

Safer Spray Foam Insulation

Finding and evaluating alternatives to
methylene diphenyl diisocyanate

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Introduction

California Department of Toxic Substances Control (DTSC) has identified two-component pressurized spray polyurethane foam (SPF) systems containing methylene diphenyl diisocyanate (MDI) as a Priority Product. SPF is commercially valuable and widespread because of its high insulation value, its ability to be sprayed onto surfaces or into cavities, and other useful properties. MDI is a key component of SPF because its strong crosslinking imparts SPF with short curing time (easy foaming, quickly becoming rigid and stable) and longevity (chemical and physical stability). However, SPF systems with MDI have been declared a Priority Product because of MDI's potential to cause asthma in SPF installers. Other components of SPF are not considered in this study. This project's goals were to: 1) Identify alternative materials and/or processes to meet SPF's performance specifications while reducing hazards and 2) Recommend frameworks for evaluating alternatives in terms of both function and health hazard.

Function of MDI-Based Spray Foam

Spray polyurethane foam performs exceptionally as insulation. Therefore, any SPF alternative must also have high performance. Key functional properties for spray foam insulation, according to our research and industry experience, as well as discussions with an industry representative, include: insulation value, longevity, sprayability, fire / mold / pest resistance, status quo compatibility, and material cost.

Insulation value is not only important commercially, but also environmentally. Since energy use constitutes 80-90% of an average building's lifetime environmental impacts (as measured by life-cycle assessment), effective insulation is one of the top priorities for building sustainability (1). It is also one of the most cost-effective carbon abatement strategies, actually paying a profit through reduced energy use (2). Insulation effectiveness is measured in "R-value", where higher numbers are better, and SPF provides R 6 to 7 per inch of thickness. These R-values are some of the highest in the market, roughly double the value of cheaper insulation such as fiberglass batting (3). Sprayability is another key function of SPF; it allows the insulation to fill gaps and thus stop air leaks. Such leaks, called "infiltration", are responsible for up to 40% of heat loss in buildings (4), so preventing these leaks provides a significant advantage. To be sprayable, the polyurethane liquid formulation must 1) adhere to surfaces and 2) solidify within seconds. (The formulation also expands as it adheres and solidifies, though the expanding is not a necessary attribute, and if not planned for properly can cause problems (5).) Surface adhesion is important both so that the product does not settle over time in a cavity, and

also so that a cavity is not needed--rather, SPF can be sprayed onto any surface, such as warehouse walls, ceilings, or under floors. Finally, quick solidifying times (called “setting up”) are also crucial. If a material takes too long to solidify (more than a few seconds or a minute), it can drip down from ceilings and walls, even if it adheres well.

Longevity is another key function of spray foam insulation, and it includes various factors--material longevity and resistance to fire, mold, and pests. Material longevity is important because insulation is usually sealed within walls, floors, and ceilings, so in order to replace it, one must destroy significant portions of a building's finishes, either interior or exterior (sometimes both). SPF is generally warrantied to last 20-30 years, so any replacement must have similar longevity. Fire resistance is a key function because it is legally required by building codes (6), for obvious safety reasons. MDI-based polyurethane foam is partly fire resistant due to polyurethane's inherently stable chemical bonds and aromaticity, but also because other chemical flame retardants such as chlorophosphonates are added (7). These flame retardants have their own potential health hazards, not considered in this study. Mold and mildew resistance is an important function because growth of mold or mildew within walls causes health problems for occupants, like “sick building syndrome” (8). SPF resists mold and mildew by having closed-cell pores of gas, where each bubble is separate from its neighbor and no air or water vapor permeates between pores (9). The polyurethane composition is also not a nutrient medium for fungi, which prevents mold and mildew from growing on SPF surfaces. Pest resistance is an important function because insects and rodents present potential health hazards living in building walls, floors, and ceilings. Additionally, pests reduce the effectiveness of the insulation by boring holes in the insulation, which can lead to air infiltration and heat loss, as described above. SPF's chemistry is physically strong as well as being non-nutritive and unattractive in taste to insects or rodents, so it is often advertised as inherently pest resistant (10).

Finally, material cost and status-quo compatibility are important because the architecture industry is extremely cost-driven and extremely conservative. The industry is averse to risk partly because of concern for building longevity, and partly because the low profit margins of most construction discourage investments in new technologies unless they have a high return on investment (11). SPF is a decades-long established industry, so alternatives that can either be drop-in replacements for chemicals, or that have their own long-established industries, are much more likely to be adopted by architects and construction firms. Cost is especially critical. SPF is already at the very high end of affordability for insulation (12), so alternatives should ideally be less expensive per unit of R-value. Status-quo compatibility is beneficial, but if an alternative product has obviously better performance or cost, builders will invest in new equipment and procedures.

Physical/Chemical Properties of MDI

All the high-performance properties of SPF listed above arise from its chemical composition. SPF is comprised of a variety of chemicals that are mixed together to yield an insulating foam. One of these chemicals, which is critical to the structure of SPF, is the crosslinking agent: methylene diphenyl diisocyanate (MDI). MDI is a highly electrophilic compound and is therefore very reactive toward nucleophiles. This reactivity allows the material to polymerize quickly in the presence of mild nucleophilic reagents and also undergo a variety of transformative processes with different complement reactants.

Due to the reactivity of MDI, the chemical constituents of SPF must be separated into two different components, an “A-side” and a “B-side”, until just before mixing. The A-side is comprised of the isocyanate (usually a mixture of MDI with short oligomers and polymeric material). The B-side is comprised of the remaining materials: the polyols (~35%) flame retardants (~25%), blowing agents (~20%), catalysts (~10%), and surfactants (~10%). (13).

When SPF is applied, the two components are pressurized and fed into a spray gun where the two components mix for a fraction of a second, are heated to ~100–140 °F and pressurized to 1000 psi (14). Once they begin mixing, a complex set of chemical reactions begins to occur. Over the time span of a couple minutes, the reactions will convert the starting materials into insulating foam.

The chemical processes are outlined below (**Figure 1**): When an isocyanate and an alcohol meet, an addition reaction occurs yielding a urethane group. Isocyanates are strong electrophiles and will react almost immediately with even mild nucleophiles, like alcohols, amines, or water. The highly reactive nature of the isocyanate is critical to the properties of the final foam. For example, when an isocyanate group reacts with residual water in the atmosphere, instead of forming a urethane group, a terminal amide and carbon dioxide gas are formed. The formation of CO₂ gas is very important to the foaming of the product. The reactivity of the isocyanate also results in an extremely stable bond, imparting SPF with its characteristic rigidity and longevity.

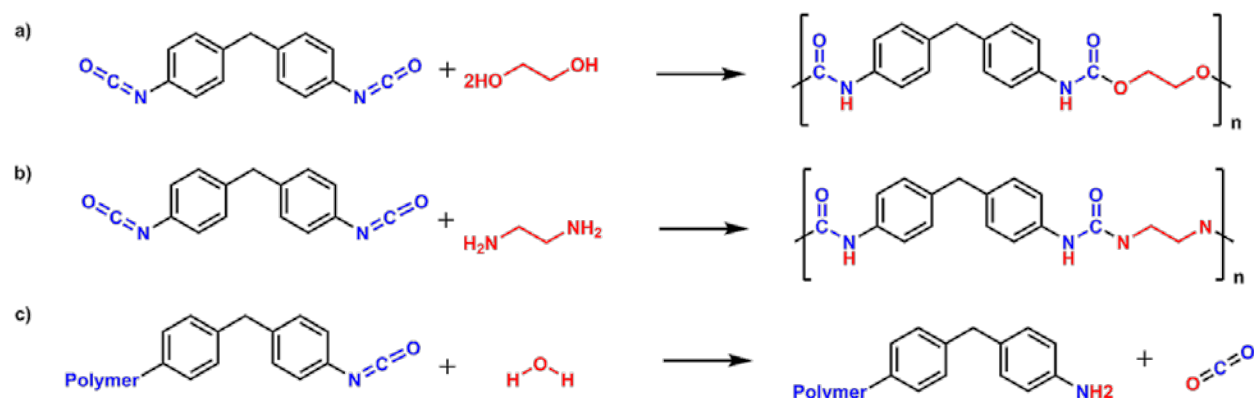


Figure 1. Outline of MDI reactivity with various nucleophiles. a) Reaction of MDI with a generic polyol to form a polyurethane. b) Reaction of MDI with a generic amine to form a polyurea. c) Reaction of a generic polymer with an isocyanate end group with water to form a polymer with a terminal amine and carbon dioxide.

Hazards of MDI

While MDI is an essential component of SPF, it presents a host of health hazards ranging from irritation to severe lung damage. Industries that use MDI may expose workers to MDI either through inhalation or dermal contact (15). Acute exposures (exposures that last < 24 hours) to MDI generally result in irritation of the upper respiratory tract and lungs with symptoms of headache, sore throat, cough, and chest tightness (16). MDI can also induce sensitization, creating MDI antigens that elicit an allergic response the next time a “sensitized” individual encounters MDI through that exposure pathway. As a respiratory sensitizer, MDI may lead to hypersensitivity of the airways after inhalation. A sufficiently high single inhalation exposure, multiple low-level exposures, or a combination of both may induce respiratory sensitization, resulting in occupational asthma or hypersensitivity pneumonitis (17,18). After respiratory sensitization, subsequent inhalation exposure to MDI—even as low as 0.05 parts per billion—may trigger pulmonary symptoms like bronchial hyper-responsiveness and airflow obstruction (19,20). For sensitized individuals, there is no known threshold exposure to prevent respiratory symptoms from occurring (16,21). MDI is also a dermal irritant and skin sensitizer capable of inducing allergic contact eczema (22). Several reports suggest that dermal exposure increases the risk for respiratory sensitization and cite occupational settings with prevalent MDI skin exposures and non-detectable air concentrations (23,24). The association between dermal exposure and isocyanate-induced asthma initiated the hypothesis that MDI causes systemic sensitization from skin exposure, leading to asthma upon MDI inhalation exposure (16).

In SPF, MDI exposure may occur during application, curing time, and thermal degradation of the product (25). Once SPF cures, MDI remains in the rigid material and will not be

released to the environment unless the polyurethane thermally degrades from fire or heat-generating processes (like drilling and welding) (26). Although SPF solidifies in seconds, it may take 23 to 72 hours to fully cure (27). Curing time varies largely according to formulations and environmental conditions. The SPF application releases vaporized and aerosolized MDI in concentrations exceeding recommended exposure limits. Crespo and Galan (1999) measured MDI aerosols in the range of 7.52-39.1 ppb from SPF applications (28). One study found 20% of spray foam aerosols were of respirable size ranges (29). Vapor-phase MDI has an estimated atmospheric half-life of 15 hours (from photochemical hydroxyl radical degradation) (30), while particle-phase MDI undergoes wet or dry deposition. Although the Occupational Safety & Health Administration (OSHA) requires personal protective equipment (PPE) for handling MDI, workers may be exposed to MDI through accidental or intentional violations, resulting in potentially severe health effects. (25). Additionally, second-hand MDI exposures from SPF applications may occur, endangering bystanders who may not have PPE (31).

As a class of chemicals, isocyanates are the leading cause of occupational asthma in the United States and other industrialized countries (32). The National Institute for Occupational Safety and Health (NIOSH) has attributed several cases of respiratory diseases and fatalities to occupational MDI exposure from polyurethane products (15,33). For its MDI findings, NIOSH focused primarily on truck bed lining operations (with spray-on polyurethane coatings) and extends its warning of MDI hazards to other industries that use MDI in similar manner (15). To ensure occupational health, SPF applications should reduce or eliminate MDI exposure through safer controls, engineering techniques, or substitution.

Methods

Potentially countless sprayable insulation alternatives may exist, but limited time and resources always limit investigations of alternatives. We searched standard chemistry literature for MDI replacements; we searched polyurethane industry patent data (generously provided by the industry partner, as well as free online resources) for both MDI replacements and alternatives to SPF as a whole; we searched other architectural industry sources for whole SPF alternatives; and we spent the bulk of our time searching biological literature for potential biomimetic MDI replacements or whole SPF alternatives. Our biomimicry searches largely stemmed from a compilation of biological strategies for crosslinking developed by Mark Dorfman at Biomimicry 3.8.

Function Evaluation

Each strategy was then evaluated from a “Function” perspective, comparing the proposed strategy to SPF’s current functionality across six different categories. Function scores for all of these categories ranged from 1 to 4, with “1” being worst, “2” being acceptable but worse than existing SPF, “3” being comparable to SPF, and “4” being better than SPF. Then an overall score was calculated as a weighted average of scores from all these categories (discussed below). We determined scores for all these categories based on published data for commercial products where available (both manufacturer claims and third-party reviews), though these were only available for existing MDI-based SPF and two alternative strategies. For other alternatives, scores were estimated based on chemical or physical data published on the components of that strategy. Once the strategy was broken down into chemicals (or representative chemicals for those strategies with undefined chemical makeup) these chemicals were evaluated by a variety of chemical and physical properties as a means to predict the end product’s characteristics. For example, we assumed strategies that only replaced MDI as the crosslinking agent (but left the rest of the spray foam system similar) would have functional properties scoring the same as MDI-based SPF, except where specific published data showed otherwise. Properties for reported chemicals were obtained from a variety of sources, including SciFinder and Chemspider. The six functional property categories are explained below:

Insulation: How well a material prevents heat transfer.

Insulation value comprised 15% of the overall score because although it is the primary purpose for insulation, applicators may simply choose to apply more of a poorly insulating foam to make up the difference in insulation value. As mentioned above, insulation performance is measured by R-value. Doubling the R-value means half the flow of heat through a given construction. An insulation material’s performance is measured in R-value per inch, so that a

given construction may achieve R 6 by having a one inch thickness of R 6/in. insulation, or by having a 2 inch thickness of R 3/in. insulation. A standard 2"x4" framed building has wall cavities 3.5" deep (not 4" as the name implies), so insulation with R 3/in. filling the cavity would provide R 10 insulation, a respectable value for many climates. Buildings are also sometimes framed with 2"x6" studs, which at R 3/in. would provide R 16, a high value. Ceiling joists are often even deeper, and empty attics or below-floor crawl spaces can have significantly more room for insulation. Not every building has these opportunities, but it is common enough we considered it a viable workaround. Numeric scores are as follows:

- 1: $R < 3/\text{in.}$
- 2: $R \text{ } 3\text{-}5/\text{in.}$
- 3: $R \text{ } 5\text{-}7/\text{in.}$
- 4: $R > 7/\text{in.}$

Longevity / Stability: How long the product is expected to last.

Longevity / Stability comprised 20% of the overall score because it is critical for insulation to last decades. Insulation sits within walls, so replacing it means destroying the wall interior or exterior in order to access the insulation. In addition, insulation's location inside walls conceals it from building occupants and maintenance personnel, blinding them to possible insulation deterioration. They would only notice insulation deterioration if they were paying strict attention to energy bills or getting complaints from occupants about sickness from mold. Longevity value was extrapolated from the chemical composition of the product. Numeric scores are as follows:

- 1: product likely needs replacement within 10 years.
- 2: 10 - 20 year life
- 3: 20 - 30 year life.
- 4: > 30 year life.

Sprayability: Whether the material can be sprayed uniformly, adheres well, sets up quickly, fills gaps, and its likely application labor cost.

Sprayability comprised 20% of the overall score because it is crucial to both the product category and its insulation performance. Sprayability improves insulation performance by stopping air infiltration from outside, and by filling gaps so there is no "thermal bridging" (heat flowing around insulation) through empty air within the building envelope. Sprayability is also part of the definition of spray foam--without it, the insulation would be rolled batts or rigid foam boards, which are different markets. Uniformity of spraying is important to have consistent R-values and surfacing. Adhering is required to avoid settling or falling from

ceilings. Setting up quickly is required to avoid dripping down surfaces. Application labor cost includes both hours on site and in training that may be incurred by equipment complexity, personal protective equipment requirements, strict procedures, or other factors. Numeric scores are as follows:

- 1: a non-sprayable material (e.g. batting or block insulation).
- 2: an increased application cost, worse adhesion, or longer cure time.
- 3: application cost, adhesion, and cure time similar to status quo.
- 4: improvement in these aspects compared to status quo.

Status Quo Compatibility: How well the proposed technology fits with current manufacturing systems, application equipment, and procedures.

Status-Quo Compatibility comprised 15% of the overall score because while it is important to ease industry adoption, it is not crucial. If industry perceives an alternative product to be sufficiently advantageous, it will adopt the alternative product even if the alternative is completely incompatible with current equipment and practices. This score includes equipment and procedures for manufacturing the liquid reagents (for current SPF, the “A” side and “B” side mixes), for storing and transporting them to building sites, for applying the product to buildings, and for cleanup of building sites. For example, current application equipment includes a two-tank system, hoses carrying the liquid reactants to a handheld nozzle, and apparatus to pressurize the tanks and heat the nozzle, as well as full-body protective equipment with respirator. Numeric scores are as follows:

- 1: no current ingredients, manufacturing methods, or application equipment and procedures can be used with the new alternative.
- 2: a large percent of ingredients, manufacturing, and application remain the same, but switching to the new system will incur costs in equipment and/or training.
- 3: switching will incur minor equipment / training costs.
- 4: an ingredient replacement with no change in manufacturing methods or application equipment or procedures.

Fire / Mold / Pest Resistance: How well the product would resist combustion, fungal growth and pests.

Fire, Mold, & Pest Resistance comprised 10% of the overall score because even though these properties are important, they can also be achieved by other means. Separate products or additives within the product can be used to supply these properties. Building walls, ceilings, and floors are already conglomerates of many products to provide different functional properties. SPF already has additives to improve its flame retardance, for example. Flame

retardance is measured by ASTM E84 standards (34), among others, with a Class 1 rating being the best; it is required by many building codes nationwide. Mold and pest resistance are more difficult to measure, so we estimated based on manufacturer claims and/or literature describing what chemistries are or are not growth media for fungus, and what chemistries are or are not edible to insects or rodents. Numeric scores are as follows:

- 1: ASTM E84 Class 3 fire rating or a lack of rating, and/or no resistance to mold or pests
- 2: Class 2 fire rating and/or less resistance to mold or pests than MDI spray foam.
- 3: Class 1 fire rating and similar mold & pest resistance to MDI spray foam with similar use of chemical additives (e.g. PBDE flame retardants).
- 4: Class 1 fire rating plus mold and pest resistance similar to or better than MDI spray foam, with fewer (or no) additives.

Material Cost: How expensive the material ingredients would be.

Material Cost comprised 20% of the overall score because it is another crucial property. The building industry is extremely cost-driven, and insulation is often under-used in order to cut costs. SPF insulation is already beyond the price range of many builders and architects, so to be viable in the real world, alternative products must have reasonable costs. Material cost does not include application labor cost, as that is included in “sprayability” above. Numeric scores are as follows:

- 1: likely total material cost for all ingredients over 50% higher than MDI spray foam
- 2: likely material cost 20-50% higher
- 3: likely material cost within 20% of MDI spray foam
- 4: likely material cost 20% less than MDI spray foam, or lower.

Table 1 below shows the functional scoring for MDI-based spray polyurethane foam, with each column showing a different functional property score, their weightings listed below each column, and the resulting overall score at the right end of the table. In this and all future tables, a score of “1” is colored red, “2” is purple, “3” is blue, and “4” is green.

Table 1. Functional score table for MDI-based spray polyurethane foam.

	Insulation R-Value	Longevity / Stability	Sprayability	Status-Quo Compatibility	Fire, Mold, & Pest Resistance	Material Cost	Overall Functional Score
MDI (current practice)	3	3	3	4	3	3	3.2
Percent of Overall Score	15%	20%	20%	15%	10%	20%	

Hazard Evaluation

To assess the hazards of our alternatives, we created an evaluation framework for health and environmental toxicity. We selected the six hazard criteria and grouped several endpoints together for simplification. We chose not to examine physical hazards like flammability or reactivity. We also did not include other human and environmental damage measurements such as climate change, acidification, or ozone depletion--we only assessed toxicity.

We broke down each alternative into its composite chemicals and compiled toxicological information for these compounds. To identify associated health and environmental hazards, we used the Pharos Project database to screen our chemicals against authoritative lists. We recorded qualitative hazards data for our six hazard criteria from the authoritative lists. When the chemicals were not included in authoritative lists, we searched additional sources for hazards information, including the Hazardous Substances Data Bank (HSDB), Material Safety Data Sheets (MSDS), OpenTox, and EPI Suite.

For the evaluation framework, we created a numerical ranking scheme adapted from from GreenScreen v.1.2. and its grouping of the Globally Harmonized System (GHS) of Classifying and Labelling of Chemicals (35). Our ranking scheme ranged from 1 to 4, with a score of “1” indicating high hazard for an endpoint and a score of “4” indicating safety or minimal hazard for an endpoint. To obtain an overall health and environment score, we calculated a weighted average of our six hazard criteria (discussed below). We prioritized long-term human health effects for occupational settings to address DTSC’s concerns about MDI exposure to SPF installers. We fully recognize that hazard weights are subjective for each population of interest, and that others may weigh these categories differently. The six hazard categories are explained below:

Sensitization: induces allergic response through inhalation or dermal exposure.

Sensitization comprises 20% of the overall score because although it is not as severe a health problem as cancer or acute toxicity, it is the reason MDI was labeled a Priority Product in SPF insulation. Our project scope aims to reduce the risks of asthma, leading us to weigh heavily on sensitization. For the numeric scoring, we prioritized respiratory over contact sensitization. Numeric scores are as follows:

- 1: Known respiratory sensitizer
 - High frequency of occurrence (GHS Category 1A)
- 2: Suspected respiratory sensitizer OR Known contact sensitizer

- Respiratory - low to moderate frequency of occurrence (GHS Category 1B)
- Contact - high frequency of occurrence (GHS Category 1A)
- 3: Possible respiratory sensitizer OR Suspected contact sensitizer
 - Respiratory - based on available adequate data: negative studies, no structural alerts, and GHS not classified
 - Contact - low to moderate frequency of occurrence (GHS Category 1B)
- 4: Improbable respiratory sensitizer OR Possible/Improbable contact sensitizer
 - Respiratory - based on strong evidence for negative studies
 - Contact - based on available adequate data: negative studies and no structural alerts, and GHS not classified

Acute Toxicity: produces toxic effects from exposures of less than 24 hours.

Acute toxicity comprises 15% of the overall score because most toxicological data present it as a critical metric for evaluating hazards in high exposure scenarios. Although the animal data endpoints for lethal dose and lethal concentrations do not easily translate to human risk, acute toxicity provides a baseline for comparison. Numeric scores are as follows:

1: Very high.

Threshold values for any route of exposure (GHS Category 1 or 2):

- Oral LD₅₀ (mg/kg) \leq 50
- Dermal LD₅₀ (mg/kg) \leq 200
- Inhalation - Gas or Vapor LC₅₀ (mg/L) \leq 2
- Inhalation - Dust/Mist/Fumes LC₅₀ (mg/L) \leq 0.5

2: High.

Threshold values for any route of exposure (GHS Category 3):

- Oral LD₅₀ (mg/kg) > 50-300
- Dermal LD₅₀ (mg/kg) > 200-1,000
- Inhalation - Gas or Vapor LC₅₀ (mg/L) > 2-10
- Inhalation - Dust/Mist/Fumes LC₅₀ (mg/L) > 0.5-1.0

3: Moderate.

Threshold values for any route of exposure (GHS Category 4):

- Oral LD₅₀ (mg/kg) > 300-2,000
- Dermal LD₅₀ (mg/kg) > 1,000-2,000
- Inhalation - Gas or Vapor LC₅₀ (mg/L) > 10-20
- Inhalation - Dust/Mist/Fumes LC₅₀ (mg/L) > 1-5

4: Low.

Threshold values for any route of exposure (GHS Category 5 or from available adequate data: negative studies, no structural alerts, and GHS not classified):

- Oral LD₅₀ (mg/kg) > 2,000

- Dermal LD₅₀ (mg/kg) > 2,000
- Inhalation - Gas or Vapor LC₅₀ (mg/L) > 20
- Inhalation - Dust/Mist/Fumes LC₅₀ (mg/L) > 5

Carcinogenicity or Mutagenicity: causes cancer or gene mutations.

Carcinogenicity or Mutagenicity comprises 20% of the overall score because carcinogens and mutagens present imminent risk for chronic, disabling, and/or fatal effects. Numeric scores are as follows:

- 1: Known carcinogen or mutagen.
 - Known or presumed for any route of exposure (GHS Category 1A or 1B)
- 2: Suspected carcinogen or mutagen
 - Suspected for any route of exposure or limited/marginal evidence of carcinogenicity in animals (GHS Category 2)
- 3: Possible carcinogen or mutagen
 - Based on available adequate data: negative studies, no structural alerts, and GHS not classified
- 4: Improbable carcinogen or mutagen
 - Based on strong evidence of negative studies

Endocrine Disruption, Reproductive or Developmental Toxicity: disrupts hormones, reproductive systems, or child development.

Endocrine Disruption, Reproductive or Developmental Toxicity comprises 20% of the overall score because these have the potential to induce long-lasting harm that can be transferred to the next generation. Chemicals that affect the hormonal system, reproductive organs, or child development may occur at very low exposures. Numeric scores are as follows:

- 1: “Known” endocrine disruptor, reproductive toxicant, or developmental toxicant
 - Endocrine - based on evidence of endocrine activity and related human health effects
 - Reproductive / Developmental - presumed or known for any route of exposure (GHS Category 1A or 1B)
- 2: “Suspected” endocrine disruptor, reproductive toxicant, or developmental toxicant
 - Endocrine - based on evidence of endocrine activity
 - Reproductive / Developmental - suspected for any route of exposure or limited/marginal evidence of reproductive or developmental toxicity in animals (GHS Category 2)
- 3: “Possible” endocrine disruptor, reproductive toxicant, or developmental toxicant

- Endocrine - based on available adequate data: negative studies and no structural alerts
 - Reproductive / Developmental - based on available adequate data: negative studies, no structural alerts, and GHS not classified
- 4: “Improbable” endocrine disruptor, reproductive toxicant, or developmental toxicant
- Endocrine - based on strong evidence for no or non-toxic effects on endocrine activity
 - Reproductive / Developmental - based on strong evidence for negative studies

Persistence or Bioaccumulation: resists degradation or accumulates in bodies.

Persistence or Bioaccumulation comprises 10% of the overall score because it does not present immediate and debilitating hazards at the application phase for SPF installers. Persistence and bioaccumulation are important in the life cycle assessment of alternatives to ensure proper evaluation of end-of-life effects, but they are not a high priority for our population of concern. Persistence metrics were based on half-lives according to media and measurement. Bioaccumulation metrics were based on Bioaccumulation Factor (BAF), Bioconcentration Factor (BCF), the octanol-water partition coefficient ($\log K_{ow}$) and monitoring data. Numeric scores are as follows:

1: Very high

- Persistence
 - Soil/Sediment $t_{1/2} > 180$ days or recalcitrant
 - Water $t_{1/2} > 60$ days or recalcitrant
 - Air $t_{1/2} > 5$ days or recalcitrant
- Bioaccumulation
 - BAF $> 5,000$ L/kg
 - $\log K_{ow} > 5$

2: High

- Persistence
 - Soil/Sediment $t_{1/2} > 60$ days
 - Water $t_{1/2} > 40$ days
 - Air $t_{1/2} > 2$ days
 - Evidence for long-range environmental transport
- Bioaccumulation
 - BAF $> 1,000$ L/kg
 - $\log K_{ow} > 4.5$
 - Biomonitoring data: evidence for bioaccumulation

3: Moderate

- Persistence

- Soil/Sediment $t_{1/2} > 16$ days
 - Water $t_{1/2} > 16$ days
 - Suggested evidence for long-range environmental transport
 - Bioaccumulation
 - $BAF > 500$ L/kg
 - $\log K_{ow} > 4$
 - Biomonitoring data: suggestive evidence for bioaccumulation
- 4: Low
- Persistence
 - Soil/Sediment $t_{1/2} \leq 16$ days
 - Water $t_{1/2} \leq 16$ days
 - Air $t_{1/2} \leq 2$ days
 - Bioaccumulation
 - $BAF \leq 500$ L/kg
 - $\log K_{ow} \leq 4$

Aquatic Toxicity or Ecotoxicity: toxic to aquatic life or ecosystems

Aquatic Toxicity or Ecotoxicity comprises 15% of the overall score because even though our priority was human health, we acknowledge the importance of hazards to other animals and ecosystems as well. Aquatic toxicity metrics consist both of acute and chronic aquatic toxicity, which were based on GreenScreen's prioritization of GHS. Ecotoxicity metrics were based on New Zealand's hazard classifications under Hazard Substances and New Organisms Act (36). Numeric scores are as follows:

- 1: Very high
 - Aquatic Toxicity - evidence for very toxic effects to aquatic life (GHS Category 1)
 - Ecotoxicity - evidence for very ecotoxic effects
- 2: High
 - Aquatic Toxicity - evidence for toxic effects to aquatic life (GHS Category 2)
 - Ecotoxicity - evidence for ecotoxic effects
- 3: Moderate
 - Aquatic Toxicity - evidence for harmful effects to aquatic life (GHS Category 3)
 - Ecotoxicity - evidence for harmful effects for ecosystems
- 4: Low
 - Aquatic Toxicity - evidence for minimal harmful effects to aquatic life
 - Ecotoxicity - evidence for minimal harmful effects for ecosystems

Screening each component chemical against authoritative lists and/or quantitative threshold values, we scored the composite chemical for each hazard criteria. If there were no hazard data for a composite chemical, we denoted the data gap with an asterisk (*). From the composite chemicals, we report the range of scores for each hazard criteria. The quantity of asterisks signifies the number of composite ingredients with data gaps for the hazard criteria. “UNK” denotes data gaps for all the composite chemicals for an alternative. Full details regarding the ranking of the composite chemicals are found in the **Appendix**.

Table 2 below shows the health & environment scoring for conventional MDI-based SPF. Each column contains a different hazard criteria score, with the percent weightings shown at the bottom of each column. The resulting overall score is located at the right end of the table. Once again, in this and all future tables, a score of “1” is colored red, “2” is purple, “3” is blue, and “4” is green. Highly uncertain overall scores are color-coded fading from the low-end color (rounded down to the next nearest color) to the high-end color (rounded up to the next nearest color if the score is within .3 of the next color).

Table 2. Health & environmental score table for MDI-based spray polyurethane foam.

	Sensitization	Acute Toxicity	Carcinogen / Mutagen	Endocrine / Reproductive / Development	Persistence / Bioaccum.	Aquatic Tox / Ecotoxicity	Overall Health & Env. Score
MDI (current practice)	1	1	2	UNK	UNK	UNK	1.2 – 2.6***
Percent of Overall Score	20%	15%	20%	20%	15%	10%	

Results: Alternative Strategies

Below are listed the eight alternative strategies we investigated, with descriptions of their chemistry, functionality scores, and health hazard scores. They are grouped into three categories: chemical replacement alternatives (which only replace MDI and still form polyurethane bonds), industry strategies (existing products that can replace SPF as a whole), and biomimetic strategies. They are listed in order from least radical (closest to a drop-in replacement) to most radical (requiring extensive research and development).

We also investigated other strategies that are not described in detail here because we deemed them less promising in both the short- and long-term for either function or health properties. To summarize: Mycelium grown-in-place insulation such as Ecovative was dismissed because it requires baking the insulation to kill mycelia after growth, which is difficult to do on-site in a building. Bio-foam O-linking to carbohydrates or bio-foam protein catalyzed by metal and proteinaceous biopolymer hydrogels were dismissed because they were less well-researched or developed than other biomimetic strategies and did not appear to have any obvious functional or health advantages. Microbial transglutaminases were dismissed because in addition to being less-well-researched and not having obvious advantages, their chemistry also appears to be associated with Alzheimer's disease, which could be an unfortunate substitution. Besides the eight strategies listed here, there may be many other promising contenders.

Chemical Replacement Alternatives

On the “less radical” end of the spectrum are replacement technologies that seek primarily to make the Priority Product safer. In this case, we can achieve this goal either by modify MDI to reduce exposure, or we can replace the isocyanate-polyol pairing with alternative chemicals that will yield a foam similar to polyurethane foam. These strategies can broadly be viewed as “Drop-In Replacement” strategies, whereby simple chemical modifications to or replacements of the Priority Product (and as few other components as possible) result in minimal disruption to the industry.

Polymeric MDI (pMDI)

What is it: Polymeric MDI (pMDI) is a nonspecific polymer form of MDI; pMDI has chemical and physical properties similar to MDI, but has a higher molecular weight than monomeric MDI.

Inspiration / precedence: Generally, an increase in molecular weight of a chemical correlates to a decrease in that chemical's health impacts. Therefore it would make sense that in order to decrease the hazard of free isocyanates, one could simply increase the molecular weight of the isocyanate used via polymerization. Additionally, isocyanate mixtures of MDI and short polymeric forms of MDI are already used in commercial applications.

Chemistry: As seen in **Figure 2**, pMDI is a polymeric version of MDI where isocyanate functionalized phenyl rings are linked together by methylene bridges. What is important to note is that the isocyanate groups are unreacted, just as in monomeric MDI. Therefore, the same chemistries should be available to this molecule as MDI.

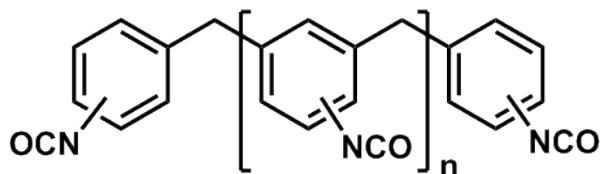


Figure 2. Chemical structure of pMDI. Polymer is comprised of aromatic isocyanates linked together by methylene bridges.

Functional advantages & disadvantages: pMDI scores a “3” for insulation because the product of SPF with pMDI should functionally be the same as the SPF with MDI. The same reasoning is applied to the longevity score. Since the product will be the same, the longevity of the product should be the same as that of SPF with MDI. Therefore our longevity score is a “3”. The same is true of sprayability as pMDI and MDI have similar physical properties. So pMDI scores a “3”. As far as status-quo compatibility is concerned, pMDI comes as close to being as non-disruptive as possible. However, while pMDI is commercially available from chemical manufacturers like Bayer, Sigma-Aldrich and Dow, it is difficult to obtain pMDI of high average molecular weights. Most suppliers supply manufacture pMDI with a relatively low average molecular weight meaning that statistically there is a relatively large percentage of monomeric MDI, between 30-60% present in the polymer mix (37). This monomeric material would have to be separated from the polymer in order to satisfy the condition that the strategy be MDI free. Therefore, it would have to be subjected to a purification step, which may include a size exclusion chromatographic technique. However, due to the highly reactive nature of isocyanates, it is likely that much material would be lost in this purification process. Such material loss would most likely increase the price of these materials. Therefore, this added purification step leads to a lower status-quo compatibility score of “3”. For fire, mold, and pest resistance” pMDI again scores a “3” as the product is expected to be the same as that of the MDI SPF. Finally, the material cost scores “3” because

although cost may increase with the added purification steps as described above, the costs of the rest of the SPF system will remain the same. **Table 3** below summarizes the functional scores and the resulting overall score.

Table 3. Functional score table for pMDI-based spray polyurethane foam.

	Insulation R-Value	Longevity / Stability	Sprayability	Status-Quo Compatibility	Fire, Mold, & Pest Resistance	Material Cost	Overall Functional Score
Polymeric MDI (pMDI)	3	3	3	3	3	3	3.0

Health / environmental advantages & disadvantages: Occupational health studies suggest that polymerized isocyanates pose similar sensitization hazards as monomeric isocyanates, prompting us to score pMDI with “1” for respiratory sensitization (17,38,39). These studies indicate that around 110°C (230°F), the polymeric chains of pMDI decompose into monomeric MDI (30). What remains unclear is whether this thermal decomposition barrier is higher or lower than that of the thermal barrier to reaction with nucleophiles, which would render the isocyanates into polyurethane. What additionally remains unclear is whether or not the MDI detected in the “decomposition vapor” evolved from the decomposition of pMDI or whether the MDI detected was present in the pMDI at the onset. Most industrial settings use a mixture of pMDI and monomeric MDI, making it difficult to distinguish the health effects of pure pMDI. Given the various formulations and molecular weights of pMDI, it is unclear whether polymerized isocyanates above a threshold molecular size would be too large to be respired or dermally absorbed, effectively reducing risks for sensitization. While we believe pMDI is a promising strategy, further research into its hazards is necessary before substituting it for MDI in SPF. **Table 4** below summarizes the different health category scores and the resulting overall score.

Table 4. Health & environmental score table for pMDI-based spray polyurethane foam.

	Sensitization	Acute Toxicity	Carcinogen / Mutagen	Endocrine / Reproductive / Development	Persistence / Bioaccum.	Aquatic Tox / Ecotoxicity	Overall Health & Env. Score
Polymeric MDI (pMDI)	1	1	UNK	3	UNK	UNK	1.4 – 2.8***

Non-Isocyanate Polyurethane (NIPU)

What is it: Non-Isocyanate Polyurethanes (NIPU) are polyurethanes made from non-isocyanate precursors. Most commonly researched are a class of NIPU that react cyclic carbonates with polyamines to create the desired crosslinked urethane structure (40).

Inspiration / precedence: Just as in the business world, usage of highly reactive isocyanates in chemical reactions is also an issue in the academic world. Therefore there has been much research in the area of making the synthesis of polyurethanes greener. Much research was invested in determining if sustainable bio-based alternatives could be used instead. It was determined that by using relatively benign and biologically abundant materials like soybean oil and sunflower oil one could in fact make greener polyurethane (41,42). These natural oils could easily be modified by epoxidation followed by CO₂ sequestration to form the desired cyclic carbonate. If this relatively lengthy route is unattractive, then there are even more ways to achieve a polymer with cyclic carbonate functionality from different approaches, including polymerization of unsaturated cyclo-carbonate monomers, copolymerization of unsaturated cyclo-carbonate monomers with vinyl ester monomers, reaction of oligomeric chlorohydrin ether with carbonate of alkaline metals, or reaction of oligomeric polyols with an acid chloride of carbonic acid (43).

Chemistry: Urethane groups will form when isocyanates and alcohol groups react with one another. However, there are other means to the same end. Urethanes are a chemical functional group belonging to a class of functional groups known as carbamates. Carbamates have the generic formula R₂N(CO)OR and can be formed using a variety of transformative chemical processes, the simplest of which is the reaction of isocyanates with polyols via the Curtius Rearrangement, which current SPF technology employs. However, by modifying the end functional groups of the starting materials, urethanes are achievable via a new reaction. The reaction of cyclic carbonates and amines will also yield urethanes (**Figure 3**).

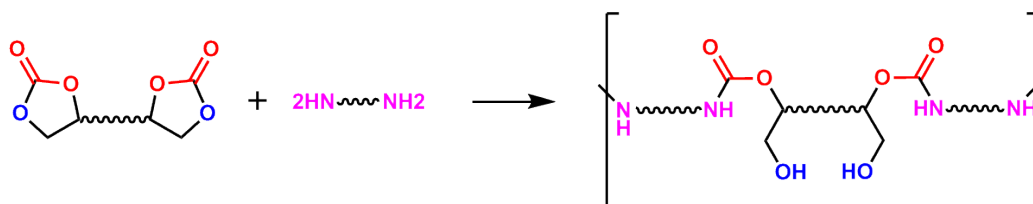


Figure 3. Representative chemical reaction between cyclic carbonate dimer and a diamine.

Functional advantages & disadvantages: The primary strengths of NIPU lie in its structural similarity to isocyanate polyurethane (IPU), the glut of chemical research available, and its burgeoning commercial viability and use. In reference to structural similarity, just as we saw for the product formed from pMDI, NIPU scores “3” in many categories since the product is expected to have the same chemical and physical properties.

Therefore, for insulation, longevity, and fire, pest, and mold resistance, we suspect that NIPU SPF will have comparable properties as MDI SPF and score the strategy a “3” in those three categories. In reference to the large amount of research available with regards to NIPU, there has been much research done in the academic arena. So while there is much known about the chemistry of NIPU, it is yet unknown how this chemistry will translate to commercial application. Therefore for sprayability, we were unable to give it a score as that factor is largely unknown. However, in reference to its burgeoning commercial viability, companies like Nanotech industries has been developing and using NIPU for coatings in industrial settings. In talking with one of their representatives, they have assured us that within the year, they will have converted their technology to a foam. However, while we can almost be assured that this strategy will be sprayable and foam, we must still rate it “UNK”. Additionally, with regard to status-quo compatibility, we expect this to be a mildly disruptive strategy. Different materials will have to be used, different application parameters and preparations are almost certain. Therefore, we rate NIPU “2” on that front. Finally, there are still unknowns as far as material properties and costs are concerned. However, we can reasonably estimate that the materials needed for this process will be within 20% of the cost of materials for SPF to ~50% more expensive which is why we gave this strategy a “2-3”. **Table 5** below summarizes the functional scores and the resulting overall score.

Table 5: Functional score table for NIPU-based spray polyurethane foam.

	Insulation R-Value	Longevity / Stability	Sprayability	Status-Quo Compatibility	Fire, Mold, & Pest Resistance	Material Cost	Overall Functional Score
Non-Isocyanate Polyurethane (NIPU)	3	3	UNK	2	3	2 - 3	2.6 - 2.8*

Health / environmental advantages & disadvantages: For NIPU, we selected representative cyclic carbonates (vinyl ethylene carbonate, propylene carbonate acrylate, and propylene carbonate methacrylate) and diamines (1,2-ethanediamine, 1,4-butanediamine, and isophoronediamine). Anticipating the scarcity in hazard information for the cyclic carbonate polymers, we instead chose to evaluate the cyclic carbonate precursors: limonene, soybean oil, linseed oil, and epoxidized linseed oil. For sensitization, 1,2-ethanediamine scores a “1” and isophoronediamine a “2” as recognized and suspected asthmagens, respectively. Limonene scores a “3” for possible sensitization hazards. For acute toxicity, all three diamine compounds demonstrate very potent dermal and oral acute toxicity, earning them scores of “1”. Limonene comprises a low hazard for acute toxicity and scores “4”. Data gaps prevail for carcinogenic and mutagenic effects, as well as endocrine, reproductive, and developmental effects. The diamines have varying data for persistence and bioaccumulation. 1-2-ethanediamine exists briefly in air as its main

environmental compartment (scoring a “4”), 1,4-butanediamine has low bioaccumulation potential (scoring a “4”), and isophoronediamine persists for over a year in its main environmental compartment of water (scoring a “1”). The cyclic carbonate precursor, limonene, exists very briefly in air and scores a “4”. For environmental toxicity, 1,2-ethanediamine (score of “2”) exhibits higher ecotoxicity to terrestrial vertebrates than 1,4-butanediamine (score of “3”). Isophoronediamine scores a “3” for its possible harm to aquatic life. Of the cyclic carbonate precursors, limonene produces very potent aquatic toxicity and scores a “1”, while soybean oil and epoxidized linseed oil contribute low hazards to water and earn scores of “4”. **Table 6** below summarizes the different health category scores and the resulting overall score.

Table 6. Health & environmental score table for NIPU-based spray polyurethane foam.

	Sensitization	Acute Toxicity	Carcinogen / Mutagen	Endocrine / Reproductive / Development	Persistence / Bioaccum.	Aquatic Tox / Ecotoxicity	Overall Health & Env. Score
Non-Isocyanate Polyurethane (NIPU)	1 – 3****	1 – 4***	UNK	UNK	1 – 4***	1 – 4*	1.0 – 3.8*****

Blocked Isocyanates

What is it: Blocked isocyanates are isocyanates which are modified reversibly by a “blocking group”. This blocking group can be any nucleophile but not such a good nucleophile that the reaction between it and the isocyanate is irreversible and not such a bad nucleophile that the reaction is easily reversible at ambient temperatures. The reason this reaction must be reversible is illustrated in **Figure 4**. Once the blocking group is added chemically to the isocyanate, it can then be removed by heating the material to form the isocyanate *in situ*, and the isocyanate may then react with the polyol to form the standard SPF.

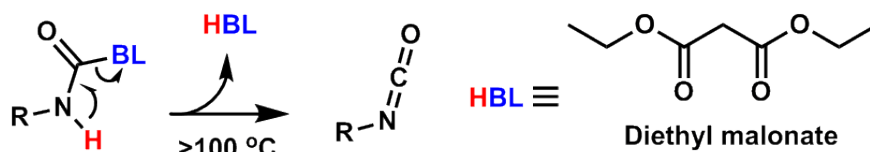


Figure 4. Representative unblocking reaction of a blocked isocyanate to form a reactive isocyanate and reform the blocking agent. As an example, the blocking agent can be a benign chemical like diethyl malonate.

Inspiration / precedence: The idea here is to keep the polyurethane foaming chemistry exactly the same, while reducing the application exposure to workers. There is plenty of

academic literature regarding the use of blocked isocyanates in coatings (coil coating, electro-coating, powder coating, automotive coating, insulating coating for wires, coating for plastics), sealants, and adhesives (44).

Chemistry: Blocked isocyanates are isocyanate molecules which contain a thermally labile leaving group (blocking group) covalently bound to the isocyanate carbon (45). The deblocking temperature of a blocked isocyanate depends on the structure of the isocyanate and the blocking agent, the chemical nature and the amount of curing catalyst and the deblocking reaction media. The most widely commercially used blocking agents are alcohols, phenols, oximes, -caprolactam, dibutyl malonates, amides and imides (44,46–48). Blocked isocyanates can act as a drop-in replacement for isocyanates in the “A-side” component of SPF application apparatus. While physical properties of these blocked isocyanates are largely unreported, it is conceivable that choice of the proper blocked isocyanate will yield a material which can act as a replacement in the “A-side” component. Additionally, the reported unblocking temperatures of blocked isocyanates, which are in excess of 100 °C or 212 °F, are well above the application temperatures of ~100 °F (49,50). This means that during application, there would be almost no likelihood of exposure to free isocyanates. Once all of the components are sprayed onto a surface, the material can be heated above the unblocking temperature at which point the blocked isocyanate will unblock yielding the reactive isocyanate which will then readily and rapidly reacted with any polyol, amine, or water present thus forming the desired polyurethane foam without ever exposing workers to free isocyanates (**Figure 5**).

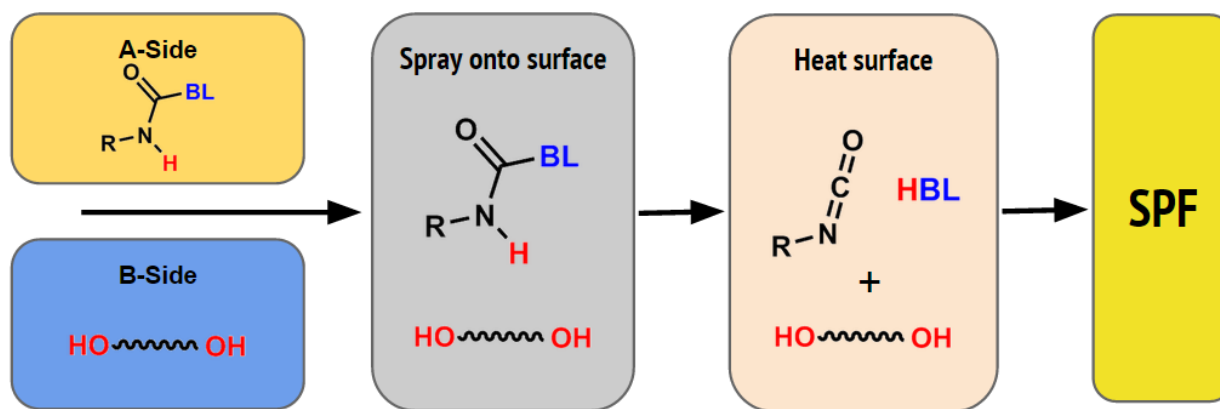


Figure 5. Representative scheme of blocked isocyanate application. The “A-side”, containing the isocyanate and the B-side containing the typical B-side mixture, will be kept separate and then sprayed in. The surface would then be heated, forming the reactive isocyanate, which would result in the reaction with polyols to form the SPF.

Functional advantages & disadvantages: The advantage of this technique lies in the fact that, aside from the unblocking aspect, the chemistry is exactly the same. Therefore, as

we've seen in the previous two techniques, we expect the final product to have comparable properties to MDI SPF. So product function scores like insulation, longevity, and fire / pest /and mold resistance" are scored a "3". Additionally, we expect that the blocked isocyanates can act as an exact drop-in replacement chemical in the "A-side" component of the SPF system. These materials, having suspected similar physical properties to their unblocked counterparts, we expect will have comparable sprayability to MDI SPF, and therefore score a "3" in that category. Additionally, we suspect that there would be some disruption in trying to determine which blocked isocyanates will unblock at a reasonable temperature, and determining how to heat the sprayed product once it has been applied. Therefore, this strategy scores a "2" in status-quo compatibility. With concern to material cost, we expect that the added material needed for blocking in addition to the reagents needed to block the material will increase the material cost, but not by more than an extra 50%. Therefore we rate this strategy a "2" in that category. Finally, an additional disadvantage, or unknown, is determining if during heating of the sprayed mixture, there will be off-gassing of free isocyanates. However, this off-gassing will most likely be minimal as unblocking temperatures tend to be well below the boiling point of MDI (314 °C). Although, if an industrially viable heating method is found, workers would not have to be present during the time-frame of heating. Thus, if any MDI is off-gassed, no one will be present to come in contact with it. **Table 7** below summarizes the functional scores and the resulting overall score.

Table 7. Functional score table for blocked isocyanate-based spray polyurethane foam.

	Insulation R-Value	Longevity / Stability	Sprayability	Status-Quo Compatibility	Fire, Mold, & Pest Resistance	Material Cost	Overall Functional Score
Blocked Isocyanates	3	3	3	2	3	2	2.7

Health / environmental advantages & disadvantages: We investigated the hazards of three composite chemicals for blocked isocyanates: MDI, diethyl malonate, and the representative blocked isocyanate tetraethyl ester-2,2'-[methylenebis(4,1-phenyleneiminocarbonyl)]bis-propanedioic acid. There is little to no hazard data reported on these blocked isocyanates. The primary concern with usage of this class of molecule is that in order for the polyurethane forming reaction to proceed, these blocked isocyanates must first thermally extrude their blocking group to form an isocyanate, which then reacts in a conventional SPF fashion. It is still unclear when this unblocking would occur, and how/if users would be exposed to isocyanates. The primary concern revolves around potential exposures to MDI, increasing the risk for respiratory sensitization and leading to a score of "1" for sensitization. MDI and diethyl malonate are both very potent acute toxicants and score "1" for acute toxicity. The acute toxicity hazards associated with diethyl

malonate comprise mainly of oral exposure, rather than inhalation or dermal like MDI. MDI is a suspected human carcinogen, contributing a score of “2” to the carcinogenicity endpoint. No hazards data exists for the endocrine, reproductive, or developmental effects of these chemicals. Diethyl malonate is predicted to have low persistence and low bioaccumulation potential, scoring a “4” for those endpoints. Diethyl malonate also presents a low aquatic hazard and scores a “4” for aquatic toxicity. **Table 8** below summarizes the different health category scores and the resulting overall score.

Table 8. Health & environmental score table for blocked isocyanate-based spray polyurethane foam.

	Sensitization	Acute Toxicity	Carcinogen / Mutagen	Endocrine / Reproductive / Development	Persistence / Bioaccum.	Aquatic Tox / Ecotoxicity	Overall Health & Env. Score
Blocked Isocyanates	1**	1*	2**	UNK	4**	4**	2.0 – 2.6*

Industry strategies

Many commercial insulation products exist that compete with SPF. While most of these are not sprayable, at least two strategies can be viewed as “Drop-In Replacement” strategies which replace all of SPF, not just the MDI component. As these are existing products, they would likely result in minimal disruption to the building industry, though they could cause significant disruption to the SPF industry.

Foamed Concrete

What is it: Foamed Concrete is a sprayable cementitious foam made primarily of magnesium oxide, water, polyvinyl alcohol, and a dispersant.

Inspiration / precedence: Dozens of varieties of foamed concrete have existed in industry for decades. Most of these are for lighter-weight structures, but at least one product, Air Krete, has long been used only for building insulation.

Chemistry: Many variations may be possible, but the specific instance of foamed concrete studied here was Air Krete. Its ingredients are 60-70% water, 15% magnesium oxide, 15-20% polyvinyl alcohol (PVA), roughly 1% barium metaborate (a cross-linker), and up to 1% Tamol dispersant. Tamol dispersant is a sodium salt of maleic anhydride copolymers, comprised of 75% water, 25% sodium polycarboxylate, and less than 0.1% “Individual residual monomers” (51). The PVA and dispersant make the mixture into a sprayable foam

with fine open-celled pores, then the magnesium oxide and water react to form magnesium hydroxide $[Mg(OH)_2]$, which is the concrete that solidifies the foam. Figure 6 below shows the material itself in close-up, as well as an installer spraying it into a wall.



Figure 6. Foamed concrete material in close-up, and being applied.

Images from aircrete-europe.com and exteriorsoflansing.com.

Functional advantages & disadvantages: Foamed concrete scores “2” for insulation value because its R-value per inch is likely much lower than standard SPF (R 3.7 per inch rather than R 6-7). In recent years the manufacturer has claimed R 6 for a new formulation, but its evidence uses non-standard testing that many do not consider credible (52). Foamed concrete scores “4” for longevity because its cementitious composition makes it extremely stable. It is not as robust as solid concrete, because the thinness of its cement membranes around air pockets make it somewhat brittle (brittle enough that a person can crumble it with their hand, not as strong as SPF), but as long as it is inside a wall or away from physical damage, it should last for decades. Similarly, it scores “4” for fire, mold, and pest resistance because its cementitious chemistry makes it very inert. It is inherently fireproof, without need for flame-retardant chemical additives and if it is in a fire, it does not emit the toxic decomposition gases that SPF does when burning (51,52). It is not a nutrient for mold or mildew, and is inedible to insects, mice, and other pests (53). It scores “4” for sprayability because its setup time and cure time are already comparable to SPF, with little shrinkage (51), and it should lower the labor cost of application because it requires less safety equipment and procedures. It scores “3” for status-quo compatibility because although it does require different equipment from SPF, and all its ingredients are different, its application equipment and procedures exist, there is no need for product development. Finally, it scores “3” for material cost, because its ingredients are comparable to or less expensive than SPF (52). **Table 9** below summarizes the functional scores and the resulting overall score.

Table 9. Functional score table for foamed concrete insulation.

	Insulation R-Value	Longevity / Stability	Sprayability	Status-Quo Compatibility	Fire, Mold, & Pest Resistance	Material Cost	Overall Functional Score
Foamed Concrete	2	4	4	3	4	3	3.4

Health / environmental advantages & disadvantages: The final product of magnesium hydroxide has low health risk and is sometimes even taken medicinally as “milk of magnesia”. Therefore, we investigated the hazards of 4 composite chemicals: magnesium oxide, PVA, Tamol, and barium metaborate. For sensitization, there were data gaps for all the composite chemicals. For acute toxicity, Tamol requires high concentrations to induce lethal inhalation toxicity and earns a score of “4”. Barium metaborate presents a very potent acute inhalation hazard and scores a “1”. Data gaps prevail for carcinogenicity and mutagenicity. Magnesium oxide presents pregnancy risks for metal fume inhalation beyond a threshold value and scores a “3”. The application of foamed concrete occurs at room temperature and does not require additional heating (52). Developmental risks from magnesium oxide fumes may arise from accidental or end-of-life incineration. Although magnesium oxide is environmentally persistent, its score of “1” does not properly characterize its toxicity since magnesium oxide is a naturally occurring mineral. For aquatic toxicity and ecotoxicity, magnesium oxide and PVA present low hazards to water, earning scores of “4”. Barium metaborate may be slightly harmful to crustaceans and scores a “3”. **Table 10** below summarizes the different health category scores and the resulting overall score.

Table 10. Health & environmental score table for foamed concrete insulation.

	Sensitization	Acute Toxicity	Carcinogen / Mutagen	Endocrine / Reproductive / Development	Persistence / Bioaccum.	Aquatic Tox / Ecotoxicity	Overall Health & Env. Score
Foamed Concrete	UNK	1 – 4**	UNK	3***	1***	3 – 4*	1.7 – 3.5***

Cellulose Spray

What is it: “Wet spray” cellulose insulation is recycled newspaper, ground up and made into a sprayable foam insulation by combining it with polyvinyl alcohol and boric acid. (This does not describe “dry cellulose”, which is simply loose fill blown into cavities.)

Inspiration / precedence: Waste newspaper has been used as insulation in homes since the 1800’s (54). However, this untreated newsprint was prone to settling, housing pests,

and mold. “Wet spray” cellulose is a modern (decades old) product to fix these problems. It is sometimes favored by green builders both because of its non-toxicity and because of its low embodied energy / low resource use, due to its recycling of a waste product from another industry (newsprint).

Chemistry: Other cellulose sources may be used, but recycled newsprint is the most common. The newsprint is ground into fine flecks, which provide microscopic air spaces between and inside cellulose fibers; these flecks are mixed with polyvinyl alcohol (PVA) so they stick to each other and to surfaces. The PVA holds the cellulose fibers in place, and the cellulose fibers give the material its (moderate) strength as well as its insulation value. In addition to these ingredients, 20% of the mixture is boric acid, added to resist fire, mold, mildew, and pests. **Figure 7** below shows the material itself in closeup, as well as an installer spraying it into a wall.



Figure 7. Cellulose spray material in closeup, and being applied.

Images from sustainableschmidt.com and staticflickr.com.

Functional advantages & disadvantages: Cellulose spray scores a “2” for insulation value because its R-value per inch is half that of standard SPF (R 3 per inch rather than R 6-7). For many applications this is not a problem (as mentioned in Methods, a standard 2”x4” framed building with R 3/in. provides nearly R 12 insulation), but for demanding insulation applications, or applications where volume is limited, it could be a problem. However, emerging technologies such as Phase Change Materials (PCM) in cellulose spray may radically improve insulation effectiveness for some climates; Oak Ridge National Labs has found that “maximum peak-time cooling loads in the house containing PCM were 35% to 40% lower”. Cellulose spray scores a “3” for longevity & stability, because it lasts decades without degrading or settling as dry cellulose fill does (55). It scores “4” for sprayability because it is already “foamed” (i.e. has microscopic air pores inside and between cellulose fibers) when it is blown in, so it does not have a setup time, only time for adhesive PVA to set; in addition, it should have lower application cost because it requires less safety equipment and procedures. It scores “3” for status-quo compatibility because although it does require different equipment from SPF, and all its ingredients are different, its application equipment and procedures exist, there is no need for product development. It

scores “2” for fire, mold, and pest resistance because although it does seem to have resistances similar to SPF, it achieves them by a large percentage of boric acid additive, which has health concerns (listed below). Cellulose spray scores a “4” for material cost because it is much less expensive than SPF--up to $\frac{1}{3}$ - $\frac{1}{4}$ the price per unit R-value as SPF (12). **Table 11** below summarizes the functional scores and the resulting overall score.

Table 11. Functional score table for cellulose spray insulation.

	Insulation R-Value	Longevity / Stability	Sprayability	Status-Quo Compatibility	Fire, Mold, & Pest Resistance	Material Cost	Overall Functional Score
Cellulose Spray	2	3	4	3	2	4	3.2

Health / environmental advantages & disadvantages: We investigated the hazards of cellulose (for recycled newspaper), boric acid, and PVA. The European Commission (EC) and US EPA recognize cellulose as an inherently safe material, earning it scores of “4” across the six hazard criteria. For sensitization, data gaps for boric acid and PVA resulted 4**, drawing the numerical value from cellulose’s score to populate the hazard endpoint field. For acute toxicity, boric acid demonstrates very potent acute effects and scores a “1”, while PVA has unknown effects. Boric acid and PVA have unknown carcinogenicity and mutagenicity, leading us to populate the hazard endpoint field with cellulose’s score. In contrast to the unknown effects of PVA, boric acid exhibits endocrine disruption activity, reproductive toxicity, and developmental toxicity and scores a “1” for that endpoint. Boric acid has a very lengthy vapor phase atmospheric half-life, scoring a “1” for persistence. The high persistence score for boric acid may inaccurately reflect its persistence since soil adsorption captures its main environmental fate. Due to data gaps concerning boric acid’s soil degradation half-life, we opted to include its atmospheric half-life. Boric acid and PVA both present low hazards to aquatic toxicity, scoring a “4” for aquatic toxicity. Table 12 below summarizes the different health category scores and the resulting overall score.

Table 12. Health & environmental score table for cellulose spray insulation.

	Sensitization	Acute Toxicity	Carcinogen / Mutagen	Endocrine / Reproductive / Development	Persistence / Bioaccum.	Aquatic Tox / Ecotoxicity	Overall Health & Env. Score
Cellulose Spray	4**	1 – 4*	4**	1 – 4*	1 – 4*	4	2.7 – 4.0***

Biomimetic Strategies

In addition to the Chemical and Industrial strategies we investigated, we also investigated 3 strategies that were biomimetically inspired. While there has been some research conducted with respect to these strategies, these are for the most part, the most “radical” suggestions. This mostly means that there is still much research to be done towards converting these strategies to structural, insulating foams. However, we find that these strategies hold the most promise for long-term, greener designs.

Protein-Based Crosslinking

What is it: Proposed protein-based spray foam adapted from soy-based wood adhesives.

Inspiration / precedence: The tenacious blue sea mussel, *Mytilus edulis*, uses proteinaceous byssal threads to anchor itself to tidal substrates (**Figure 8**). Despite being in an aqueous and turbulent environment, the mussel artfully masters surface adhesion, earning it considerable attention from the biomimetic field. The mussel byssal threads consist of a high proportion of 3,4-dihydroxyphenylalanine (DOPA), which have catechol functional groups (56). The catechol groups offers strong hydrogen-bonding and an affinity for metal complexation, allowing for a high degree of crosslinking (57). Industrial translation of marine adhesive proteins (MAPs) has produced soy-based wood adhesives.

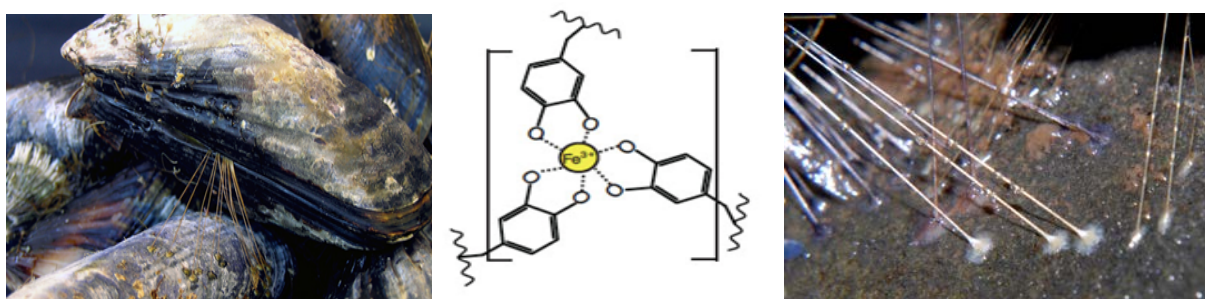


Figure 8. (Left) Blue sea mussel. (Middle) Iron-catechol complex. (Left) Byssal thread securing mussel to rocky substrate. Images from reefland.com and societyforscience.org

Chemistry: Soy-based wood adhesives highlight techniques to crosslink proteins, which could potentially be translated into a sprayable foam application. Initial attempts at developing soy-based adhesives consisted of grafting additional phenolic, hydroxyl, amine, and/or thiol functional groups on to the protein structure (58,59). With more reactive side chains, the modified soy protein may covalently bond with an amine/amide compound to bind lignocellulosic composites together. The modified soy proteins, however, exhibited

poor adhesive performance compared to synthetic resins (such as phenol formaldehyde), prompting researchers to re-approach the design. Rather than modifying soy proteins, researchers mixed a stronger crosslinking agent with soy protein to enhance adhesive capabilities (60). Ashland Inc. has successfully developed a commercially competitive soy-based wood adhesive, Soyad, which consists of soy protein, polyamidoamine-epichlorohydrin (PAE) resin, and a non-urea diluent (61). The PAE resin is a wet-strength agent often used in papermaking and contains a highly reactive hydroxy-azetidinium group (the cationic four-membered ring structure) that can crosslink with the amine and carboxyl terminals of soy protein (**Figure 9**) at elevated temperatures (60). The use of Soyad in composite wood involves mixing the ingredients (with the PAE resin added last), applying them to wood panels, and then curing the panels with heat (120°C) and pressure (200 psi) (60,61).

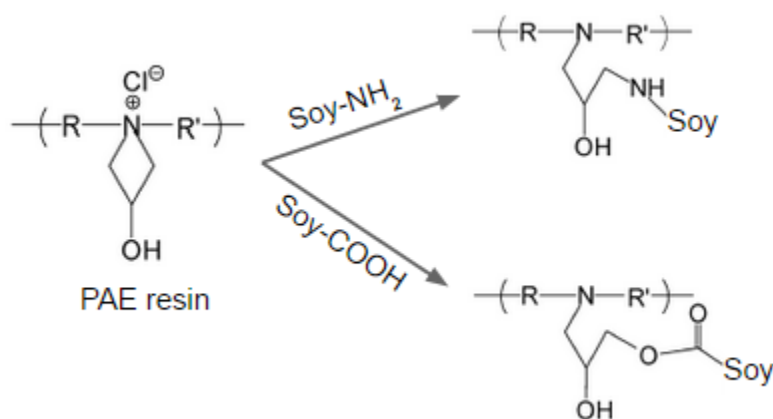


Figure 9. Reaction pathways for Soyad ingredients: PAE resin crosslinks with the amine side chain of soy flour (top reaction) or carboxyl side chain (bottom reaction). Adapted from Li et al. 2004.

Functional advantages & disadvantages: The greatest advantage of this strategy lies in the fact that the chemistry behind the resin has been thoroughly researched. First, it is unknown whether or not this strategy can be converted into an insulating foam. Second, the properties of this foam are entirely unknown. While we believe that if converted to a foam, it would not be a terrible insulator, we cannot with any surety say how well it will insulate. Therefore for insulation we've scored this strategy a "2-4". Additionally, while we know nothing about this material as a foam, we can extrapolate from its chemical makeup that it is a relatively stable material. Therefore for longevity / stability we score this strategy a "3". Additionally, multiple technical hurdles exist to convert wood adhesives into a foam for SPF applications. Currently, conventional polyurethane wood adhesives are formulated with any insulating gases, so their potential to foam will require further development and research (14). For soy-based wood adhesives, Kaichang Li of Oregon

State University confirms that Soyad’s peanut-butter-like consistency would not be conducive to foaming (62). Li, however, postulates that formulation alterations could feasibly produce SPF drop-in replacements and has expressed interest in developing a non-isocyanate polyurethane spray. Based on wood adhesive chemistry, protein-based spray foams may require heating to evaporate any aqueous solution and facilitate curing – an impractical inconvenience for insulation professionals. Therefore this material scores a “3” for sprayability. With regard to status-quo compatibility, we expect this strategy to be relatively disruptive as the chemical components would be changed entirely, although the application could still feasibly remain the same. Therefore, we score it a “2”. From a fire, mold, and pest resistance perspective, we can expect this material to score between “2-3” based on its chemical makeup. Finally, we were unable to assess its material cost and so we rated it “UNK”. **Table 13** below summarizes the functional scores and the resulting overall score.

Table 13. Functional score table for protein crosslinking based insulation

	Insulation R-Value	Longevity / Stability	Sprayability	Status-Quo Compatibility	Fire, Mold, & Pest Resistance	Material Cost	Overall Functional Score
Protein Cross-Linking	2 - 4	3	3	2	2 - 3	UNK	2.5 - 3.0**

Health / environmental advantages & disadvantages: We used the composition of Soyad to evaluate the potential hazards of our proposed protein-based spray foam. Anticipating (and finding) a dearth of information for the PAE polymer, we used PAE’s precursors for our assessment and included polyamidoamine (for the generic backbone) and epichlorohydrin (the primary crosslinking agent in creating the hydroxy-azetidinium group). We also investigated the hazards of soy flour. Polyamidoamine yielded no hazards information, leaving the evaluation to rely upon epichlorohydrin and soy flour. Both ingredients contribute to sensitization: epichlorohydrin is a suspected respiratory and recognized contact sensitization (scoring a “2”) and soy flour has been suggested as a possible cause of occupational asthma (scoring a “3”) in the baking industry (63). If these components are incorporated in the proposed protein-based spray foam, applicators will be required to don PPE. As the only chemical with hazards data for the other criteria endpoints, epichlorohydrin exhibits potent acute toxicity (score of “1”), suspected carcinogenic and mutagenic effects (score of “2”), suspected endocrine and reproductive effects (score of “2”), environmental persistence (score of “1”), and very high ecotoxicity (score of “1”). Based on the biodegradability of proteins, we assumed low persistence for soy flour and scored it a range of “3-4” for that endpoint. From the evaluation, epichlorohydrin constitutes the largest hazard across all our criteria endpoints and offers potential for safer substitution in PAE production or in PAE use overall. Current research

for soy-based wood adhesives focus on reducing the use of petroleum-based ingredients (the polyamidoamine component) rather than finding less toxic alternatives to epichlorohydrin (64). **Table 14** below summarizes the different health category scores and the resulting overall score.

Table 14. Health & environmental score table for protein crosslinking based insulation.

	Sensitization	Acute Toxicity	Carcinogen / Mutagen	Endocrine / Reproductive / Development	Persistence / Bioaccum.	Aquatic Tox / Ecotoxicity	Overall Health & Env. Score
Protein Cross-Linking	2 – 3*	1**	2**	2**	1 – 4*	1**	1.6 – 1.8*

Polysaccharide-based Crosslinking

What is it: Proposed polysaccharide-based spray foam adapted from chitosan hydrogels.

Inspiration / precedence: A biochemical process, sclerotization, involves crosslinking proteins to stabilize arthropod cuticles. Sclerotization strengthens, thickens, and armorizes the soft exoskeleton of freshly molted arthropods, endowing them with rigid cuticles to survive in the environment (**Figure 10**).



Figure 10. Arthropods and their sclerotized exoskeletons.
Images from flickr.com, wageningenur.nl, thedragonflywoman.com

During sclerotization (**Figure 11**), the enzyme tyrosinase oxidizes a low molecular weight compound with a catechol functional group and generates *o*-quinones (65). The *o*-quinones undergo subsequent protein crosslinking reactions to produce a hardened cuticle. The phase change from soft starting materials to strong end-products appealed to us as spray foam applications depend on transforming liquid spray into a rigid foam

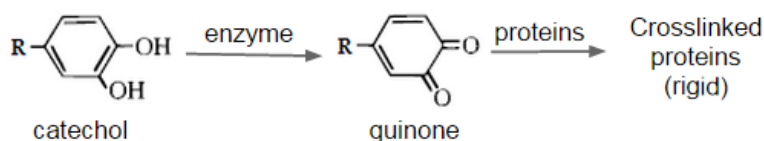


Figure 11. Simplified overview of sclerotization.
Adapted from Yamada et al. 2000.

Chemistry: Development of chitosan-based adhesives highlight techniques to cross-link polysaccharides. These techniques could potentially be used to create a polysaccharide-based spray foam. The selected polysaccharide, chitosan, is derived from commercially available, renewable, and derived from crustacean processing waste. Generally, chitosan-based adhesives involve three components: chitosan, phenolic compounds, and enzymes (65,66). During the mixing of the three ingredients, the enzymes would oxidize the phenolic compounds into quinone compounds, which would react with chitosan to produce a gel with water-resistant and adhesive properties (**Figure 12**). Researchers have investigated chitosan/dopamine/tyrosinase systems for glass adhesives and chitosan/various phenolic compounds/laccase for wood adhesives and measured notable adhesive capabilities for end-product. However, there are still inconsistencies regarding the relationships between viscosity, adhesion strength, functional group variation (for the phenolic compounds), and reaction times. Further development and fine-tuning is necessary to understand the essential properties and requirements in creating a chitosan-based adhesive.

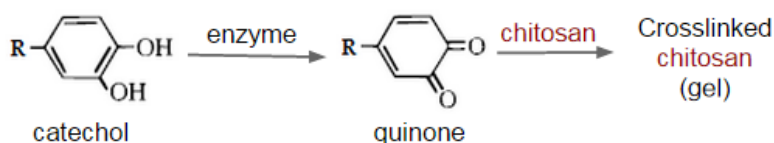


Figure 12. Proposed reaction pathway chitosan-based adhesive.
Adapted from Yamada et al. 2000.

Functional advantages & disadvantages: Functionally, there is not much we can currently say about this strategy, as it is undeveloped. The strategy would need to be researched more thoroughly before any sort of functional application can be determined. This kind of foam would be bioinspired, like soy-based adhesives. Therefore we imagine that its constituents would be biologically benign. Energetically this could be a very low energy technique from an application perspective. However, all of our fields, with the exception of status-quo compatibility are rated “UNK”. Obviously, status-quo compatibility gets rating of “1” as this strategy would be very disruptive. **Table 15** below summarizes the functional scores and the resulting overall score.

Table 15. Functional score table for polysaccharide crosslinking based insulation

	Insulation R-Value	Longevity / Stability	Sprayability	Status-Quo Compatibility	Fire, Mold, & Pest Resistance	Material Cost	Overall Functional Score
Polysaccharide Cross-Linking	UNK	UNK	UNK	1	UNK	UNK	UNK

Health / environmental advantages & disadvantages: Basing our potential polysaccharide-based spray foam on the chitosan-based wood adhesive, we investigated selected chitosan, laccase, and a generic phenolic compound as our composite chemicals. Since the chitosan-based wood adhesive requires further fine-tuning to select an ideal phenolic compound, we did not identify a specific phenolic compound to evaluate and left it as an unknown data gap as a placeholder for future investigation. Data gaps populate most of our hazard criteria, except for two endpoints. Laccase may possibly induce sensitization if inhaled and scores a “3” for sensitization. Laccase also presents a low aquatic hazard, scoring a “4” for aquatic toxicity. **Table 16** below summarizes the different health category scores and the resulting overall score.

Table 16. Health & environmental score table for polysaccharide crosslinking based insulation.

	Sensitization	Acute Toxicity	Carcinogen / Mutagen	Endocrine / Reproductive / Development	Persistence / Bioaccum.	Aquatic Tox / Ecotoxicity	Overall Health & Env. Score
Polysaccharide Cross-Linking	3**	UNK	UNK	UNK	UNK	4**	2.0 – 3.8****

Self-polymerizing by pH

What is it: Self-polymerizing by pH is when a single liquid reagent (probably a complex protein) strongly cross-links itself when exposed to salt and a pH change from 7 (or similar) to 6.3 or below.

Inspiration / precedence: This strategy is inspired by spider silk, which has remarkable physical properties but self-polymerizes at ambient temperature and pressure in water-based chemistry. It is the only instance of the phenomenon of which we are aware, so we believe synthetic analogs should be investigated.

Chemistry: Spider silk proteins “major ampullate spidroin” type 1 and 2 both turn from a liquid protein into a polymer by being exposed to salt (sodium chloride) catalyst and changing the surrounding environment from pH from neutral (7) to below 6.3 (mildly acidic, like bread or potatoes) (67). **Figure 13** below summarizes the reaction graphically.

In spiders, this occurs as the liquid passes through the spider's spinneret to extrude it into threads; it could just as well occur as it passes from a tank through a handheld nozzle like an SPF installer's spray gun. (Note: spidroin 1 protein self-assembles in a few days at any pH, but at pH 6.3 it self-assembles into a solid in less than five minutes.) This has not only been observed in nature, but synthesized in labs. The patent for synthetically creating such polymers from spidroin protein says "In one embodiment, the polymer is a fiber, film, *foam*, net or mesh" (68). (Emphasis added.) Unfortunately, the protein itself is difficult to synthesize--only a few grams of it have ever been produced at a time, despite researchers trying to scale up synthetic spider silk production for decades. One of the closest attempts came from Canadian researchers at the turn of the last century genetically engineering goats to produce milk with spider protein (69). We are not aware of anyone artificially synthesizing any chemical besides spidroin protein that self-polymerizes when exposed to salt and a pH change, though we believe it should be possible.

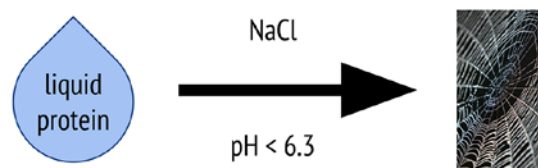


Figure 13. Liquid protein catalyzed by salt and pH self-polymerizes.

Functional advantages & disadvantages: Because this strategy has only been accomplished in the lab, and even then only a few grams of material at a time, it is obviously not yet a commercially viable solution. As we do not know what chemistry would be used to imitate spider protein's self-polymerization, we cannot begin to attempt scoring its functional properties. Its insulation value, longevity, etc. might be unacceptable or might actually be better than SPF, depending on the ease of product development. In spiders, the same protein can form multiple different kinds of silk with different mechanical and adhesive properties (70). The only score we can give with reasonable confidence is a status-quo compatibility of "1" because it will almost certainly not use status-quo installation equipment or procedures. However, we believe the strategy is worth researching as a long-term alternative to SPF, because in principle it could be a very high-performance material with low toxicity and low cost. Salt is certainly low-cost, as are chemicals to bring a solution to pH 6.3, or pH change could be accomplished electrostatically with only one consumable chemical ingredient. Costs would initially be high as with any new technology, but in the long-term, costs might become low because a single ingredient is inherently easier to install than a multi-ingredient mix. **Table 17** below summarizes the functional scores and the resulting overall score.

Table 17. Functional score table for pH self crosslinking based insulation.

	Insulation R-Value	Longevity / Stability	Sprayability	Status-Quo Compatibility	Fire, Mold, & Pest Resistance	Material Cost	Overall Functional Score
pH Self Cross-Linking	UNK	UNK	UNK	1	UNK	UNK	UNK

Health / environmental advantages & disadvantages: Similar to the functionality scores, we cannot estimate with any confidence what the health impacts of self-polymerization by pH would be, because no industrial-scale versions exist. Therefore all endpoints are scores as “unknown”. However, we believe the strategy is worth researching in the long-term, because in principle it could be entirely non-toxic. We were unable to find toxicity studies of major ampullate spidroin 1 or 2, but because they are long-chain proteins found commonly in nature worldwide, they are likely to be very low-toxicity. Sodium chloride certainly scores as non-toxic because it is an essential nutrient in appropriate quantities, and this application would only use it as a catalyst, so it would not be required in large quantities. If an acid solution is added to bring the pH down to 6.3 it may not need to be a strong acid, since 6.3 is only mildly acidic; or as mentioned above, this might be accomplished electrostatically, with no need for acid additives. If the solution has only one ingredient, and that ingredient is a long-chain protein, the product would likely be very non-toxic. However, a commercially-viable industrial imitation of spider silk will likely not be made of spidroin. It will likely use very different chemistry for its self-polymerization, so we did not assume toxicity ranges for unknown chemistries. **Table 18** below summarizes the different health category scores and the resulting overall score.

Table 18. Health & environmental score table for pH self crosslinking based insulation.

	Sensitization	Acute Toxicity	Carcinogen / Mutagen	Endocrine / Reproductive / Development	Persistence / Bioaccum.	Aquatic Tox / Ecotoxicity	Overall Health & Env. Score
pH Self Cross-Linking	UNK	UNK	UNK	UNK	UNK	UNK	UNK

Results: Evaluation Framework

Trying to choose the best alternative from a list with twelve different independent variables is a daunting task for the most committed person, and requires subject matter expertise. Most experts on spray foam's functionality will not be experts on its chemical toxicity, and vice-versa. Therefore, we unified the six separate functionality properties in a single overall functionality score, which is a weighted average of the six individual functionality scores. See **Table 19** below for results; see the Methods section above for explanations of the different categories and why they were weighted as they are. This functional scoring system was reviewed by an industry representative. The scores are informed estimates as described above, but serve as indicators for future research and development.

Table 19. Functionality evaluation table.

	Insulation R-Value	Longevity / Stability	Sprayability	Status-Quo Compatibility	Fire, Mold, & Pest Resistance	Material Cost	Overall Functional Score
MDI (current practice)	3	3	3	4	3	3	3.2
Foamed Concrete	2	4	4	3	4	3	3.4
Cellulose Spray	2	3	4	3	2	4	3.2
Polymeric MDI (pMDI)	3	3	3	3	3	3	3.0
Protein Cross-Linking	2 - 4	3	3	2	2 - 3	UNK	2.5 - 3.0**
Non-Isocyanate Polyurethane (NIPU)	3	3	UNK	2	3	2 - 3	2.6 - 2.8*
Blocked Isocyanates	3	3	3	2	3	2	2.7
Polysaccharide Cross-Linking	UNK	UNK	UNK	1	UNK	UNK	UNK
pH Self Cross-Linking	UNK	UNK	UNK	1	UNK	UNK	UNK
Percent of Overall Score	15%	20%	20%	15%	10%	20%	

Health and environmental scores counted ten endpoints to attempt a comprehensive representation of toxicity to humans and other plants and animals, and grouped them into six categories for simplicity. See **Table 20** below; see the Methods section above for explanations of the different categories and why they were weighted as they are. These scores do not include other environmental impacts such as climate change, resource depletion, or land use. This scoring system was reviewed by a representative of California DTSC. The scores are informed estimates as described above, but serve as indicators for future research and development.

Table 20. Chemical health and environmental evaluation table.

	Sensitization	Acute Toxicity	Carcinogen / Mutagen	Endocrine / Reproductive / Development	Persistence / Bioaccum.	Aquatic Tox / Ecotoxicity	Overall Health & Env. Score
MDI (current practice)	1	1	2	UNK	UNK	UNK	1.2 – 2.6***
Foamed Concrete	UNK	1 – 4**	UNK	3***	1***	3 – 4*	1.7 – 3.5***
Cellulose Spray	4**	1 – 4*	4**	1 – 4*	1 – 4*	4	2.7 – 4.0***
Polymeric MDI (pMDI)	1	1	UNK	3	UNK	UNK	1.4 – 2.8***
Protein Cross-Linking	2 – 3*	1**	2**	2**	1 – 4*	1**	1.6 – 1.8*
Non-Isocyanate Polyurethane (NIPU)	1 – 3****	1 – 4***	UNK	UNK	1 – 4***	1 – 4*	1.0 – 3.8*****
Blocked Isocyanates	1**	1*	2**	UNK	4**	4**	2.0 – 2.6*
Polysaccharide Cross-Linking	3**	UNK	UNK	UNK	UNK	4**	2.0 – 3.8*****
pH Self Cross-Linking	UNK	UNK	UNK	UNK	UNK	UNK	UNK
Percent of Overall Score	20%	15%	20%	20%	15%	10%	

Of course, products must be evaluated by both functionality and health / environment at once. Since different companies, regulators, or other interested parties may have very different values of function vs. health, we did not presume to assign weights to calculate an overall single score per product alternative. **Table 21** below simply presents the two scores next to each other, for readers to make their own decisions.

Table 21. Summary evaluation table, showing overall functionality and chemical hazard scores.

	Function	Health & Env.
MDI (current practice)	3.2	1.2 – 2.6***
Foamed Concrete	3.4	1.7 – 3.5***
Cellulose Spray	3.2	2.7 – 4.0***
Polymeric MDI (pMDI)	3.0	1.4 – 2.8***
Protein Cross-Linking	2.5 - 3.0**	1.6 – 1.8*
Non-Isocyanate Polyurethane (NIPU)	2.6 - 2.8*	1.0 – 3.8*****
Blocked Isocyanates	2.7	2.0 – 2.6*
Polysaccharide Cross-Linking	UNK	2.0 – 3.8*****
pH Self Cross-Linking	UNK	UNK

Conclusion & Recommendations

This study investigated eight alternatives to existing MDI-based medium-density polyurethane spray foam, and developed an evaluation method to score alternatives by key functional properties and health / environmental endpoints. The eight spray foam alternatives we examined in detail fell into three categories: replacements for MDI alone that would leave the rest of spray foam's chemistry similar, replacements for all of spray polyurethane foam's chemistry that are already commercial spray insulation products, and biomimetic strategies replacing all of spray foam's chemistry.

Our evaluation method to score alternatives by functionality and low toxicity attempted to balance completeness and rigor with simplicity of communicating results to non-experts. Both functional and health / environmental scores ranged from 1 (worst) to 4 (best). Functional scores counted six properties we considered most important for product performance and commercial viability. The overall functional score was 20% longevity / stability, 20% sprayability, 20% material cost, 15% insulation value, 15% status quo compatibility, and 10% fire / mold / pest resistance. Higher percentages are more crucial for the product to be commercially viable, lower percentages are easier to work around. Health and environmental scores counted ten endpoints to attempt a comprehensive representation of toxicity to humans and other plants and animals, and grouped them into six categories for simplicity. These scores do not include other environmental impacts such as climate change, resource depletion, or land use. The overall health / environmental score was 20% sensitization, 20% carcinogenicity / mutagenicity, 20% endocrine disruption / reproductive harm / developmental harm, 15% acute toxicity, 15% toxicity to fish or mammals, and 10% persistence / bioaccumulation. The functional scoring system was reviewed by an industry representative, while the health / environmental scoring system was reviewed by a representative of California DTSC.

Scoring the eight MDI spray foam alternatives by functionality and low toxicity showed the best alternatives in the short term are likely to be foamed concrete, cellulose spray, and polymeric MDI (pMDI). In terms of functionality, each of these should cause only minor technology disruption while providing a product with long life, fire / mold / pest resistance, good sprayability, and costs comparable to or lower than existing MDI-based spray foam. Foamed concrete and cellulose spray both have the advantage of being existing commercial products, but both have the disadvantage of providing significantly less insulation (nearly half the R-value per inch), which can be an environmental concern as well as a commercial concern. In terms of health and environment, all three of these alternatives are likely to cause less sensitization, acute toxicity, carcinogenicity / mutagenicity, endocrine / reproductive / developmental harm, aquatic toxicity / mammalian ecotoxicity, and be less persistent / bioaccumulative. However, there is a great

deal of uncertainty in these health estimates, not only for the alternatives to MDI-based spray foam, but for MDI itself. In particular, pMDI needs further study of sensitization to determine if it is actually an improvement over MDI.

Two other spray foam insulation alternatives that are not currently viable options but that might cause greater improvements in the long term are non-isocyanate polyurethane (NIPU) and pH self crosslinking. NIPU may be able to replace MDI in an otherwise similar spray form chemistry with lower toxicity than pMDI, foamed concrete, or cellulose spray, if research and development commercialize clean formulations. Self crosslinking driven by pH is a biomimetic strategy for which no known industry analog exists, but which might use a single non-toxic ingredient (such as a protein) to self-cross-link when exposed to a salt catalyst and a pH change. No one can yet say whether these strategies would function as well or be healthier than other alternatives, but we believe they are worth investigating.

Searching for a healthier replacement to MDI-based spray foam insulation has just begun, and there are many important gaps for future research and development to fill: First, many knowledge gaps should be filled by researchers in academia, industry, or government to determine the toxicity of existing MDI spray foam and all the alternatives with more certainty. Second, technology gaps should be filled by industry and academia to commercialize new cleaner chemistries listed here, or improve the functionality of existing cleaner chemistries listed here. Finally, industry and academia should investigate other potential alternatives we are not yet aware of or did not have time to investigate. Polyurethane spray foam is a large industry serving the important function of reducing building energy use; it deserves concerted attention to make it an excellent industry for its workers as well.

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