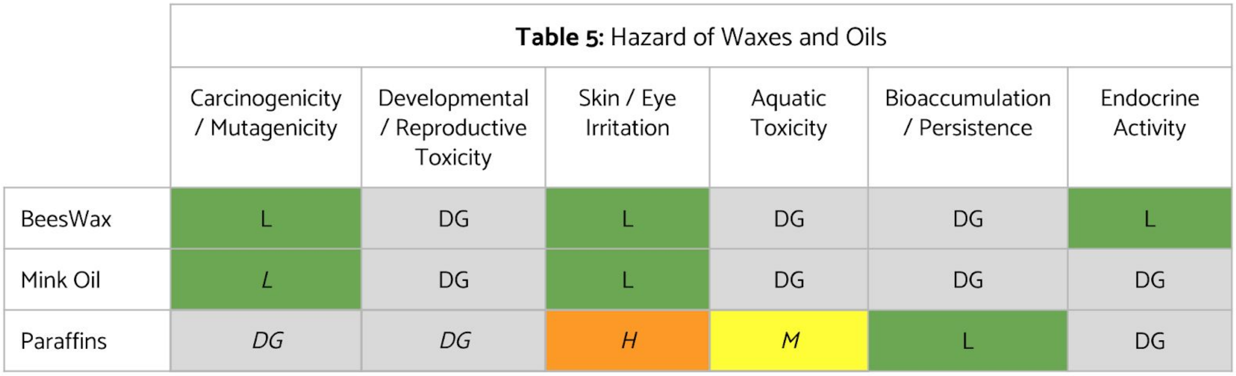

Table 5: Hazard of Waxes and Oils

	Carcinogenicity / Mutagenicity	Developmental / Reproductive Toxicity	Skin / Eye Irritation	Aquatic Toxicity	Bioaccumulation / Persistence	Endocrine Activity
BeesWax	L	DG	L	DG	DG	L
Mink Oil	*L*	DG	L	DG	DG	DG
Paraffins	*DG*	*DG*	*H*	*M*	L	DG

Alternative Recommendation: Biopolymers

Strategy D: Chitosan

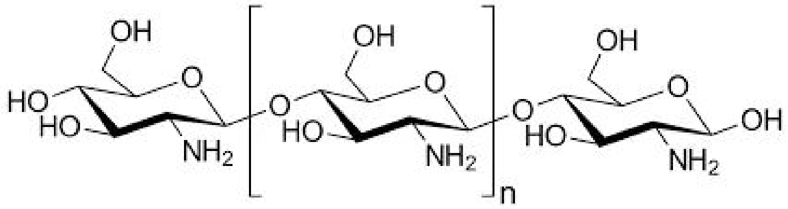

Figure 6. The structure of chitosan, illustrating its acetylated and deacetylated units.

Background:

Chitosan is the second most abundant polymer in nature, only behind cellulose.[39] Composed of randomly repeating β-(1-4)-linked D-glucosamine (deacetylated units) and *N*-acetyl-D-glucosamine (acetylated units), Chitosan is a linear polysaccharide that encompasses a whole category of biopolymers[19] (Figure 6). These biopolymers differ in their length and deacetylation amount, resulting in compounds with different physical and molecular properties. The amino group on chitosan has a pKa of 6.5, meaning that chitosan is a cationic polymer; in acidic and neutral solutions, chitosan solubilizes,[40] so it can be applied through aerosol or spray methods.

Bio-based sources of chitosan include crustacean shell waste, like shrimp and crab shells, and the cell walls of fungi[39] (Figure 7). Under basic conditions at high temperatures, crustacean chitin deacetylates to form chitosan, while in fungi, this process of chitin deacetylation is not necessary.[39] Because of chitosan's versatility, it is currently used in agricultural pest management,[41] biomedical applications,[42] and the food industry.[43] One company, Tidal-Vision, produces a chitosan based product called Tidal-Tex™ that imparts antimicrobial activity on textiles and clothing, but carpet treatments are not included.[44] Chitosan presents promising features in the carpet industry because of its hydrophobic properties and antimicrobial activity.[45]

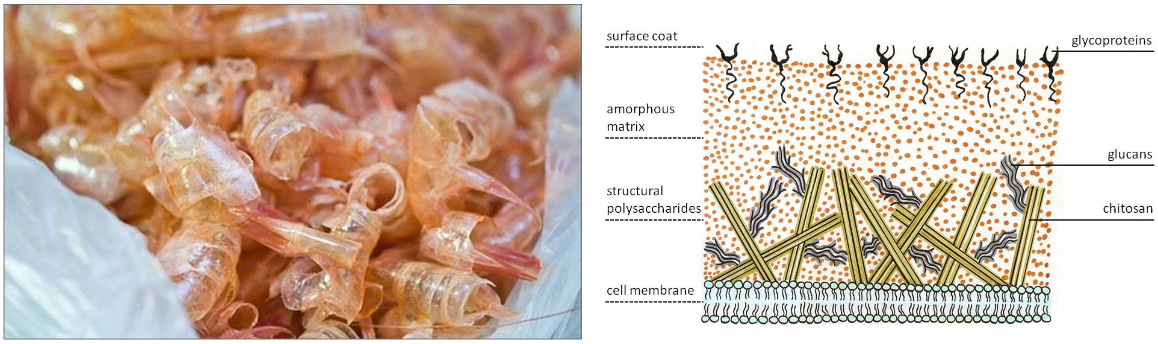

Figure 7. Chitosan is found in shrimp shell waste (left) and fungal cell walls[46] (right).

Inspiration:

Chitosan is a versatile class of polymers and its application uses are quite broad. Since it is a naturally abundant polymer, we were interested in learning more about its properties specifically relating to hydrophobicity and antimicrobial activity. Our hope was that materials currently considered as waste and thrown into landfills could be turned into beneficial products for consumers to use.

Technical Performance:

Chitosan presents useful qualities regarding hydrophobicity and antimicrobial activity, making it a possible alternative solution for repelling water-based stains. The structure of chitosan includes several opportunities for hydrogen bonding between chitosan and the nylon carpet fibers (Figure 8). This bonding interaction alters the mechanical properties of the carpet by increasing the number of functional groups available to catch water molecules.[47] When chitosan binds to the carpet, it forms a coat or protective layer on the surface; once water based stains are spilled onto the carpet, chitosan is able to hydrogen bond with those molecules and prevent the spills from permeating the carpet. Hydrogen bonding plays an important role in chitosan's hydrophobic properties, for it allows chitosan to bind to both the carpet and the stain itself, effectively allowing chitosan to serve as a barrier. The water contact angle between chitosan and polyester fabric was 102°, while the water contact angle between chitosan and cotton was 130°; [47] a water contact angle for chitosan and nylon-6 fibers was not found. Since both angles are greater than 90°, this indicates that chitosan exhibits hydrophobicity when applied to fabrics. Oleophobic contact angles were not determined for chitosan.

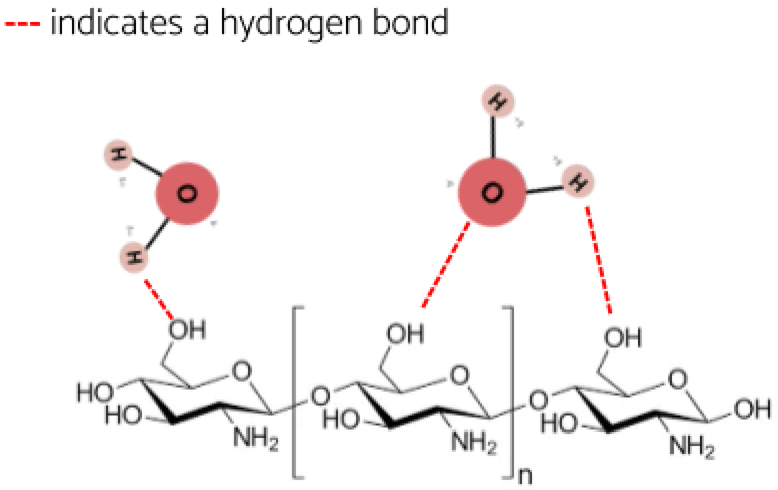

Figure 8. Chitosan is capable of Hydrogen bonding with water-based spills, preventing them from sinking into the carpet.

Chitosan's antimicrobial properties provide an opportunity for carpet cleaning alongside carpet protection. As mentioned before, chitosan is a cationic polymer, meaning that it is positively charged. The charged amino group of chitosan interacts with the cell wall of microbes, causing protein and intracellular constituents to degrade.[48] Chitosan only has antibacterial properties in acidic conditions because it is not very soluble in solutions where the pH is higher than 6.5.[49] Additionally, chitosan directly interacts with the cell walls of *Aspergillus niger* spores, creating a fungistatic effect.[48] These spores are commonly found in carpets and flooring, so chitosan's ability to inhibit its growth is noteworthy.

For durability, Ye et al. found lasting antimicrobial properties on clothing for up to 50 washes,[50] which is more than double the 20 wash threshold considered to be a durable antibacterial finish. The researchers measured durability by covalently attaching a chitosan shell to an amphiphilic nanoparticle core and applying it to cotton fabric; the treated fabric had bacterial reduction greater than 99%,[50] indicating that chitosan has strong antibacterial properties. While the durability data does not specifically address carpets, the main theme is that chitosan has the potential to prevent bacterial and fungal growth on fabric.

Along with antimicrobial properties, chitosan-based dyes exhibit self-healing properties, allowing them to partially repair mechanical properties damaged by breaks or nicks.[45] At the microscopic level, carpets can be damaged by the repetition of foot traffic and overuse. Once the fiber has been damaged, a mobile phase is induced, creating a mass transport mechanism whereby chitosan restores the chemical bonds that have been broken and seals the cracks[45] (Figure 9). If chitosan-based dyes are introduced into the nylon-6 fabric, the self healing properties of chitosan can repair the carpet before stains embed themselves into the microscopic holes, which can help maintain carpet cleanliness.

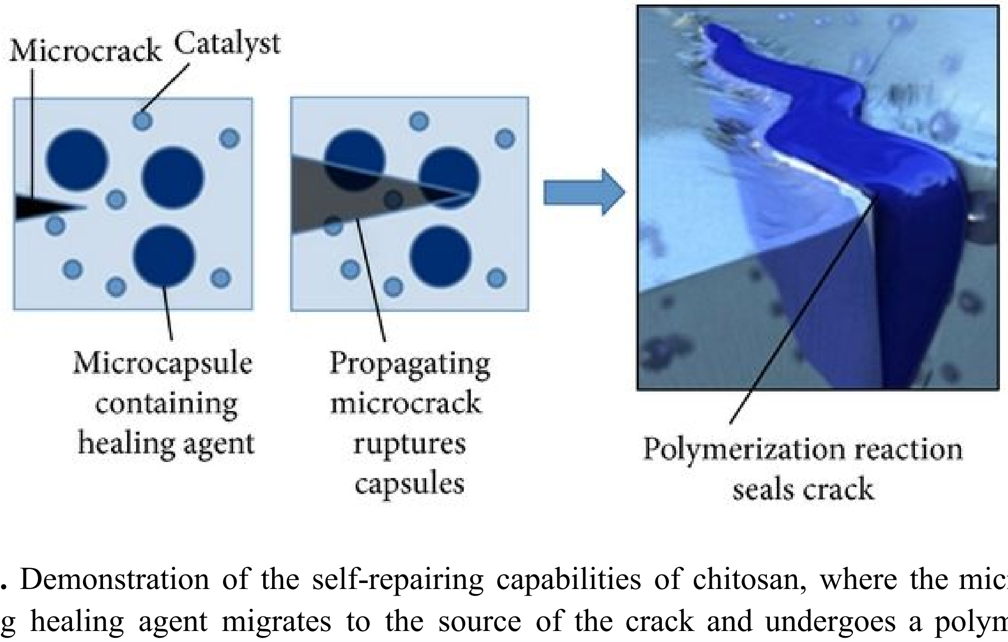

Figure 9. Demonstration of the self-repairing capabilities of chitosan, where the microcapsule containing healing agent migrates to the source of the crack and undergoes a polymerization reaction to resolve the damage. This schematic is from Atay et al.[45]

Human and Environmental Health Hazards:

When looking at the human and environmental health hazard endpoints (Table 6), chitosan performs relatively well. Chang et al. tested seven forms of chitosan, all with varying molecular weights, and found that chitosan exhibits antimutagenic properties because of its ability to decrease the effectiveness of mutagens.[51] However, chitosan has a GHS category 2 rating for skin irritation, and a GHS category 2A rating for eye irritation, meaning that it is a relatively potent skin irritant and a serious eye irritant.[52] These factors necessitate the need for caution when using chitosan as a product, so it would be beneficial for consumers to use proper protection equipment (PPE) if available. One major concern from an environmental standpoint is chitosan's aquatic toxicity. Since chitosan is a cationic polymer with antimicrobial properties, higher doses of chitosan lead to higher levels of acute aquatic toxicity in fish, specifically zebra mussels and rainbow trout.[53] Rainbow trout in particular are quite sensitive to chitosan, even at low concentrations; their gills are affected by chitosan at concentrations ranging from 0.075 ppm to 0.75ppm.[54] In contrast to the aquatic toxicity hazard, chitosan biodegrades relatively easily into nontoxic components. The level of deacetylation affects the biodegradability rate; higher amounts of deacetylation correspond to faster degradation rates.[55] In stark contrast to Scotchgard products, chitosan is not persistent in the environment and it is biodegradable.[56]

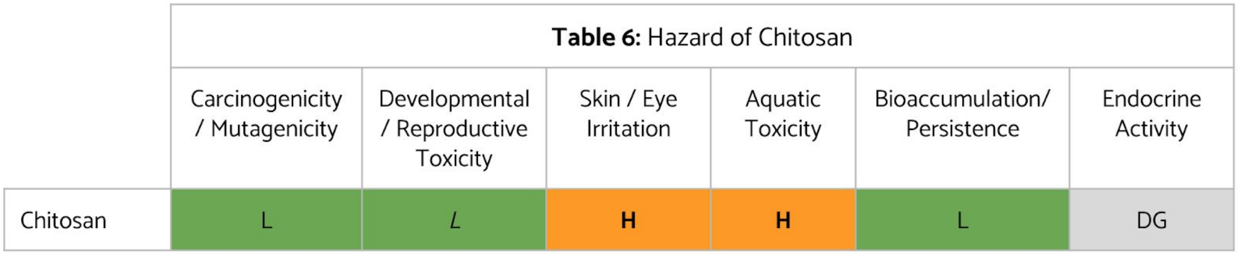

Table 6: Hazard of Chitosan

	Carcinogenicity / Mutagenicity	Developmental / Reproductive Toxicity	Skin / Eye Irritation	Aquatic Toxicity	Bioaccumulation/ Persistence	Endocrine Activity
Chitosan	L	*L*	**H**	**H**	L	DG

Conclusion:

Chitosan is a naturally abundant polymer that can be easily sourced from bio-based crustacean shell waste, providing an outlet for waste to be recycled into a useful product. It has antimicrobial and self-healing properties that have the potential to instill both carpet protection and cleanliness, and it is soluble in solutions of acetic acid, a safer solvent, when the pH is below 6.[57] However, chitosan exhibits acute aquatic toxicity, it has poorer long term hydrophobicity, and it loses the ability to flow at high concentrations.[47] Furthermore, chitosan may have the potential to impart oleophobicity, but more research is needed to determine the best way to accomplish this goal. Overall, chitosan presents beneficial properties that can adequately impart hydrophobic properties on carpet fibers, but its greatest strength is its antimicrobial activity.

Alternative Recommendation: Biopolymers

Strategy E: Cellulose Nanocrystals (CNC)

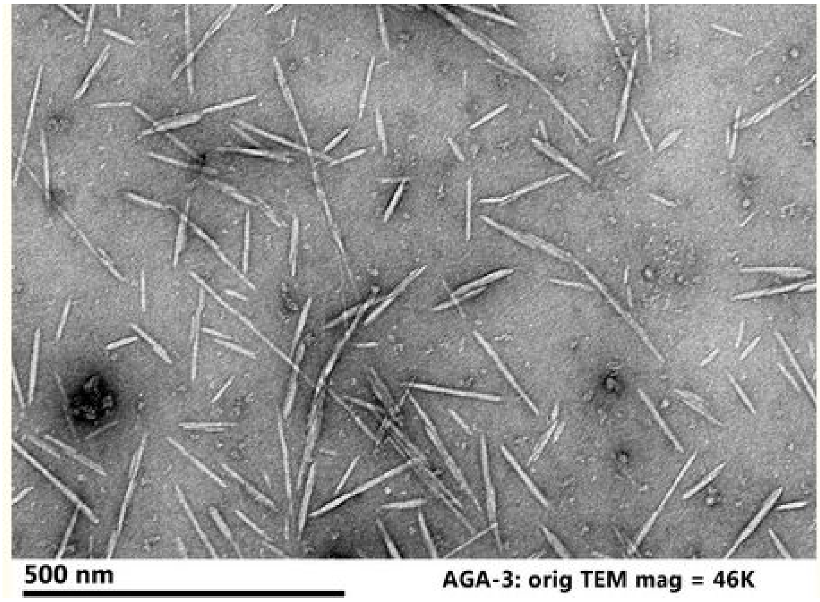

Figure 10. Magnified lignin containing cellulose nanocrystals.[58]

Background:

Cellulose is most famously known for its abundance in plants and some bacteria. In nature, cellulose is primarily in plant cell walls; in industry, this sugar is extracted from cotton fibers. Cellulose can be derivatized and used in the pharmaceutical and chemical engineering industry; some examples include use in chromatography, paints, and explosives. Some other sources for cellulose are jute, hemp, corn, flasks, rice, wheat straw, and sisal.[59] Unlike PFAS, cellulose alone is the most sustainable resource on earth and is extremely abundant and environmentally friendly. Unfortunately, it is hydrophilic and does not repel oil.[60] Therefore, pure cellulose is harder to utilize in large amounts required by industry, so derivatives are more common and utilized in greater quantities. We believe cellulose nanocrystal(s) (CNC) are the most promising cellulose derivative. They are currently utilized in industry and found in thin films, coatings, and plies for packaging applications.[61]

Inspiration:

We were inspired by the properties and utility of cellulose as a sturdy barrier in plants. This sparked our curiosity pertaining to whether cellulose or its derivatives could be used to prevent contaminants from damaging a carpet without harming environmental, human, and animal health. We particularly wondered if it could serve as a waterproof and oil-proof barrier.

Technical Performance:

The individual crystals of nanocellulose are elastic, strong, produced at a low cost and should be administered onto a carpet in the form of a powder. While mostly hydrophilic by themselves, these crystals can easily be modified with other compounds that are just as safe, biodegradable, and abundant as CNCs alone.[60]

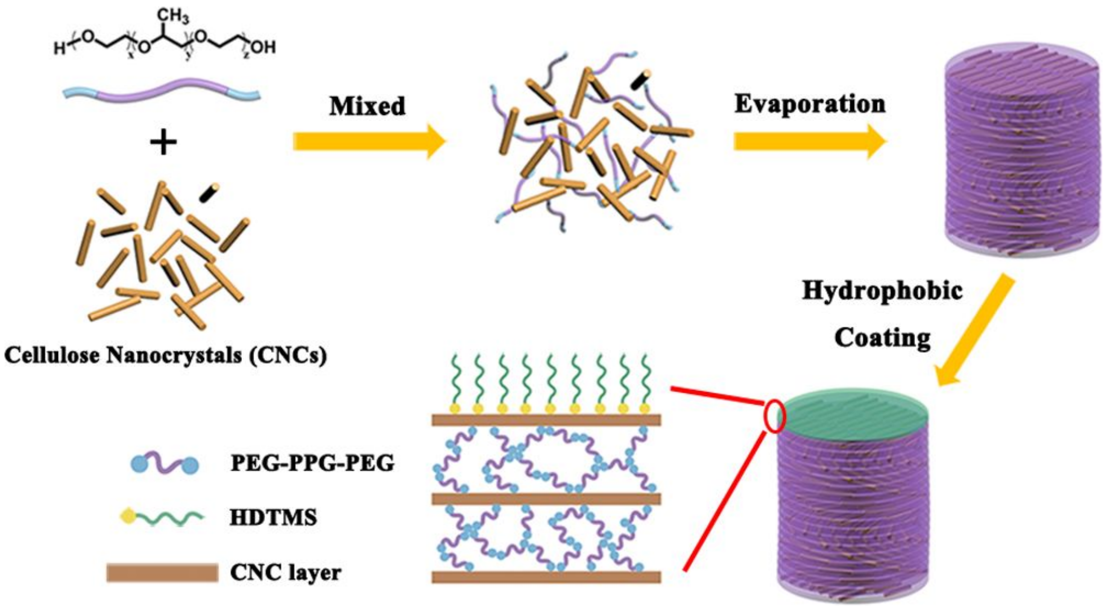

Figure 11. The process of creating CNC film infused with herein: a novel bioinspired nanocomposite film with organic-solvent-regulated variable structural color and surface hydrophobicity, also consisting of PPPTCs and hexadecyltrimethoxysilane (HDTMS).[62]

The most promising example is CNCs combined with rarasaponins (RSs) or herein (Figure 11). Rarasporins, like CNCs, avoid human health and environmental issues. When combined with CNCs, rarasporins were found to increase hydrophobicity. In this study, RSs were attached onto CNCs from bamboo shoots, and hydrophobicity was enhanced.[63] Additionally, when herein was added to CNCs, the resulting hydrophilic film surface became hydrophobic shortly after surface modification; within 2 hours, a water contact angle of up to 130.6° was achieved.[40] The whole process was operated at room temperature without destroying the ordered structure of the CNC film.[40] As for oleophobicity, this has only been attained with Fluorine-based surface decorated nanocrystals. As the focus of our class is to avoid fluourine containing chemicals like PFAS, another solution is necessary to impart oleophobicity on CNCs.[64] However, as CNCs have shown great potential for modification, there is hope that they can be combined with one or more chemicals like RSs and herein, which have low toxicities and environmental impacts, and serve as a barrier against oils.

Human and Environmental Health Hazards:

Table 7: Hazard of CNC

	Carcinogenicity / Mutagenicity	Developmental / Reproductive Toxicity	Skin / Eye Irritation	Aquatic Toxicity	Bioaccumulation/ Persistence	Endocrine Activity
CNC	L	DG	H	DG	M	DG

Although there are significant data gaps on literature and evaluations by major chemical organizations like TedX, ECHA, and Pharos, there is significant evidence to believe that CNCs are less toxic overall than PFAS and less likely to bioaccumulate (Table 7). However, data suggests some negative effects regarding cytotoxicity and immunosuppression,[12,65] but it is believed that these findings tested a concentration of CNCs too high for realistic exposure.[42] There is little data on carcinogenicity, with the exception of a study that suggests a dose dependent link between CNCs and colon adenocarcinoma.[67] However, there is little evidence of mutagenicity.[66] It was not found to irritate the eyes or skin[68] very much, although CNCs were primarily found to irritate the lungs.[69] CNCs were even believed to possibly induce sustained adverse effects in spermatocytes/spermatozoa, indicating male mice reproductive toxicity via inhalation.[69] Ultimately, there is still little data and evidence on animal and human reproductive toxicity in general, as well as endocrine activity and aquatic toxicity (Table 7). Since they are smaller compounds, there is more potential for cellulose nanocrystals to persist in the body, particularly in the lungs after chronic exposure.[66] However, there are not very many studies available on this, and the few that exist are conducted in vitro and some in vivo.[66] CNCs also surpass PFAS in its ability to biodegrade more efficiently (Table 7).[68]

Conclusion:

CNCs are increasingly better in many health and environmental hazard criteria than PFAS, despite the data gaps (Table 7). This compound surpasses PFAS in biodegradability, bioaccumulation/persistence (albeit slightly), and known low mutagenicity. Unfortunately, CNCs have not quite reached the high technical performance standard of preventing oil like PFAS has, and its washability is unknown. Luckily, there is significant potential in theoretical applications due to the high modifiability of the CNCs' structure. These need to be further explored in a lab setting to help overcome some of the technical and health challenges.

Alternative Recommendation: Silicon-Based Materials

Strategy F: Silicon Dioxide Nanoparticles

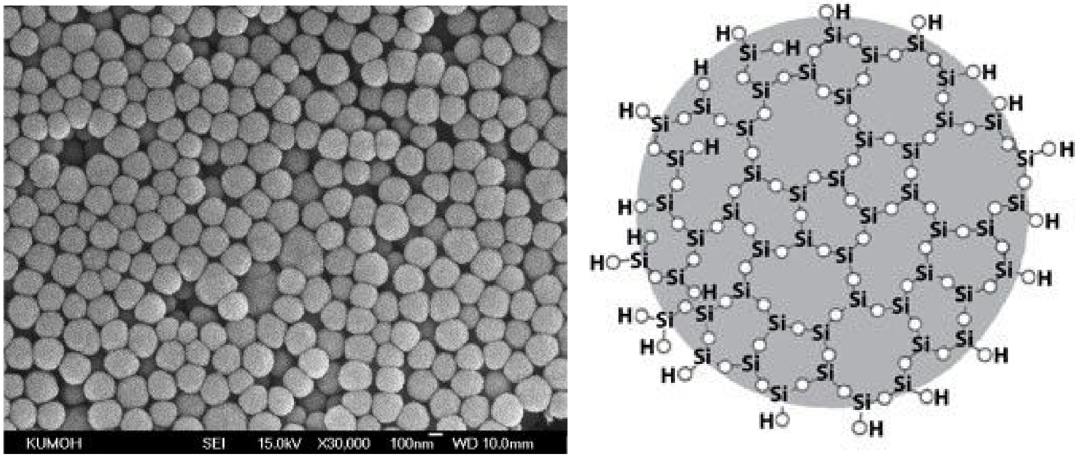

Figure 12. A scanning electron microscopy image of silicon dioxide nanoparticles[70] and general schematic of SiNPs.[71]

Background:

Silicon dioxide nanoparticles are particles on the scale of 1-500nm made up of networks of silicon-oxygen bonds, with outward-facing hydroxyl groups (Figure 12). These nanoparticles are commonly made via the sol-gel process, which combines tetraethylorthosilicate (TEOS) in ethanol with ammonium hydroxide (NH_4OH), which is used to control the size of the particle.[70] During this process, organosilanes may be added to modify the particle surface to enhance the SiNP's water-repellent properties and contribute oil repellency to the particle.

SiNPs are already a common component of fabric protectors, including shoe- and mask-protecting products from Vetro Power and carpet- and rug-protecting products from protectME. Both of these brands apply the SiNP-based formulation to fabric via a water-based spray, indicating that the use of organic solvents is unnecessary for SiNPs; they can be easily applied via a spray without the need for specialized equipment to cure the treatment. Additionally, the ubiquitous nature of SiNPs in fabric protectors and other industries attests to the economic feasibility of this aftermarket treatment strategy. Silicon and oxygen are the most abundant elements in the earth's crust, most commonly present as silicon dioxide, so they are an inherently sustainable material for industrial use.

While SiNPs are present in many fabric protecting products, their ability to coat and not leach out of a material is dependent on the type of fabric. Plant-derived fabrics such as cotton and flax are derived from cellulose, animal-derived fabrics such as silk and wool are protein-derived, and synthetic fabrics such as nylon are synthetic polymers. On a chemical level, this results in plant- and animal-derived fabrics containing many exposed hydroxyl groups, while nylon is relatively inert by comparison. When several fabric types were exposed to SiNP emulsions in water, cotton and flax retained the SiNP to a greater extent than nylon. While SiNPs can chemically adhere to nylon only through dipole-dipole interactions, much stronger covalent Si-O-C bonds can be formed between SiNPs and exposed hydroxyl groups on natural fibers. This poses a potential problem for carpet and rug treatments specifically, as the majority of carpets and rugs are composed of nylon. One potential work-around for coating nylon with SiNPs is to acidify the solution used to apply the SiNPs, which has been shown to increase adherence (Figure 13).[72]

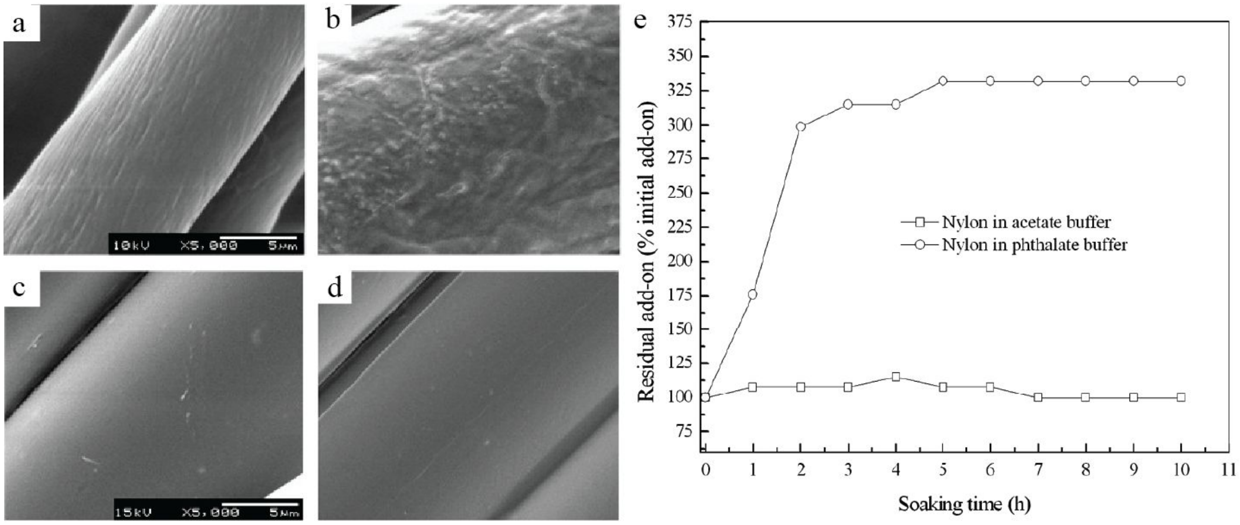

Figure 13. a) Untreated cotton fibers. b) Cotton fibers treated with silica sol. c) Untreated nylon fibers. d) Nylon fibers treated with silica sol. e) Increased add-on of silica sol to nylon in acidic solution. Modified from Li et. al.[72]

Inspiration: Physical liquid repellency

Although silicon dioxide nanoparticles (SiNPs) are an inorganic material, their method for repelling liquids is based on the physical method by which plants, such as the lotus leaf, repel water. The upper surface of lotus leaves is composed of a mixture of lipids of different chain lengths which form structures with hierarchical micro- and nanoscale rough patterning (Figure 14).[28] Rough patterning on this scale allows for air pockets to be captured between the surface and water, causing water not to adsorb onto the surface, in what is known as a Cassie-Baxter surface wetting mode (Figure 15).While additional energy can cause water to fill in these air pockets, switching to Wenzel mode, this can be avoided by altering the surface patterning and combining physical with chemical water repellency. While lotus leaves primarily repel water, this principle of physical repellency also pertains to other liquids, such as oils and solvents.

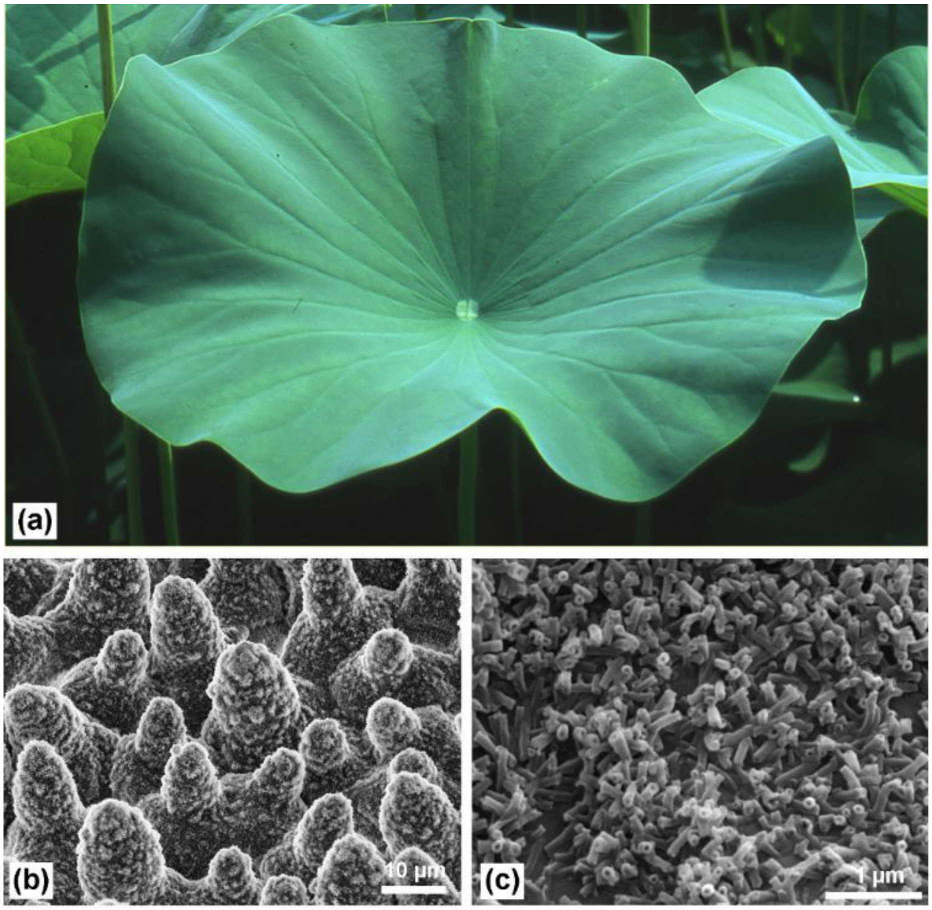

Figure 14. The lotus leaf contains hierarchical rough patterning, as demonstrated in electron microscopy images of the lotus leaf upper surface by Ensikat et. al.[73]

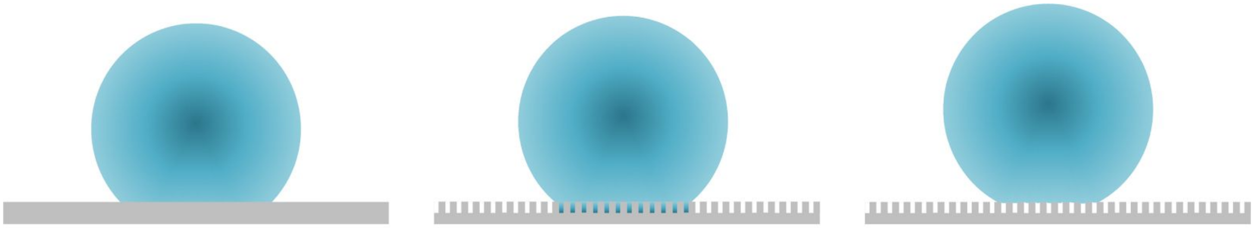
(a) Young mode (b) Wenzel mode (c) Cassie-Baxter mode

Figure 15. Surface wetting modes affected by surface patterning.[74]

Technical Performance:

In the absence of additives, silica coatings have limited ability to confer water or oil resistance. Their contact angle with water when applied to solid surfaces ranges from hydrophilic[75] to just exceeding the threshold of hydrophobicity with a water contact angle of 100°.[76] However, several additives can improve the performance of SiNPs as fabric treatments, including silicon-containing small molecules, silicone polymers, and others. Several examples of these formulations are discussed in detail below.

A superhydrophobic nylon stain- and UV-protecting solution was achieved by combining SiNPs with zinc oxide and sodium stearate.[77] While sodium stearate conferred hydrophobicity, the zinc oxide particles conferred UV resistance, which is not a crucial need for most carpets and rugs. This treatment was able to confer superhydrophobicity to the nylon fibers, with a water contact angle >150° and hydrophobicity maintained over 10 wash cycles (Figure 16). Because the primary method of water repellency was chemical, with the hydrocarbon chains of stearate providing water repellency, this strategy is unfortunately expected only to repel water-based stains and likely would not be effective against oil-based stains.

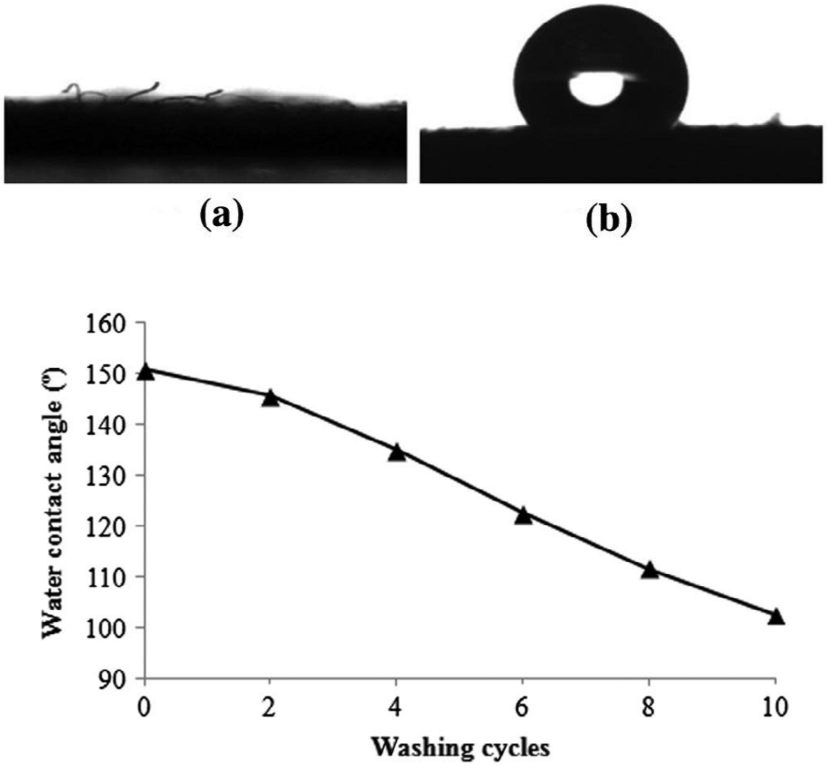

Figure 16. a) Water droplet on unmodified nylon surface. b) Water droplet on nylon surface coated with SiNP solution. Graph shows the water contact angle as a function of the number of wash cycles, where hydrophobicity is maintained for 10 washes.[77]

A second strategy for improving both the water- and oil-resistant performance of SiNPs is through the incorporation of small molecule silicon-containing compounds. By including methyltriethoxysilane (MTES) into the sol-gel formulation of SiNPs, a highly hydrophobic and oleophobic coating was produced as demonstrated by Sheen et. al. (Figure 17).[78] When applied to paper, this coating introduced a heterogeneous rough patterning to the surface (Figures 18). After applying the coating to paper, the contact angles of oil and water were 149° and 133°, respectively. Although these contact angles occur when the coating is applied to paper, the exposed hydroxyl group on cellulosic papers are similar to exposed hydroxyl groups in naturally-derived fabrics and may be expected to act similarly. On nylon, the performance may be compromised slightly, and the resistance of this formulation to washing and mechanical abrasion is unknown; therefore, testing the properties of this formulation on nylon is recommended.

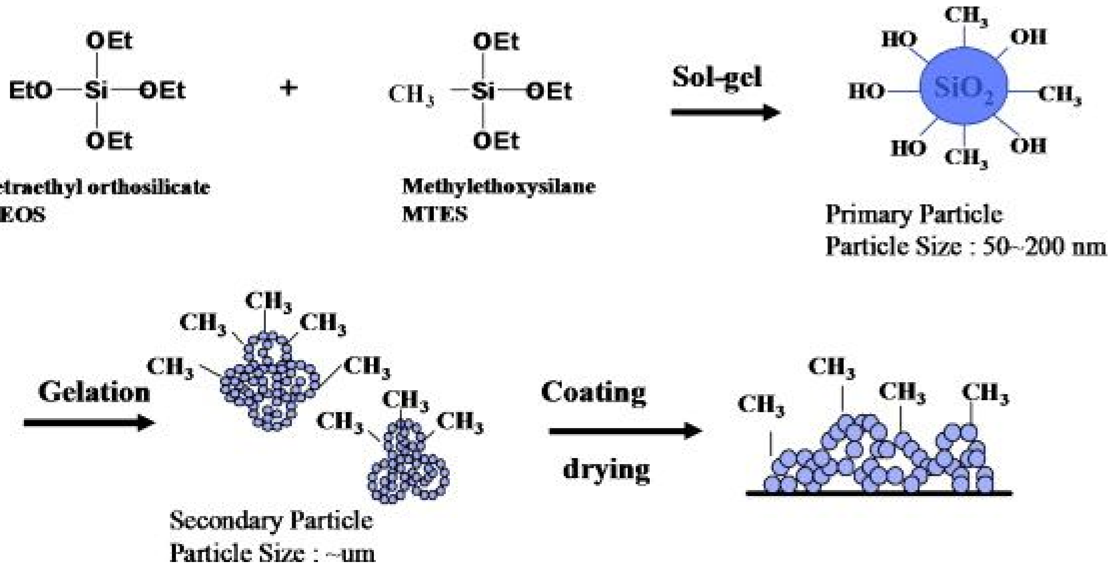

Figure 17. Process of synthesizing a SiNP-based coating to impart hydrophobicity and oleophobicity to paper.[78]

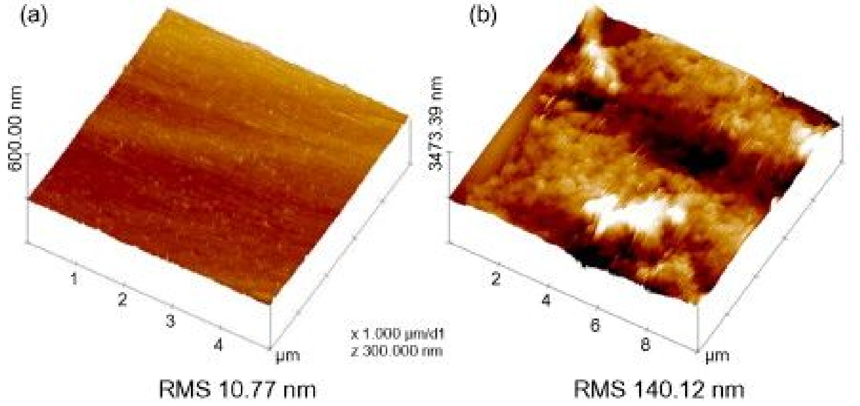

Figure 18. a) Unmodified paper surface. b) Paper surface modified with silica solution containing 37.5% methyltriethoxysilane.[78]

Human and Environmental Health Hazards:

Traditionally, chemical hazard is assessed by determining the hazard of a pure substance with a known and consistent chemical formula. Most GHS categorizations are for chemicals of this type. For nanoparticles, this type of characterization is impossible as nanoparticles are composed of populations of structures which do not all have the same structure and are not all necessarily identical in size. However, research has been been done concerning the toxicology of silicon dioxide nanoparticles and their environmental fate and effects.[79] SiNPs are not generally expected to bioaccumulate because they rapidly degrade in natural media to atomic silicon dioxide, which is already naturally abundant in terrestrial and aquatic environments.[80] Toxicity of SiNPs to algae[80] and a freshwater fish[81] would meet GHS category 4 criteria, with toxicity thresholds above those needed for a more hazardous classification.

SiNPs are present in a wide variety of common products, including cosmetics, pharmaceuticals, and food. In spite of this, their impact on human health is not fully understood. An evaluation of their potential for skin irritation revealed that SiNPs are not dermally irritating and in fact, may mitigate skin irritation due to allergic reactions to other substances.[82] In addition, no eye damage has been observed in several studies.[79] Along other health hazard endpoints, the outcomes are more concerning, although further study is needed to understand the applicability of these studies to human exposure routes and levels. When SiNPs were continuously administered over the course of several weeks to mice, respiratory irritation was observed, with sensitization also being observed when it was administered alongside a known allergen.[83] There is tenuous evidence of carcinogenicity and no in vivo evidence for mutagenicity. Additionally, no risk to mouse fetuses or mothers was demonstrated at high levels of SiNPs,[84] but a dramatic reproductive toxicity effect may be present in males.[79] Insulin resistance[85] and an increased risk of Alzheimer's disease[79] may also be caused by SiNPs, although data for each of these endpoints is limited. The ubiquity of SiNPs in common products suggests that they do not exhibit dramatic and acute toxicity. However, ubiquity is not always indicative of a lack of hazard. Overall, greater studies of SiNPs of a variety of sizes and with a variety of additives must be performed to confirm the safety of this material.

The primary component of SiNPs is TEOS. Because this is a constituent of SiNPs, there may be trace amounts in the finished SiNP product; the main concern for TEOS hazards are the manufacturers rather than consumers. The hazards of TEOS were primarily assessed by consulting GHS Japan's regulated hazard list. TEOS is moderately skin and eye irritating, meeting GHS category 2 for each. It is also severely irritating to the respiratory system, and exposure via inhalation was shown to have adverse effects on the kidney and liver in animal studies. While data regarding carcinogenicity and developmental and reproductive toxicity was sparse, in vitro data suggests that there is little risk of mutagenicity from TEOS. TEOS is biodegradable, with a 98% degradation rate within 28 days. It also has been shown not to be acutely or chronically toxic to aquatic life. A summary of the hazards of SiNPs and tetraethyl orthosilicate is displayed in Table 8.

Table 8: Hazard of SiNPs and their primary constituent, tetraethyl orthosilicate

	Carcinogenicity / Mutagenicity	Developmental / Reproductive Toxicity	Skin / Eye Irritation	Aquatic Toxicity	Bioaccumulation/ Persistence	Endocrine Activity
SiNPs	M	H	M*	L	L	L
TEOS	L	DG	M	L	L	L

The primary additives discussed above were sodium stearate, zinc oxide, and MTES. The hazards of ZnO will not be considered, as their function, UV protection, is not necessary for our desired stain protecting application. Other small molecule and polymeric siloxanes are common additives to SiNP water repellent formulations as well; these will be discussed further in the subsequent section.

Sodium stearate is present on several positive lists, including the US EPA's Safer Chemical Ingredients List. Sodium stearate health and environmental data were gathered from GHS Japan and the European Chemicals Agency (ECHA) database. The greatest human health concerns for this chemical are an ability to cause eye irritation (GHS 2A) and potentially mild skin irritation. No data was found regarding carcinogenicity, mutagenicity, developmental and reproductive toxicity, or endocrine activity. However, use of the Toxtree computational predictor of toxicity indicated that sodium stearate is likely not carcinogenic or mutagenic. Sodium stearate is considered rapidly biodegradable and thus not bioaccumulative. However, it may be hazardous to aquatic life, being classified as GHS 2. For this reason, care should be taken during the manufacture and disposal of materials containing sodium stearate.

Table 9: Hazard of SiNPs additives

	Carcinogenicity / Mutagenicity	Developmental / Reproductive Toxicity	Skin / Eye Irritation	Aquatic Toxicity	Bioaccumulation/ Persistence	Endocrine Activity
Sodium stearate	L	DG	H	H	L	DG
MTES	L	L	L	L	L	DG

MTES environmental and health data were gathered from the REACH database and GHS New Zealand. The primary concern for MTES is its flammability, which is primarily of concern in the industrial setting rather than in the finished product. It is neither a skin irritant nor an eye irritant in humans; several animal and in vitro studies have not demonstrated health hazard concern along other endpoints. However, greater confirmation is needed. No data was found for the endocrine activity of MTES. MTES hydrolyzes rapidly in water and therefore is not considered persistent. It also has not shown aquatic toxicity meriting GHS classification. Overall, this is a remarkably safe substance, although further confirmation of its safety is needed. The hazards of both MTES and sodium stearate are summarized in Table 9.

Conclusion:

Silicon dioxide nanoparticles are an earth-abundant, economically feasible carpet protecting solution that can be delivered to fabric via an aqueous spray. The incorporation of small molecule additives grants SiNPs high hydrophobic and oleophobic performance as well as moderate washability. SiNPs have little environmental impact, and while some studies have demonstrated human health concerns in animal models, further study into the hazards of SiNPs is needed. The application of SiNP/MTES formulations, currently used on paper, to nylon carpets and rugs is a promising area for further research.

Alternative Recommendation: Silicon-Based Materials

Strategy G: Silicones and Silanes

Background:

Silicone is present in a wide variety of industrial and household materials. Due to its biocompatibility, it is a common component of medical dressings and implants. Its utility ranges from cookware to a sealant used in the aerospace industry. The most common silicone is polydimethylsiloxane (PDMS), which is generated through the reaction of dimethyldichlorosilane with water.[86] By replacing the methyl groups of dimethyldichlorosilane with other groups, the properties of the resulting polysiloxane can be altered.

Inspiration:

Water is set apart from oils and other substances by its strong intermolecular forces. While oils and solvents are held together by London dispersion and dipole-dipole interactions, water experiences much higher hydrogen bonding interactions in addition to these weaker interactions. As a result, water has a much higher surface tension than oils and most other liquids. This high surface tension provides an energy barrier moving from the Cassie-Baxter to Wenzel wetting state as shown in Figure 15. This allows for physical repellency via rough surface patterning to work well. For oils, the Cassie-Baxter to Wenzel transition requires much less energy. Because of the low surface tension of oils, oil repellency must be achieved by having a low surface energy of the oil-repellent coating, or a high surface energy at the oil/coating interface.[87]

Perfluorinated compounds are extremely effective at repelling oil as well as water due to their low surface energies. Hierarchical rough surface patterning can physically decrease the surface energy of a substance without fluorination. Increasing the surface energy at the oil/coating interface is a more difficult problem, but has also been pursued. One method for increasing this surface energy is through incorporating flexibility and dynamic molecular movement into the coating; rather than rigid microscale patterning, this approach prevents liquid adherence through molecular dynamics at the oil/coating interface.[88] Silicones and silanes represent a broad, well-understood, and tailorable class of compounds through which the principles of rigid rough surface patterning and dynamic, liquid-like repellency can be explored. Examples of each of these approaches to oleophobicity are detailed in the following section.

Technical Performance:

PDMS has been used to produce a nylon fabric coating which is both hydrophobic and oleophobic. After application of TEOS from a TEOS/ethanol solution followed by heat curing to incorporate silanol groups onto the nylon fabric, the fabric was exposed to dichlorotetramethyldisiloxane vapors to allow for the formation of PDMS on the fabric. When exposed to water and a variety of commonly-encountered oils, including olive oil and canola oil, the PDMS-treated nylon exhibited both water and oil contact angles greater than 90° (Figure 19).[87]

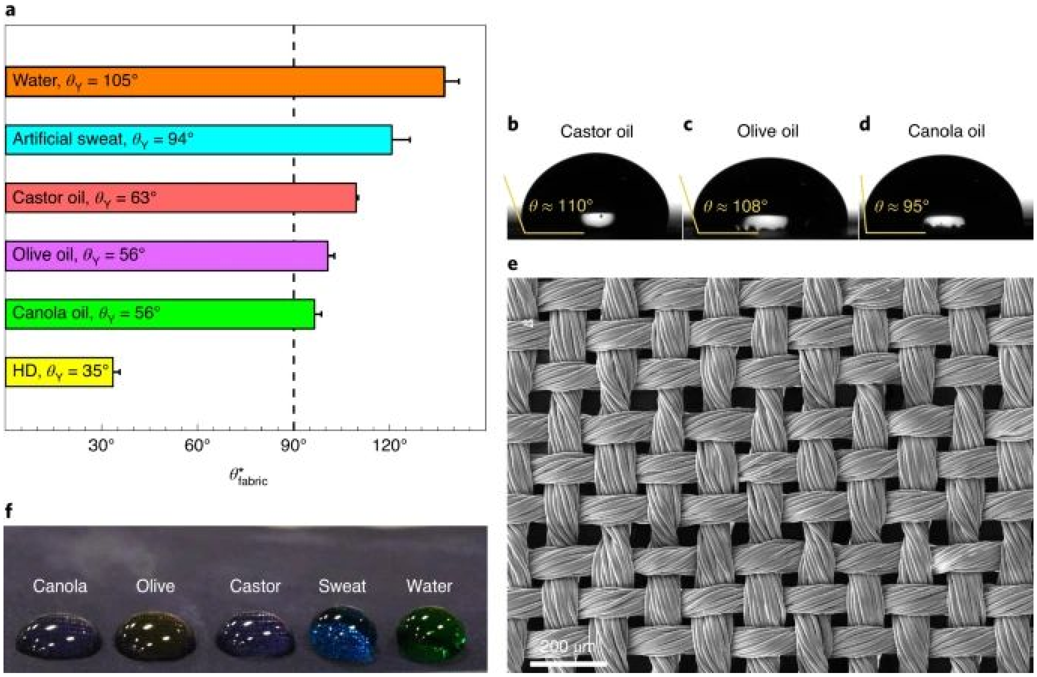

Figure 19. The oleophobic properties of PDMS treated nylon as demonstrated by Shabanian et. al.[87] a) Contact angles of water, sweat, and various oils on treated fabric. b-d) Profile of oils on treated fabric showing contact angle. e) Scanning electron microscopy image of the nylon fabric. f) colored image of each of the liquids shown in (a) excluding hexadecane.

There are several caveats to the performance of this treatment, primarily the feasibility of treating fabric in this way if the treatment is to be applied in-home by consumers. Rather than reacting the PDMS monomer directly with modified nylon fabric, it may be feasible to dissolve PDMS and apply it to nylon as a spray, as with other solutions. A drawback to this method is that PDMS is insoluble in water and may require the use of a hazardous solvent. Modifications can be made to PDMS to increase its water solubility,[89] but it is highly likely that this would compromise its stain resistant performance. Another possibility is the application of the treatment by professionals with specialized equipment. An additional uncertainty regarding this treatment is its wash fastness and abrasion resistance; these would be helpful areas for further research exploration.

A siloxane polymer functionalized with alkyl groups of varying chain lengths has also been used to create a coating that is both hydrophobic and semi-oleophobic. Specifically, tetramethoxysilane was co-condensed with alkyltriethoxysilanes of varying chain lengths. These coatings were applied to glass slides and their water and solvent contact angles measured. The water and oil contact angles of the siloxane polymer-coated slide are shown in Figure 20, with nearly all water contact angles exceeding 90° and oil contact angles as high as 40°. It is important to note that the oils used in this experiment have exceedingly low surface energies; as can be seen in Figure 19 above, a material with a hexadecane (HD) contact angle of 35° may still be oleophobic to most oils encountered in a home environment. As the chain length of the alkyl groups increases over 16, the oleophobic performance of this coating worsens. It is postulated that the higher chain length results in closer packing and less dynamic movement of the alkyl chains, with greater dynamics providing the oil barrier.[90]

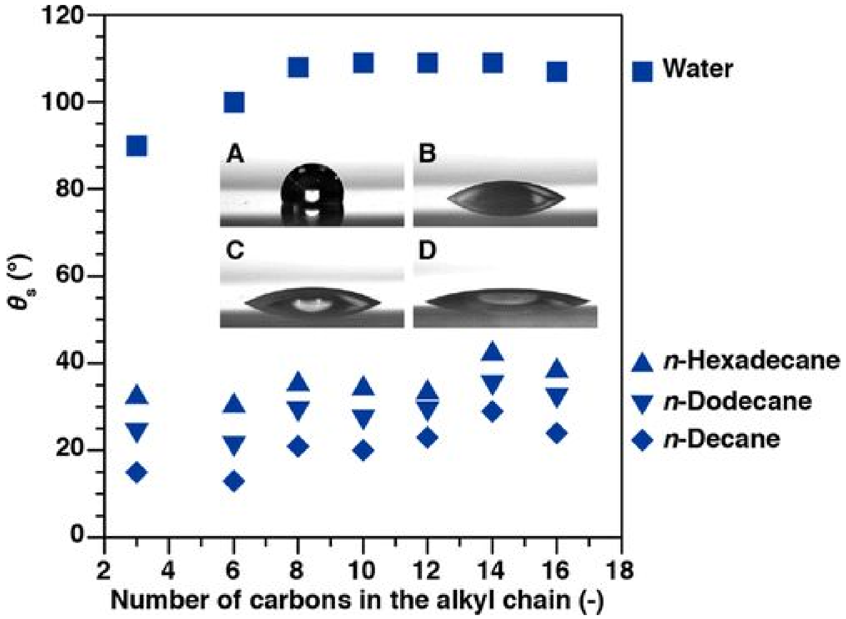

Figure 20. Water and oil contact angles of siloxane polymer functionalized with alkyl groups of various chain lengths.[90]

As for the PDMS coating above, there are several unknowns for the performance of this alkyl-functionalized siloxane polymer. These experiments were performed on spin-coated glass slides, so a delivery method for this solution to carpets still needs to be determined. Additionally, no information about the washability and durability of this coating on carpets is presently available.

Human and Environmental Health Hazards:

Assessing the hazard of polymers such as PDMS is difficult because they do not have a discrete molecular formula, and hazard can vary based on chain length. PDMS is present on several positive authoritative lists, including the US EPA's Cosmetic Ingredients Review: Safe as Used. Hazard data for this polymer was collected from the ECHA substance infocard, The New Zealand EPA's Chemical Classification and Information Database (CCID), and the Danish Advisory List for Self-Classification of Hazardous Substances. PDMS has been shown to be acutely toxic to terrestrial invertebrates and computationally predicted to be toxic to aquatic life. It is persistent, though not bioaccumulative.[91] It also causes serious eye irritation. While further toxicity data was not present on regulated substances lists, in general silicones are considered to have little toxicity and potential for carcinogenicity.[92] Several of the harms posed by siloxane polymers may also be mitigated by using polymers of a higher molecular weight.[92]

The primary constituent in the synthesis of PDMS is dimethyldichlorosilane. Trace amounts of this monomer are expected to be present in the finished polymer, so the main health concerns are exposure during manufacturing and release into the environment during manufacturing. Hazard data for dimethyldichlorosilane was gathered from the REACH registered substance factsheet. This chemical is flammable and reactive, which results in rapid degradation and hydrolysis in an aquatic environment. Its half-life is less than a minute in water, and therefore bioaccumulation and aquatic toxicity are unconcerning. Human health studies indicate that this chemical does not have long-lasting detrimental health effects, but causes skin and eye irritation. Tetramethoxysilane, a constituent of one of the aforementioned oleophobic siloxane coatings, was also evaluated using its REACH registered substance factsheet and has a very similar toxicity profile to dimethyldichlorosilane. A summary of the human and environmental hazards of silicones and their components is in Table 10.

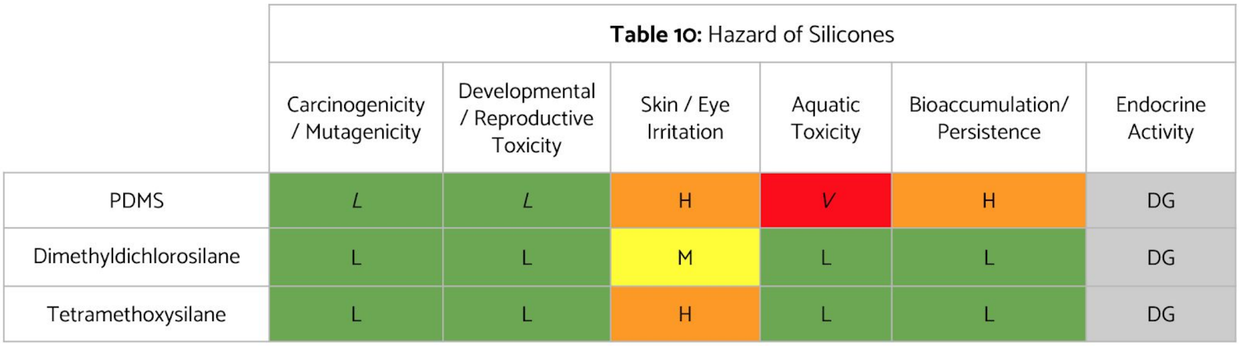

Table 10: Hazard of Silicones

	Carcinogenicity / Mutagenicity	Developmental / Reproductive Toxicity	Skin / Eye Irritation	Aquatic Toxicity	Bioaccumulation/ Persistence	Endocrine Activity
PDMS	*L*	*L*	H	*V*	H	DG
Dimethyldichlorosilane	L	L	M	L	L	DG
Tetramethoxysilane	L	L	H	L	L	DG

It is important to note that the hazards of only a few of many siloxanes have been reported here, and hazard is highly contingent on the specific siloxane or polymer used. Cyclic siloxanes in particular pose human health risks, and the hazard profile of the specific monomers used to construct silicone polymers should always be considered.

Conclusion:

Silicone is omnipresent in industrial and household items. Coatings employing the use of PDMS and modified siloxane polymers have the ability to protect fabrics from both water- and oil-based stains. Applying these polymers in a sprayable format and designing them to endure washability and abrasion are key areas of further research. There are environmental concerns for silicone polymers, and a better understanding of the health and environmental hazards of varying chain lengths of siloxane polymers is needed.

Comparison of Alternatives

Table 11 summarizes all the human and environmental hazards from the aforementioned alternatives. In terms of carcinogenicity or mutagenicity, most alternatives including bad actors have a low hazard level except SiNPs, which reach the moderate level of hazard. A similar situation describes the developmental and reproductive toxicity column, but more data gaps are present. The major concern lies in the skin and eye irritation column, as both paraffins and biopolymers present high hazards. Meanwhile, chitosan and CNCs have differing levels of hazard in environmental health, specifically for aquatic toxicity and bioaccumulation or persistence. Compared with biopolymers, SiNP alternatives are more environmentally-friendly; though there are some indications of detrimental health effects of SiNPs, this must be validated with further research. Silicones, by contrast, tend to have benign human health effects but can exhibit environmental persistence and toxicity depending on the polymer used. When it comes to the last category, endocrine activity, all the strategies appear greener than PFAS but data gaps still exist.

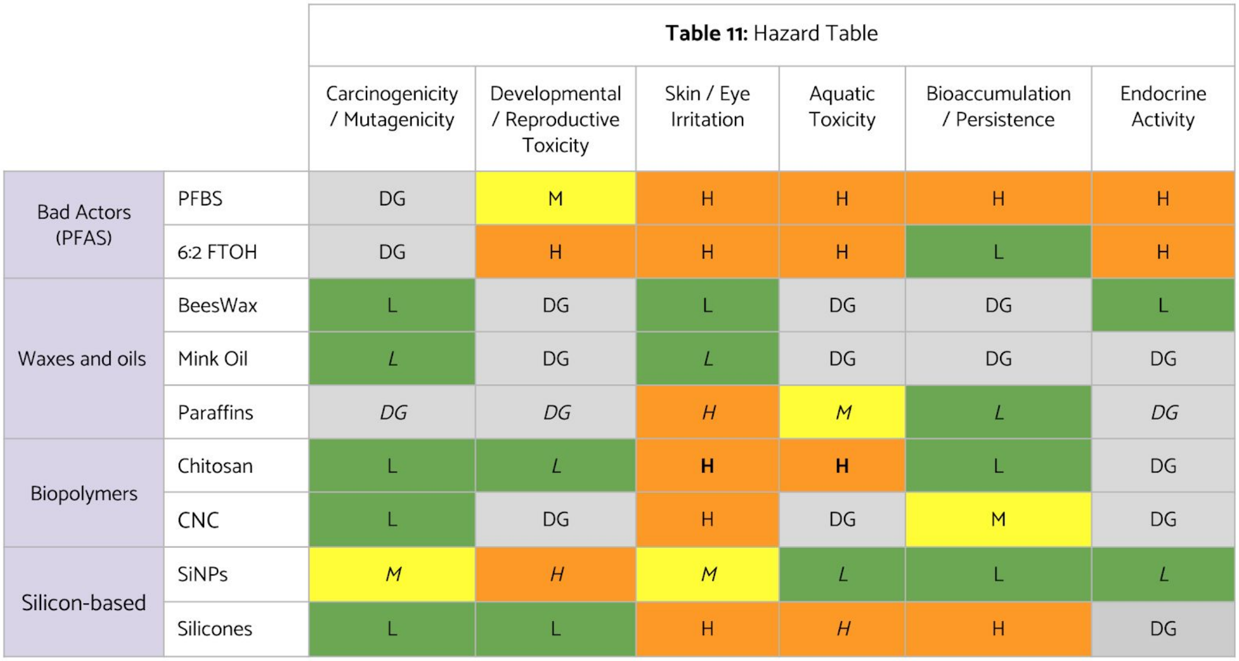

Table 11: Hazard Table

		Carcinogenicity / Mutagenicity	Developmental / Reproductive Toxicity	Skin / Eye Irritation	Aquatic Toxicity	Bioaccumulation / Persistence	Endocrine Activity
Bad Actors (PFAS)	PFBS	DG	M	H	H	H	H
	6:2 FTOH	DG	H	H	H	L	H
Waxes and oils	BeesWax	L	DG	L	DG	DG	L
	Mink Oil	*L*	DG	*L*	DG	DG	DG
	Paraffins	*DG*	*DG*	*H*	*M*	*L*	*DG*
Biopolymers	Chitosan	L	*L*	**H**	**H**	L	DG
	CNC	L	DG	H	DG	M	DG
Silicon-based	SiNPs	*M*	*H*	*M*	*L*	L	*L*
	Silicones	L	L	H	*H*	H	DG

Table 12 summarizes the performance of each strategy. All the alternatives have strong hydrophobicity; even the biopolymers have reached a moderate level of performance. In terms of water repellency, none of them except silicon-based strategies demonstrated oleophobicity without the use of PFAS. Most of their washability ranges from a low to moderate level; chitosan shows the highest durability with 50 wash cycles. Sourcing is the main reason paraffin waxes are excluded from our proposed alternative solutions because they are derived from petroleum. As for the other strategies, they are promising when considering the sources, especially chitosan and SiNPs, which come from earth-abundant materials.

Table 12: Performance Table

		Hydrophobicity (Contact Angle)	Oleophobicity	Washability	Source
Bad Actors (PFAS)	PFAS	170°	156°	120+ washes	Artificial
Waxes and oils	BeesWax	153°	DG	15 washes	Bees
	Mink Oil	Oil-based	DG	2 weeks	Mink
	Paraffin Waxes	108.9	DG	20 maxiumum	Petroleum
Biopolymers	Chitosan	102°	DG	50 washes	Crustacean exoskeletons
	CNC	>90°	w/ PFAS	DG	Cellulose isolation + Prep
Silicon-based materials	SiNPs	151°	133°	10 washes	Silicon
	Silicones	130°	100°	DG	Silicon

Conclusions

Summary of Alternatives

A comparison of our most viable aftermarket treatment alternatives to PFAS is shown in Figure 21. While PFAS outmatches our alternatives in terms of performance, particularly oil-resistant performance, its environmental and health effects are uniformly worse than the alternatives. Many of the health effects of PFAS are not immediately apparent to workers and consumers, although they are dire. In our opinion, the health and environmental risks far outweigh the benefits of their remarkable stain resistance. While PFAS is both superhydrophobic and superoleophobic, many of our proposed treatments achieve high hydrophobicity, with silicon-based materials also being oleophobic against commonly-encountered household oils. For the purposes of stain resistance in most uses, a contact angle >90° with oil and water should be sufficient. We recommend reserving PFAS-containing treatments only for cases for which super-omniphobicity is truly necessary due to health or safety concerns.

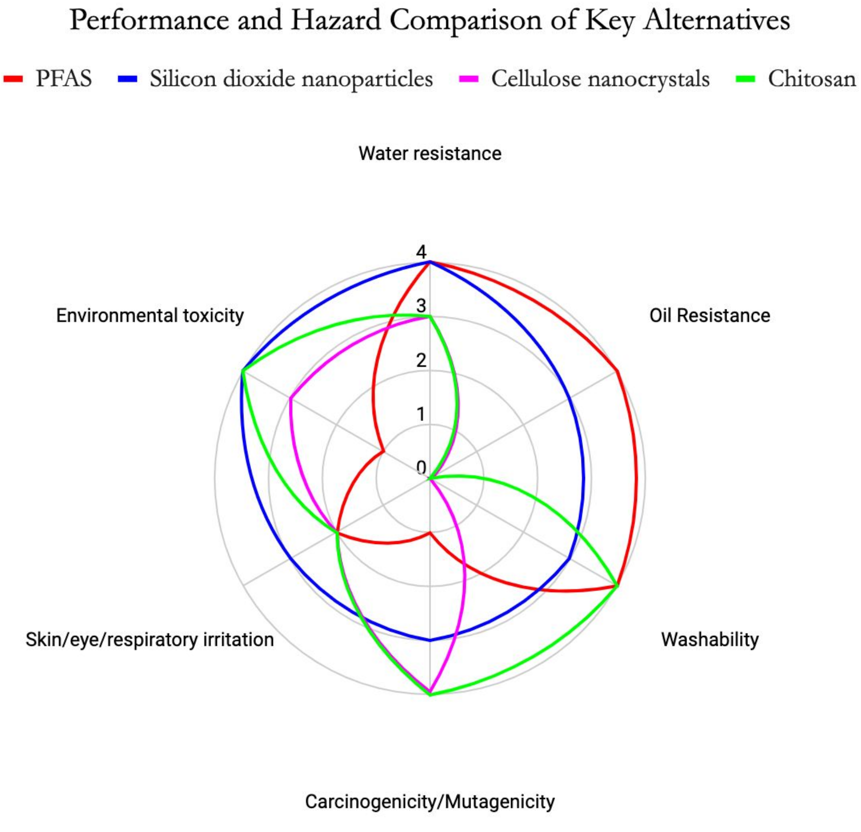

Figure 21. Comparison of PFAS to key alternatives. 4 represents the greatest performance along a technical or safety criterion, 1 is worst, and 0 is a data gap.

Waxes and Oils

Waxes and Oils are natural products with low hazard and strong hydrophobic properties, except paraffin with certain environmental concerns. They could be good inspirations of aftermarket carpet treatment products. Still, more information regarding toxicities and additives to increase oleophobicity are needed.

Biopolymers

Chitosan has potential to impart oleophobicity, but more information is needed to understand how this goal can be accomplished. The flexible and modifiable structure of cellulose nanocrystals, in combination with rarasaponins and/or herein, increase hydrophobicity of CNCs. However, they cannot be used to impart oleophobicity. Additionally, more information and research regarding toxicities and compound additive combinations is needed to increase oleophobicity; it would be beneficial to determine this in an experimental lab setting.

Silicon-based Materials

Silicon-based materials are inherently sustainable and cost-effective strategies with high stain resistant performance. While there are some human and environmental health concerns for silicon dioxide nanoparticles and silicone polymers, more research is needed to truly understand the risks of these materials, as well as their durability after application to fabric. These materials, however, are safer than PFAS and are already present in carpet-protecting formulations, so they represent a feasible way to immediately act to reduce PFAS in aftermarket treatments.

Final Recommendation/Next Steps

After a semester of research, we propose combining some of our listed alternate strategies to achieve high stain-resistant performance and introduce desirable properties not present in PFAS-containing treatments. For example, chitosan’s antimicrobial properties combined with SiNPs may produce a liquid solution that imparts strong levels of hydrophobicity and oleophobicity, as well as high levels of durability and antimicrobial activity. Combining these strategies is likely feasible, for both of them are soluble in slightly acidic aqueous solutions. We recommend exploring new ways to combine our strategies to achieve the best performance while mitigating the harmful effects of each proposed solution.

About the Authors

Amanda Bischoff is a PhD candidate in the Chemical Biology Program at UC Berkeley. As a graduate student in Matt Francis's lab, she constructs viral protein-based models of photosynthetic complexes in order to better understand the energy transfer processes of photosynthesis and has an interest in protein-based materials. Amanda used her chemical background to classify and explain the function of proposed solutions, focusing on physical strategies for conferring stain resistance.

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Samantha Vega is a UC Berkeley graduate student pursuing an Master of Public Health in Environmental Health Science with an emphasis in Industrial Hygiene. She is interested in occupational health, and researching and implementing effective controls to safeguard the health of marginalized populations. She is currently in her second year of study.

References

(1) History of PFAS and 3M https://www.3m.com/3M/en_US/pfas-stewardship-us/pfas-history/ (accessed Dec 16, 2020).

(2) Department of Toxic Substances Control https://dtsc.ca.gov/ (accessed Dec 13, 2020).

(3) Proposed Priority Product: Carpets and Rugs with Perfluoroalkyl and Polyfluoroalkyl Substances (PFASs) https://dtsc.ca.gov/scp/carpets-and-rugs-with-perfluoroalkyl-and-polyfluoroalkyl-substances-pfass/ (accessed Dec 13, 2020).

(4) Ucar, M.; Wang, Y. Utilization of Recycled Post Consumer Carpet Waste Fibers as Reinforcement in Lightweight Cementitious Composites. *International Journal of Clothing Science and Technology* **2011**, *23*, 242–248. https://doi.org/10.1108/09556221111136502.

(5) Scotchgard https://www.scotchgard.com/3M/en_US/scotchgard/ (accessed Dec 15, 2020).

(6) Renner, R. The Long and the Short of Perfluorinated Replacements. *Environ. Sci. Technol.* **2006**, *40* (1), 12–13. https://doi.org/10.1021/es062612a.

(7) Product-Chemical Profile for Treatments Containing Perfluoroalkyl or Polyfluoroalkyl Substances for Use on Converted Textiles or Leathers. 185.

(8) Classifications - CL Inventory https://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/discli/details/80228 (accessed Dec 18, 2020).

(9) Scheringer, M.; Trier, X.; Cousins, I. T.; de Voogt, P.; Fletcher, T.; Wang, Z.; Webster, T. F. Helsingør Statement on Poly- and Perfluorinated Alkyl Substances (PFASs). *Chemosphere* **2014**, *114*, 337–339. https://doi.org/10.1016/j.chemosphere.2014.05.044.

(10) Rice, P. A.; Aungst, J.; Cooper, J.; Bandele, O.; Kabadi, S. V. Comparative Analysis of the Toxicological Databases for 6:2 Fluorotelomer Alcohol (6:2 FTOH) and Perfluorohexanoic Acid (PFHxA). *Food and Chemical Toxicology* **2020**, *138*, 111210. https://doi.org/10.1016/j.fct.2020.111210.

(11) Kabadi, S. V.; Fisher, J.; Aungst, J.; Rice, P. Internal Exposure-Based Pharmacokinetic Evaluation of Potential for Biopersistence of 6:2 Fluorotelomer Alcohol (FTOH) and Its Metabolites. *Food and Chemical Toxicology* **2018**, *112*, 375–382. https://doi.org/10.1016/j.fct.2018.01.012.

(12) Farcas, M. T.; Kisin, E. R.; Menas, A. L.; Gutkin, D. W.; Star, A.; Reiner, R. S.; Yanamala, N.; Savolainen, K.; Shvedova, A. A. Pulmonary Exposure to Cellulose Nanocrystals Caused Deleterious Effects to Reproductive System in Male Mice. *Journal of Toxicology and Environmental Health, Part A* **2016**, *79* (21), 984–997. https://doi.org/10.1080/15287394.2016.1211045.

(13) Fabric Protection Market Size, Share & Trends Analysis Report By Application (Apparel, Footwear, Upholstery), By Region (North America, Asia Pacific, MEA), And Segment Forecasts, 2019 - 2025. Grand View Research 2019.

(14) Maras, M.; Vanparys, C.; Muylle, F.; Robbens, J.; Berger, U.; Barber, J. L.; Blust, R.; De Coen, W. Estrogen-Like Properties of Fluorotelomer Alcohols as Revealed by MCF-7 Breast Cancer Cell Proliferation. *Environ Health Perspect* **2006**, *114* (1), 100–105. https://doi.org/10.1289/ehp.8149.

(15) Ding, N.; Harlow, S. D.; Randolph Jr, J. F.; Loch-Caruso, R.; Park, S. K. Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) and Their Effects on the Ovary. *Human Reproduction Update* **2020**, *26* (5), 724–752. https://doi.org/10.1093/humupd/dmaa018.

(16) Ishibashi, H.; Ishida, H.; Matsuoka, M.; Tominaga, N.; Arizono, K. Estrogenic Effects of Fluorotelomer Alcohols for Human Estrogen Receptor Isoforms a and b in Vitro. *Biological and Pharmaceutical Bulletin* **2007**, *30* (7), 1358–1359.

(17) Yuan, Y.; Lee, T. R. Contact Angle and Wetting Properties. In *Surface Science Techniques*; Bracco, G., Holst, B., Eds.; Springer Berlin Heidelberg: Berlin, Heidelberg, 2013; pp 3–34. https://doi.org/10.1007/978-3-642-34243-1_1.

(18) Lanes, A. W. Carpet Protection. *Textile Progress* **1989**, *19* (3), 18–20. https://doi.org/10.1080/00405168808688931.

(19) Law, K.-Y. Water–Surface Interactions and Definitions for Hydrophilicity, Hydrophobicity and Superhydrophobicity. *Pure and Applied Chemistry* **2015**, *87* (8), 759–765. https://doi.org/10.1515/pac-2014-1206.

(20) De Smet, D.; Weydts, D.; Vanneste, M. Environmentally Friendly Fabric Finishes. In *Sustainable Apparel*; Elsevier, 2015; pp 3–33. https://doi.org/10.1016/B978-1-78242-339-3.00001-7.

(21) Paraffin Wax. *Wikipedia*; 2020.

(22) www.webcoweb.com. Paraffin application in industry http://atdmco.com/ (accessed Dec 18, 2020).

(23) Paraffin wax | chemical compound | Britannica https://www.britannica.com/science/paraffin-wax (accessed Dec 18, 2020).

(24) Jensen and Warming - 1 COWI AS 2 NIPSECT.Pdf.

(25) sharif, R.; Mohsin, M.; Ramzan, N.; Ahmad, S. W.; Qutab, H. G. Synthesis and Application of Fluorine-Free Environment-Friendly Stearic Acid-Based Oil and Water Repellent for Cotton Fabric. *Journal of Natural Fibers* **2020**, 1–16. https://doi.org/10.1080/15440478.2020.1787918.

(26) Stanley, J. S. The Effect of Paraffin Chain Salts on the Charge on Textile Fibers. *J. Phys. Chem.* **1954**, *58* (7), 533–536. https://doi.org/10.1021/j150517a005.

(27) Rehman, T.-; Ali, H. M. Experimental Investigation on Paraffin Wax Integrated with Copper Foam Based Heat Sinks for Electronic Components Thermal Cooling. *International Communications in Heat and Mass Transfer* **2018**, *98*, 155–162. https://doi.org/10.1016/j.icheatmasstransfer.2018.08.003.

(28) Critical Surface Tension and Contact Angle with Water for Various Polymers. Diversified Enterprises 2020.

(29) Ozkan, O.; Erbil, H. Y. Interpreting Contact Angle Results under Air, Water and Oil for the Same Surfaces. *Surf. Topogr.: Metrol. Prop.* **2017**, *5* (2), 024002. https://doi.org/10.1088/2051-672X/aa6e02.

(30) Zhao, Y.; Liu, E.; Fan, J.; Chen, B.; Hu, X.; He, Y.; He, C. Superhydrophobic PDMS/Wax Coated Polyester Textiles with Self-Healing Ability via Inlaying Method. *Progress in Organic Coatings* **2019**, *132*, 100–107. https://doi.org/10.1016/j.porgcoat.2019.03.043.

(31) 7 Final Report on the Safety Assessment of Sodium Lauryl Sulfate and Ammonium Lauryl Sulfate. *Journal of the American College of Toxicology* **1983**, *2* (7), 127–181. https://doi.org/10.3109/10915818309142005.

(32) Stearic acid (57-11-4) | Chemical Effects in Biological Systems https://manticore.niehs.nih.gov/cebssearch/test_article/57-11-4 (accessed Dec 18, 2020).

(33) Beeswax Beads - All-Natural Organic White Beeswax Beads https://artisanaromatics.com/shop/beeswax-beads/ (accessed Dec 18, 2020).

(34) R, R. C.; Sundaran, S. P.; A, J.; Athiyanathil, S. Fabrication of Superhydrophobic

Polycaprolactone/Beeswax Electrospun Membranes for High-Efficiency Oil/Water Separation. *RSC Adv.* **2017**, *7* (4), 2092–2102. https://doi.org/10.1039/C6RA26123J.
(35) Lanigan, R. S.; Yamarik, T. A.; Cosmetic Ingredient Review Expert Panel. Final Report on the Safety Assessment of PEG-6, -8, and -20 Sorbitan Beeswax. *Int J Toxicol* **2001**, *20 Suppl 4*, 27–38. https://doi.org/10.1080/10915810152902565.
(36) Amazon.com: Sof Sole Mink Oil for Conditioning and Waterproofing Leather, 3.5-Ounce: Sports & Outdoors https://www.amazon.com/Sof-Sole-Conditioning-Waterproofing-3-5-Ounce/dp/B003EMABT6/ref=asc_df_B003EMABT6/?tag=hyprod-20&linkCode=df0&hvadid=198081051342&hvpos=&hvnetw=g&hvrand=3369913304118870199&hvpone=&hvptwo=&hvqmt=&hvdev=c&hvdvcmdl=&hvlocint=&hvlocphy=9032086&hvtargid=pla-448733916477&psc=1 (accessed Dec 16, 2020).
(37) Final Amended Report on the Safety Assessment of Mink Oil1. *Int J Toxicol* **2005**, *24* (3_suppl), 57–64. https://doi.org/10.1080/10915810500257154.
(38) The Best Products for Maintaining and Shining Leather Shoes. *The New York Times*. April 13, 2020.
(39) Prabaharan, M. Sources of Chitosan. **2012**. https://doi.org/10.1115/1.860052_ch2.
(40) Sudhakar, Y. N.; Selvakumar, M.; Bhat, D. K. Methods of Preparation of Biopolymer Electrolytes. In *Biopolymer Electrolytes*; Elsevier, 2018; pp 35–52. https://doi.org/10.1016/B978-0-12-813447-4.00002-9.
(41) Shalaby, E. *Biological Activities and Application of Marine Polysaccharides*; BoD – Books on Demand, 2017.
(42) Kurakula, M.; N., N. R. Prospection of Recent Chitosan Biomedical Trends: Evidence from Patent Analysis (2009–2020). *International Journal of Biological Macromolecules* **2020**, *165*, 1924–1938. https://doi.org/10.1016/j.ijbiomac.2020.10.043.
(43) Manigandan, V.; Karthik, R.; Ramachandran, S.; Rajagopal, S. Chapter 15 - Chitosan Applications in Food Industry. In *Biopolymers for Food Design*; Grumezescu, A. M., Holban, A. M., Eds.; Handbook of Food Bioengineering; Academic Press, 2018; pp 469–491. https://doi.org/10.1016/B978-0-12-811449-0.00015-3.
(44) Supplier of Chitosan Antimicrobial Textile Treatments. *Tidal Vision*.
(45) Yılmaz Atay, H.; Eral Doğan, L.; Çelik, E. Investigations of Self-Healing Property of Chitosan-Reinforced Epoxy Dye Composite Coatings https://www.hindawi.com/journals/jma/2013/613717/ (accessed Dec 17, 2020). https://doi.org/10.1155/2013/613717.
(46) Zygomycota. *Wikipedia*; 2020.
(47) Roy, J.; Salaün, F.; Giraud, S.; Guan, A. F. and J. Chitosan-Based Sustainable Textile Technology: Process, Mechanism, Innovation, and Safety. *Biological Activities and Application of Marine Polysaccharides* **2017**. https://doi.org/10.5772/65259.
(48) Alonso, D.; Gimeno, M.; Olayo, R.; Vázquez-Torres, H.; Sepúlveda-Sánchez, J. D.; Shirai, K. Cross-Linking Chitosan into UV-Irradiated Cellulose Fibers for the Preparation of Antimicrobial-Finished Textiles. *Carbohydrate Polymers* **2009**, *77* (3), 536–543. https://doi.org/10.1016/j.carbpol.2009.01.027.
(49) Antibacterial action of chitosan and carboxymethylated chitosan - Fei Liu - 2001 - Journal of Applied Polymer Science - Wiley Online Library https://onlinelibrary-wiley-com.libproxy.berkeley.edu/doi/10.1002/1097-4628(20010214)79:7%3C1324::AID-APP210%3E3.0.CO;2-L (accessed Dec 17, 2020).

(50) Ye, W.; Xin, J. H.; Li, P.; Lee, K.-L. D.; Kwong, T.-L. Durable Antibacterial Finish on Cotton Fabric by Using Chitosan-Based Polymeric Core-Shell Particles. *Journal of Applied Polymer Science* **2006**, *102* (2), 1787–1793. https://doi.org/10.1002/app.24463.
(51) Chang, S.-H.; Wu, C.-H.; Tsai, G.-J. Effects of Chitosan Molecular Weight on Its Antioxidant and Antimutagenic Properties. *Carbohydrate Polymers* **2018**, *181*, 1026–1032. https://doi.org/10.1016/j.carbpol.2017.11.047.
(52) Notification Details - CL Inventory https://echa.europa.eu/information-on-chemicals/cl-inventory-database/-/discli/notification-details/79723/954936 (accessed Dec 17, 2020).
(53) Toxicity of Candidate Molluscicides to Zebra Mussels (Dreissena polymorpha) and Selected Nontarget Organisms | Elsevier Enhanced Reader https://reader.elsevier.com/reader/sd/pii/S0380133093712575?token=20E17555E547EB45BC47B52BB21C6127428CC0A3A99897CCEAC3A3BE022626A80A2A9327FF6A3C33E5E24D85A613A4AF (accessed Dec 17, 2020). https://doi.org/10.1016/S0380-1330(93)71257-5.
(54) Bullock, G.; Blazer, V.; Tsukuda, S.; Summerfelt, S. Toxicity of Acidified Chitosan for Cultured Rainbow Trout (Oncorhynchus Mykiss). *Aquaculture* **2000**, *185* (3), 273–280. https://doi.org/10.1016/S0044-8486(99)00359-2.
(55) Kean, T.; Thanou, M. Biodegradation, Biodistribution and Toxicity of Chitosan. *Advanced Drug Delivery Reviews* **2010**, *62* (1), 3–11. https://doi.org/10.1016/j.addr.2009.09.004.
(56) Matica, A. BIODEGRADABILITY OF CHITOSAN BASED PRODUCTS. **2017**, 12.
(57) Escudero-Oñate, C.; Martínez-Francés, E. A Review of Chitosan-Based Materials for the Removal of Organic Pollution from Water and Bioaugmentation. *Chitin-Chitosan - Myriad Functionalities in Science and Technology* **2018**. https://doi.org/10.5772/intechopen.76540.
(58) Production of cellulose nanocrystals from raw wood via hydrothermal treatment – Research Highlights - US Forest Service Research & Development https://www.fs.fed.us/research/highlights/highlights_display.php?in_high_id=1284 (accessed Dec 18, 2020).
(59) Lavanya, D.; Kulkarni, P.; Dixit, M.; Raavi, P. K.; Krishna, L. N. V. Sources of Cellulose and Their Applications- A Review. *International Journal of Drug Formulation and Research* **2011**, *2*, 19–38.
(60) Shankaran, D. R. Chapter 14 - Cellulose Nanocrystals for Health Care Applications. In *Applications of Nanomaterials*; Bhagyaraj, S. M., Oluwafemi, O. S., Kalarikkal, N., Thomas, S., Eds.; Micro and Nano Technologies; Woodhead Publishing, 2018; pp 415–459. https://doi.org/10.1016/B978-0-08-101971-9.00015-6.
(61) Nanocellulose in thin films, coatings, and plies for packaging applications: A review :: BioResources https://bioresources.cnr.ncsu.edu/ (accessed Dec 17, 2020).
(62) Sun, C.; Zhu, D.; Jia, H.; Yang, C.; Zheng, Z.; Wang, X. Bioinspired Hydrophobic Cellulose Nanocrystal Composite Films as Organic-Solvent-Responsive Structural-Color Rewritable Papers. *ACS Appl. Mater. Interfaces* **2020**, *12* (23), 26455–26463. https://doi.org/10.1021/acsami.0c04785.
(63) Hydrophobic Modification of Cellulose Nanocrystals from Bamboo Shoots Using Rarasaponins | ACS Omega https://pubs.acs.org/doi/10.1021/acsomega.0c02425# (accessed Dec 17, 2020).
(64) Salam, A.; Lucia, L. A.; Jameel, H. Fluorine-Based Surface Decorated Cellulose Nanocrystals as Potential Hydrophobic and Oleophobic Materials. *Cellulose* **2015**, *22* (1),

397–406. https://doi.org/10.1007/s10570-014-0507-9.

(65) Shvedova, A. A.; Kisin, E. R.; Yanamala, N.; Farcas, M. T.; Menas, A. L.; Williams, A.; Fournier, P. M.; Reynolds, J. S.; Gutkin, D. W.; Star, A.; Reiner, R. S.; Halappanavar, S.; Kagan, V. E. Gender Differences in Murine Pulmonary Responses Elicited by Cellulose Nanocrystals. *Particle and Fibre Toxicology* **2016**, *13* (1), 28. https://doi.org/10.1186/s12989-016-0140-x.

(66) Endes, C.; Camarero-Espinosa, S.; Mueller, S.; Foster, E. J.; Petri-Fink, A.; Rothen-Rutishauser, B.; Weder, C.; Clift, M. J. D. A Critical Review of the Current Knowledge Regarding the Biological Impact of Nanocellulose. *Journal of Nanobiotechnology* **2016**, *14* (1), 78. https://doi.org/10.1186/s12951-016-0230-9.

(67) Hanif, Z.; Ahmed, F. R.; Shin, S. W.; Kim, Y.-K.; Um, S. H. Size- and Dose-Dependent Toxicity of Cellulose Nanocrystals (CNC) on Human Fibroblasts and Colon Adenocarcinoma. *Colloids and Surfaces B: Biointerfaces* **2014**, *119*, 162–165. https://doi.org/10.1016/j.colsurfb.2014.04.018.

(68) Halib, N.; Ahmad, I. Nanocellulose: Insight into Health and Medical Applications. In *Handbook of Ecomaterials*; Martínez, L. M. T., Kharissova, O. V., Kharisov, B. I., Eds.; Springer International Publishing: Cham, 2017; pp 1–19. https://doi.org/10.1007/978-3-319-48281-1_5-1.

(69) 2017Tox.Pdf.

(70) Bae, G. Y.; Min, B. G.; Jeong, Y. G.; Lee, S. C.; Jang, J. H.; Koo, G. H. Superhydrophobicity of Cotton Fabrics Treated with Silica Nanoparticles and Water-Repellent Agent. *Journal of Colloid and Interface Science* **2009**, *337* (1), 170–175. https://doi.org/10.1016/j.jcis.2009.04.066.

(71) Myers, M. Current and Impending Developments in Silica Nanoparticle Use in UV-Curable Systems. *Paintings & Coatings Industry Magazine* **2011**.

(72) Li, F.; Xing, Y.; Ding, X. Silica Xerogel Coating on the Surface of Natural and Synthetic Fabrics. *Surface and Coatings Technology* **2008**, *202* (19), 4721–4727. https://doi.org/10.1016/j.surfcoat.2008.04.048.

(73) Ensikat, H. J.; Ditsche-Kuru, P.; Neinhuis, C.; Barthlott, W. Superhydrophobicity in Perfection: The Outstanding Properties of the Lotus Leaf. *Beilstein Journal of Nanotechnology* **2011**, *2* (1), 152–161. https://doi.org/10.3762/bjnano.2.19.

(74) Deng, Y.; Mager, D.; Bai, Y.; Zhou, T.; Liu, Z.; Wen, L.; Wu, Y.; Korvink, J. G. Inversely Designed Micro-Textures for Robust Cassie–Baxter Mode of Super-Hydrophobicity. *Computer Methods in Applied Mechanics and Engineering* **2018**, *341*, 113–132. https://doi.org/10.1016/j.cma.2018.06.034.

(75) Sriramulu, D.; Reed, E. L.; Annamalai, M.; Venkatesan, T. V.; Valiyaveettil, S. Synthesis and Characterization of Superhydrophobic, Self-Cleaning NIR-Reflective Silica Nanoparticles. *Sci Rep* **2016**, *6* (1), 35993. https://doi.org/10.1038/srep35993.

(76) Petcu, C.; Purcar, V.; Spătaru, C.-I.; Alexandrescu, E.; Şomoghi, R.; Trică, B.; Nițu, S.; Panaitescu, D.; Donescu, D.; Jecu, M.-L. The Influence of New Hydrophobic Silica Nanoparticles on the Surface Properties of the Films Obtained from Bilayer Hybrids. *Nanomaterials* **2017**, *7* (2), 47. https://doi.org/10.3390/nano7020047.

(77) Teli, M. D.; Annaldewar, B. N. Superhydrophobic and Ultraviolet Protective Nylon Fabrics by Modified Nano Silica Coating. *The Journal of The Textile Institute* **2017**, *108* (3), 460–466. https://doi.org/10.1080/00405000.2016.1171028.

(78) Sheen, Y.-C.; Chang, W.-H.; Chen, W.-C.; Chang, Y.-H.; Huang, Y.-C.; Chang, F.-C.

Non-Fluorinated Superamphiphobic Surfaces through Sol–Gel Processing of Methyltriethoxysilane and Tetraethoxysilane. *Materials Chemistry and Physics* **2009**, *114* (1), 63–68. https://doi.org/10.1016/j.matchemphys.2008.07.132.

(79) Murugadoss, S.; Lison, D.; Godderis, L.; Van Den Brule, S.; Mast, J.; Brassinne, F.; Sebaihi, N.; Hoet, P. H. Toxicology of Silica Nanoparticles: An Update. *Arch Toxicol* **2017**, *91* (9), 2967–3010. https://doi.org/10.1007/s00204-017-1993-y.

(80) Michel, K.; Scheel, J.; Karsten, S.; Stelter, N.; Wind, T. Risk Assessment of Amorphous Silicon Dioxide Nanoparticles in a Glass Cleaner Formulation. *Nanotoxicology* **2013**, *7* (5), 974–988. https://doi.org/10.3109/17435390.2012.689881.

(81) Vidya, P.; Chitra, K. Assessment of Acute Toxicity (LC50-96 h) of Aluminium Oxide, Silicon Dioxide and Titanium Dioxide Nanoparticles on the Freshwater Fish, Oreochromis Mossambicus (Peters, 1852). 7.

(82) Palmer, B. C.; Jatana, S.; Phelan-Dickinson, S. J.; DeLouise, L. A. Amorphous Silicon Dioxide Nanoparticles Modulate Immune Responses in a Model of Allergic Contact Dermatitis. *Sci Rep* **2019**, *9* (1), 5085. https://doi.org/10.1038/s41598-019-41493-7.

(83) Han, H.; Park, Y. H.; Park, H. J.; Lee, K.; Um, K.; Park, J.-W.; Lee, J.-H. Toxic and Adjuvant Effects of Silica Nanoparticles on Ovalbumin-Induced Allergic Airway Inflammation in Mice. *Respir Res* **2016**, *17* (1), 60. https://doi.org/10.1186/s12931-016-0376-x.

(84) Hofmann, T.; Schneider, S.; Wolterbeek, A.; van de Sandt, H.; Landsiedel, R.; van Ravenzwaay, B. Prenatal Toxicity of Synthetic Amorphous Silica Nanomaterial in Rats. *Reproductive Toxicology* **2015**, *56*, 141–146. https://doi.org/10.1016/j.reprotox.2015.04.006.

(85) Hu, H.; Fan, X.; Guo, Q.; Wei, X.; Yang, D.; Zhang, B.; Liu, J.; Wu, Q.; Oh, Y.; Feng, Y.; Chen, K.; Hou, L.; Gu, N. Silicon Dioxide Nanoparticles Induce Insulin Resistance through Endoplasmic Reticulum Stress and Generation of Reactive Oxygen Species. *Part Fibre Toxicol* **2019**, *16* (1), 41. https://doi.org/10.1186/s12989-019-0327-z.

(86) Moretto, H.-H.; Schulze, M.; Wagner, G. Silicones. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA, Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2000; p a24_057. https://doi.org/10.1002/14356007.a24_057.

(87) Shabanian, S.; Khatir, B.; Nisar, A.; Golovin, K. Rational Design of Perfluorocarbon-Free Oleophobic Textiles. *Nat Sustain* **2020**, *3* (12), 1059–1066. https://doi.org/10.1038/s41893-020-0591-9.

(88) Cheng, D. F.; Urata, C.; Yagihashi, M.; Hozumi, A. A Statically Oleophilic but Dynamically Oleophobic Smooth Nonperfluorinated Surface. *Angew. Chem.* **2012**, *124* (12), 3010–3013. https://doi.org/10.1002/ange.201108800.

(89) Dewasthale, S.; Andrews, C.; Graiver, D.; Narayan, R. Water Soluble Polysiloxanes. *Silicon* **2017**, *9* (4), 619–628. https://doi.org/10.1007/s12633-015-9334-3.

(90) Urata, C.; Masheder, B.; Cheng, D. F.; Hozumi, A. How To Reduce Resistance to Movement of Alkane Liquid Drops Across Tilted Surfaces Without Relying on Surface Roughening and Perfluorination. *Langmuir* **2012**, *28* (51), 17681–17689. https://doi.org/10.1021/la303829p.

(91) Nendza, M. Hazard Assessment of Silicone Oils (Polydimethylsiloxanes, PDMS) Used in Antifouling-/Foul-Release-Products in the Marine Environment. *Marine Pollution Bulletin* **2007**, *54* (8), 1190–1196. https://doi.org/10.1016/j.marpolbul.2007.04.009.

(92) Mojsiewicz-Pieńkowska, K.; Jamrógiewicz, M.; Szymkowska, K.; Krenczkowska, D. Direct Human Contact with Siloxanes (Silicones) – Safety or Risk Part 1. Characteristics of Siloxanes (Silicones). *Front. Pharmacol.* **2016**, *7*. https://doi.org/10.3389/fphar.2016.00132.