Potential Alternatives to PFASs in Treatments for Converted Textiles or Leathers

Below is a list of potential alternatives to perfluoroalkyl and polyfluoroalkyl substances (PFASs) in treatments for converted textiles or leathers. We identified these through our own research and outreach as of April 2022. We were able to confirm that some of these alternatives are currently used in treatment products intended for converted textiles or leathers, while for others we could only find information related to uses during textile or leather product manufacturing.

This is a **non-exhaustive list** of alternatives that Responsible Entities need to evaluate in their Alternatives Analysis, per title 22 of the California Code of Regulations, section 69505.5. The alternative chemicals and products on the list have **not been vetted for safety or performance** and listing them here does **not constitute an endorsement** by DTSC. We do not have full information on product composition, and we did not identify and evaluate all the potential factors (i.e., hazard traits) relevant for a complete Alternatives Analysis. Instead, it is the Responsible Entity's duty to assess the safety and performance of these alternatives in the Alternatives Analysis.

1. CHEMICAL ALTERNATIVES KNOWN TO BE USED IN TREATMENTS FOR CONVERTED TEXTILES OR LEATHERS

1.1. Silicones/siloxanes

- **Description:** Polysiloxanes, also known as silicones, are polymers composed of repeating units of siloxane functional groups (e.g., $[\text{-O-SiR}_1\text{R}_2\text{-}]_n$). Silicones found in a variety of commercial products contain a rigid rough surface patterning that allows them to repel liquids effectively and be used as water repellent agents. Different functional groups, including fluorine-containing ones, may be added to silicones. Only silicones that do not meet the Buck et al. (2011) definition of PFASs can be considered alternatives to the Chemical of Concern in this Priority Product.

- **Known hazard traits:** An example silicone that may be used in treatment products is polydimethylsiloxane, or PDMS (Shabanian et al. 2020). While PDMS is generally considered inert and without adverse effects, it can contain cyclic siloxane impurities known as D4 and D5 that are

persistent and bioaccumulative (Holmquist et al. 2016). The following hazard traits have been identified for D4 and D5:

- D4: Aquatic toxicity and reproductive toxicity (ECHA 2022a)
- D5: Reproductive toxicity, hepatotoxicity, digestive system toxicity, immunotoxicity, possible carcinogenicity and neurotoxicity (OEHHA 2007)

- **Example products:**
  - Atsko, Inc. Silicone Water-Guard Aerosol (Atsko, Inc. 2016)
  - Crown General Purpose Silicone Lubricant Spray (Aervoe Industries Incorporated 2019)
  - Kiwi Camp Dry Heavy Duty Water Repellent (S.C. Johnson 2018)
  - Fiebing's Snow Proof Silicone Water & Stain Repellent (Fiebing Company, Inc. 2015)

1.2. Silicon dioxide nanoparticles

- **Description:** Silica or silicon dioxide (SiO_2) is naturally occurring. Silica, including nano-silica, comes in two shapes – amorphous and crystalline. Crystalline silica can be inhaled deep into the lungs and causes silicosis and cancer. Amorphous silica is less respirable, but that distinction may be less clear with nano-size particles. Nano-amorphous silica seems to be more commonly used in products. When nano-silica adheres to the textile, it forms nano-sized air pockets that water cannot penetrate, thus creating a hydrophobic or super hydrophobic surface (Mendoza and Yu 2021; Patti et al. 2021).

- **Known hazard traits:** One concern with this alternative is potential neurotoxicity and genotoxicity. A 6-month study of rats exposed to amorphous nano-silica through a nose cone demonstrated that the particles translocated to the brain through the olfactory nerve and the weight of the brain decreased (Sutunkova et al. 2017). In addition, the researchers noted increased fragmentation of DNA in bone marrow (Sutunkova et al. 2017).

- **Example products:**
  - Vetro Power Fabric & Leather Protection (Vetro Power 2022)
  - protectME Fabric Protector Spray (protectME 2022a)
  - protectME Premium Footwear Protector (protectME 2022b)
  - Nanoman Fabric + Textile Protective Coating (Nanoman 2022)

1.3. Polyurethanes

- **Description:** Polyurethanes are a diverse class of polymers that can be used to form protective films on surfaces (Sworen et al. 2018). Polyurethane resins are composed of isocyanates and polyol building blocks and are considered inert once polymerized. Polyurethanes can be dispersed in water by incorporating hydrophilic segments into the polymer (Honarkar 2018). Such

waterborne polyurethanes can be used on converted textiles to avoid exposure to isocyanates. Because these waterborne polyurethanes are already polymerized, the potential exposures to hazardous prepolymer ingredients are expected to be reduced. They do not require potentially hazardous solvents and are generally viewed as "greener" than regular polyurethanes (Noreen et al. 2016). Different fabrics or consumer goods may require the application of different polyurethanes to provide the specific intended function, such as water repellency or spot-removal. Some polyurethanes meet the side-chain fluorinated polymer definition in Buck et al. (2011), and are thus PFASs. Only polyurethanes that are not PFASs can be considered alternatives to the Chemical of Concern in this Priority Product.

- **Known hazard traits:** The hazards associated with polyurethanes arise from their component chemicals. Because polyurethanes are a class of polymers rather than one single chemical, their hazard traits are dependent on the isocyanate/polyol combinations used during synthesis. The following is not a comprehensive list of potential chemicals used in polyurethane formulations, but rather the ingredients most expected to lead to harmful exposure from products based on our market research:
    - Methylene diphenyl diisocyanate, or MDI (Chemical Abstract Services Number (CAS RN) 101-68-8), a polyurethane building block: dermatotoxicity, immunotoxicity, neurotoxicity, respiratory toxicity (DTSC 2022)
    - Toluene (CAS RN 108-88-3), a solvent used for MDI suspension: cardiovascular toxicity, developmental toxicity, hepatotoxicity and digestive system toxicity, immunotoxicity, nephrotoxicity and other toxicity to the urinary system, neurotoxicity, ocular toxicity, ototoxicity, and respiratory toxicity (DTSC 2022)

- **Example products:**
    - WP Waterproof Sealant & Adhesive (Gear Aid 2022a)
    - WP Repair Kit (Gear Aid 2022b)
    - FC Fast Cure Seam Sealant (Gear Aid 2022c)
    - TF Tent Fabric Sealant (Gear Aid 2022d)

1.4. Acrylates

- **Description**: Acrylic polymers, or acrylates, are a class of polymers used for a variety of fabric care purposes. Acrylic polymers can be formed from various chemical building blocks, including butyl acrylate, methyl methacrylate, butyl methacrylate, and acrylic acid. Acrylates can be applied to a wide range of products such as carpets, rugs, upholstery, handbags, purses, shoes, boots, wallets, belts, furniture, laundry, and car interiors (Bissell 2019; Apple Brand 2022; Johnson 2022). While acrylic polymers can be both fluorinated and non-fluorinated (Danish Environmental Protection Agency 2015), only those that do not meet the definition of PFASs

according to Buck et al. (2011) can be considered alternatives to the Chemical of Concern in this Priority Product.

- **Known hazard traits:** Data regarding the biological and environmental fates of some acrylic polymers are lacking. However, the following acrylic polymers are used in relevant products and have known hazard traits:
    - Polymethyl methacrylate (PMMA) (CAS RN 9011-14-7): predicted as likely to meet criteria for carcinogenicity, mutagenicity, and reproductive category 1A or 1B toxicity (ECHA 2021)
    - Polyacrylic acid (CAS RN 9003-01-4): wildlife survival impairment (Aquatic Acute 1, Aquatic chronic 2), ocular toxicity (Eye Dam. 1), respiratory toxicity (STOT SE 3), and reactivity in biological systems (Acute Tox. 4) (ECHA 2022b)

- **Example products:**
    - Garde Rain and Stain Repellent (Apple Brand 2022)
    - Pro Max – Bissell (Bissell 2019)
    - Marine and Boat Fabric Guard (Chemical Guys 2019)
    - SC Johnson Shout Triple-Action Laundry Stain Remover (Johnson 2022)
    - Oxiclean Laundry Stain Remover (Church & Dwight 2022a)
    - Oxiclean Max Force Laundry Stain Remover Gel Stick (Church & Dwight 2022b)

1.5. Paraffin waxes/hydrocarbons

- **Description:** Paraffin waxes, which are mixtures of hydrocarbons, are white or colorless solids derived from petroleum or oil shale. Paraffins have a general formula of C_nH_{2n+2} and consist of branched (iso), cyclic, straight-chain, and aromatic alkanes (Speight 2002). As used in treatments for converted textiles and leathers, this alternative is usually an emulsion of paraffins made up of metal salts (commonly aluminum, zinc, and zirconium) and fatty acids like stearic acid (Danish Environmental Protection Agency 2015). Paraffin emulsions containing metal ions create asymmetrical macromolecules with a polar head and hydrophobic tail. These molecules self-orient on textile surfaces, with the more polar metal salts binding to the textile surface and allowing the hydrophobic hydrocarbon chains to face outwards and protect the textile surface from water (Danish Environmental Protection Agency 2015).

- **Known hazard traits:** As a class, paraffin waxes include thousands of potential molecular isomeric variations (Speight 2002), each with potentially unique hazard profiles. Each of the example products we identified in our research contained one of the paraffin waxes listed below. In addition, zirconium acetate (CAS RN 7585-20-8), a common component of paraffin emulsions, displays dermatotoxicity (Skin Irrit. 2), ocular toxicity (Eye Dam. 1, Eye Irrit. 2), and wildlife survival impairment (Aquatic Chronic 4) (PubChem 2022a).

- C13-14 Isoparaffin (CAS RN 64742-47-8): respiratory toxicity (Asp. Tox. 1), neurotoxicity (STOT SE 3), wildlife survival impairment (Aquatic Chronic 2), and dermatotoxicity (Skin Irrit. 2) (ECHA 2022c)
- C9-12 Isoparaffin (CAS RN 90622-57-4): respiratory toxicity (Asp. Tox. 1), wildlife survival impairment (Aquatic Chronic 2-4), and reactivity in biological systems (Acute Tox. 4) (ECHA 2022d)
- C12-14 Isoparaffin (CAS RN 68551-19-9): respiratory toxicity (Asp. Tox. 1) and neurotoxicity (STOT SE 3) (ECHA 2022e)

- **Example products:**
  - Vectra 16 and 22 (Vectra Enterprises, Inc. 2009)
  - Thompsons Water Seal Fabric Seal (The Thompson's Company 2021)
  - Collonil Carbon Pro (Collonil 2021)
  - Carpet and Fabric Protector (Ultra Chem Labs 2021)

1.6. Derivatives of fatty acids

- **Description:** Fatty acids are carboxylic acids containing aliphatic chains of varying length and degree of saturation. Naturally occurring fatty acid derivatives used as repellent treatments include beeswax ($C_{15}H_{31}COOC_{30}H_{61}$) and mink oil (triglycerides of 14 to 20 carbon chain fatty acids) (Cosmetic Ingredient Review Expert Panel 2005; C. R. et al. 2017). Other fatty acid derivatives used in treatment formulations include fatty acid modified melamine (Schindler and Hauser 2010; Danish Environmental Protection Agency 2015) and emulsions of metal salts of fatty acids and paraffins (Danish Environmental Protection Agency 2015).

- **Known hazard traits:** Mink oil can pose a low hazard for skin/eye irritation and may enhance the dermal penetration of other chemicals (Cosmetic Ingredient Review Expert Panel 2005).

- **Example products:**
  - Heavy Duty Fabric Wax (Otter Wax 2022)
  - Sno-Seal Wax (Atsko, Inc. 2022)
  - Mink Oil (Moneysworth and Best 2021)

1.7. Titanium dioxide nanoparticles

- **Description:** Titanium dioxide (TiO_2) nanoparticles are particles formed from titanium dioxide with a diameter of 100 nm or less. TiO_2 nanoparticles absorb energy from light and use that energy to react with and degrade organic contaminants, thus imparting self-cleaning properties (Prorokova et al. 2020). The hydrophobic nature of TiO_2 also makes it useful in terms of preventing water-based stains.

- **Known hazard traits:** TiO_2 (airborne, unbound particles of respirable size) is on DTSC's Candidate Chemical List because it is on the Prop 65 list as a carcinogen and on the International Agency for Research on Cancer (IARC) Carcinogen list 2B (possible carcinogenic to humans) (DTSC 2022). TiO_2 is also persistent and can release metal ions into the environment (WAP Sustainability Consulting 2021).

- **Example products**[1] (U.S. EPA 2010):
    - NanoCotz
    - Iconic Zone's Nano TiO2 PCO Liquid
    - T-2

2. OTHER CHEMICAL ALTERNATIVES KNOWN TO BE USED DURING TEXTILE OR LEATHER PRODUCT MANUFACTURING

These chemicals are known alternatives to PFASs for use during the manufacturing of textile or leather products. It is unclear if these chemicals are currently used in treatments for converted textiles or leathers, or if they could be used in such products.

2.1. Dendrimers

- **Description:** The term "dendrimer" refers to a nanoscale physical structure characterized by uniform tree-like structures (Namligoz et al. 2009; Atav 2018; Najafi et al. 2021; Rudolf Group 2022). Dendrimers prevent water, soil, and dirt particles from sticking to the surface of textiles, thus imparting self-cleaning properties; this is known as the "lotus effect" (Haule and Nambela 2022). Dendrimers can have varied chemical compositions, such as hydrocarbon-, polyurethane-, and siloxane-based (KEMI 2015; Danish Environmental Protection Agency 2015; Atav 2018). Only dendrimers that do not contain PFASs can be considered alternatives to the Chemical of Concern in this Priority Product.

[1] *These products were identified in 2010 and may have been discontinued.*

- **Known hazard traits:** Pandit (2021) calls dendrimers "*green materials*" and Mulder (2021) calls them "*friendlier chemicals*" than fluorocarbons, zirconium acetate, and titanium dioxide nanoparticles, with the caveat that "*the true safety of using dendrimers is dependent on the actual structure and the impregnation method*." The main potential hazard traits identified in the literature for dendrimer-based products are ocular toxicity, dermatotoxicity, respiratory toxicity, and aquatic toxicity (Åkerblom and Göranzon 2014; Danish Environmental Protection Agency 2015). However, these hazard traits are based on individual components of specific dendrimer formulations (e.g., organic silicon compound, organic acid, acetic acid, functionalized polymer, cationic surfactant, hydrophilic group, cross-linker), and it is unclear if they are relevant to specific dendrimers that could be used as PFAS alternatives in the Priority Product. Many of the physicochemical properties of dendrimers are also determined by their terminal groups (Atav 2018).

- **Example products:**
    - BIONIC FINISH® ECO, including the RUCO-DRY ECO series (Rudolf Group 2022)
    - Nicca (NICCA 2022)
    - OrganoTex® (OrganoTex 2022)

2.2. Silanes

- **Description:** Silanes are chemicals with the general formula Si_nH_{2n+2}. They are analogous to alkanes but based on silicon instead of carbon. A variety of silanes appear to be used to treat fabrics for water repellency (Mondal et al. 2018; Makowski 2020; Mendoza and Yu 2021; Dow Chemical). In some cases, combinations of alkyl and chlorine-substituted silanes are used to react and form a siloxane oligomer on the textile, which may impart hydrophobicity (Mondal et al. 2018; Makowski 2020). Other reports credit the alkyl chain length on the silane for the hydrophobicity (Roe et al. 2012). In addition, silanes may be modified with different functional groups, including chlorine, so that they react with the textile surface. Various functional groups, particularly chlorine, make silanes good coupling agents, meaning that they can bind to both organic and inorganic molecules. Because of this, they may be used to modify many of the nanoparticles that are used to create hydrophobicity and other properties on textiles, such as SiO_2 and TiO_2 nanoparticles (Makowski 2020; Ahangaran and Navarchian 2020; Mendoza and Yu 2021). Some silanes are fluorinated and meet the PFAS definition in Buck et al. (2011), therefore they cannot be considered alternatives to the Chemical of Concern in this Priority Product.

- **Known hazard traits:** Silanes can be reactive and flammable; when heated, some chlorinated silanes may decompose into hydrogen chloride and phosgene (PubChem 2022b). A PubChem review of CAS numbers of silanes used to treat textiles (e.g., 75-78-5, 149-74-6, 75-79-6, 919-30-2) indicates many are corrosive or irritants. Furthermore, some silanes used to treat textiles are

flagged for other hazard traits. For example, chlorotrimethylsilane (CTMS, CAS RN 75-77-4) is persistent, mobile, and toxic (PMT) and is categorized as very persistent and very mobile (vPvM) and carcinogenic. Dimethoxydimethylsilane (CAS RN 1112-39-6) is a reproductive and chronic toxicant and is vPvM and PMT (Arp and Hale 2019).

- **Example products:**
  - Silane coupling agents for textiles (Hengda 2022)

2.3. Melamine

- **Description:** Surface coating resins based on melamine (1,3,5-triazine-2,4,6-triamine, CAS RN 108-78-1) used as stain repellent treatments on textiles include the following polymers: melamine-formaldehyde, melamine-urea-phenol-formaldehyde, methylated melamine-formaldehyde, and melamine-urea-formaldehyde (Zheng and Salamova 2020). Combinations of stearic acid, formaldehyde, and melamine are also used as repellent treatments for surfaces (Schindler and Hauser 2010). Additional polymers may exist for other textile applications. Cyanuric acid, ammeline, and ammelide are common byproducts or impurities from the melamine manufacturing process and can also be used in combination with melamine to produce resins (Zheng and Salamova 2020).

- **Known hazard traits:** Melamine is on DTSC's Candidate Chemicals List due to its listing as an IARC group 2B carcinogen (potentially carcinogenic to humans) (DTSC 2022). Melamine may cause damage to the kidney and bladder (Zheng and Salamova 2020). Additionally, melamine resins are commonly formed in conjunction with formaldehyde, which is a known carcinogen. Formaldehyde is on DTSC's Candidate Chemical List, citing carcinogenicity, hepatotoxicity, digestive system toxicity, ocular toxicity, and respiratory toxicity (DTSC 2022).

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