Identifying Greener Solutions: Biomimetic Chemical Alternatives for Fabric Finishing at Levi Strauss & Co.

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PH 290.2 – GREENER SOLUTIONS

December 19, 2013

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1.0 INTRODUCTION

1.1 The Levi's Challenge

Levi Strauss & Co. partnered with the Biomimicry Institute and UC Berkeley's Greener Solutions Course in order to tackle a challenge: replace toxic chemistry currently used in the fabric finishing process with "greener" chemical alternatives. Two chemical groups on Levi's restricted substances list, formaldehyde-based resins and di-isocyanates, have been targeted for reduced use or total elimination in the later stages of garment finishing. Below, Table 1 summarizes the potential health hazards associated with each of these chemicals.

Levi's seeks to eliminate these hazardous substances at a stage in the garment process where there is greatest potential for occupational exposure. Formaldehyde-based resins are used in permanent press fabric finishing in Levi's Docker's Line, and di-isocyanate chemistry is used in to impart a water-repellent finish in their line of commuter jeans. These finishes are subject to significant performance and cost constraints, which safer conventional chemical approaches have not yet been able to match.

For the duration of the fall semester, our class has investigated biologically based chemical strategies found in nature as inspiration to develop "greener" chemical solutions. This challenge is illustrative of Levi's enthusiasm in pioneering more environmentally friendly and health protective strategies in their garment manufacturing process.

Table 1. Chemicals on Levi's Restricted Substances List Targeted for Reduced Use

Chemical	Use	Exposure	Summary of Health Effects
Di-isocyanates	A major component of polyurethane coatings	Used in a vapor or aerosol form. Skin absorption may be a significant source of exposure; est. 280,000 US workers exposed annually (1)	TDI Group 2B carcinogen: *possibly carcinogenic to humans*. Supported by animal evidence. (2) Respiratory sensitization produces asthma May cause contact irritation of skin, eyes, nose, and upper respiratory tract.
Formaldehyde-based resins	Used to impart wrinkle-resistance during wear and laundering to cotton and cotton polyester blend fabrics (3)	Readily absorbed via respiratory tract. Highest continuous exposures measured in: varnishing of furniture and wooden floors; textile finishing; the garment industry; fur treatment; and in manufactured wood production mills. (4)	Nasopharyngeal irritation, causes contact skin irritation, asthma. (IARC monograph, 2012). Group 1 carcinogen: causes cancer in humans (nasopharyngeal and leukemia) (IARC monograph, 1987). Strong weight of evidence from numerous human and animal studies (5)

1.2 Goals

In the context of this project, our goal is to investigate crosslinking strategies[1] in natural protein and polysaccharide networks as potential biomimetic replacements for hazardous formaldehyde-based resins or di-isocyanate-based chemistries used in durable press and durable water-repellent (DWR) fabric finishes.

We have identified a limited list of alternative approaches to chemical crosslinking that are less hazardous to human health and the environment through the following steps:

1. Translating biological crosslinking inspirations into chemical solutions for fabric finishing
2. Evaluating promising solutions for technical feasibility
3. Evaluating promising solutions for health and environmental impacts

Rather than focusing on finding alternatives to one fabric finishing treatment (durable press or DWR), we chose to look broadly at biomimetic solutions for crosslinking cellulose. Once we identified feasible cellulose crosslinkers, we then determined which fabric finishing process each solution was most suited for.

1.3 Scope & Limitations

We prioritized our investigation on the health and environmental impacts centered on the latest stage of the garment manufacturing process, the finishing process, where formaldehyde-based resins and di-isocyanates are applied to cured fabrics. At this stage, exposure of chemicals to workers is potentially quite high, as these processes are labor intensive and involve extensive handling of garments by textile workers. As such, we will not address or evaluate health or environmental hazards outside of the finishing process. Assessing environmental (and social) impacts in the larger supply chain (chemical manufacturing, product shipping, disposal of product and byproducts generated during the fabric or garment manufacturing process) are beyond the scope of this report.

1.4 Hazard vs. Risk Management Framework

In many developing countries, manufacturing facilities have few health and safety protections in the form of occupational standards for their workers. If such regulations are in place, they often lack adequate enforcement. A substantial motivating factor for this project is to examine avenues through which occupational exposure hazards can be reduced. However, the challenge of making such an impact on a globally diverse and widespread supply chain is systematically difficult. As we will discuss below, Levi's outsources much of its labor to hundreds of contracted factories around the world. In light of the broad complexity of the garment manufacturing process, Levi's has opted to operate within a hazard management (vs. risk management) framework by investing in research to develop greener chemistry. Managing hazards (i.e. using inherently safer, less toxic chemicals) is a more achievable goal than managing risk (trying to change procedures and practices so that the actual process is inherently less hazardous) (6).

[1] A crosslink is a bond that links one chain of polymers to another. These bonds may be covalent or ionic. Crosslinking is used both in nature and in the textile industry. In the context of the textile industry, crosslinking imparts special properties to fabrics such as durability, tensile strength, stain resistance, and water resistance.

2.0 BACKGROUND & CONTEXT

This background section is meant to introduce some of the broader issues associated with our project, from how we understand and define "greener" to some of the stakeholder issues involved. Though this section could have included many other topic areas, these two were determined to be essential in helping to define what we are doing, why we are doing it, and whom we are doing it for.

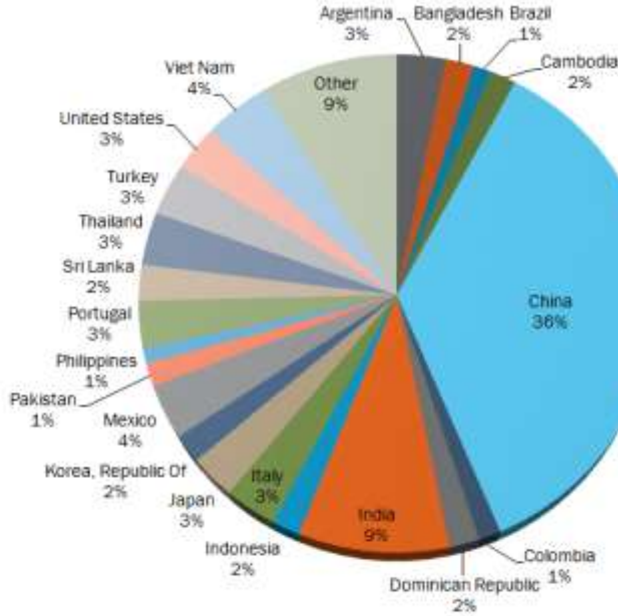
2.1 Stakeholders

In 2011, Levi Strauss & Co. (Levi's) and thirteen other major textile entities established the Zero Discharge of hazardous Chemicals (ZDHC) Group. This was partly in response to Greenpeace's Detox campaign, a challenge to major clothing brands to eliminate the use of hazardous chemicals from their supply chains and products. Levi's recent focus has been to follow the roadmap laid out by the ZDHC and provide greater transparency around the chemicals used in their supply chain, as well as create concrete plans for the elimination of the most hazardous substances used in their production process.

Levi Strauss & Co.

Levi's is easily identified as iconic through its 501® jeans, though one has to remember that they are more so a brand manager today than a manufacturer. Essentially, they outsource manufacturing to the third world where labor and environmental regulations are economically favorable, as is the norm for any multinational. According to their 2012 corporate report, Levi's operates over 470 company stores and employs over 17,000 people; additionally, if you include workers within their entire supply chain, that number jumps to 315,000 (7). The connection to make here is that as a clothing brand, their pulse is relative more progressive within corporate social responsibility but still exists within a greater system where managing risk rather than eliminating hazard is the norm. Another viewpoint is with 97% of their contracted or licensed factories located overseas, 279 of them in China alone, the ability to manage risk is made difficult by geography, culture, and distance. In consideration of these challenges, Levi's has opted to use a hazard management approach as opposed to a risk management framework. In light of the broad complexity of the garment manufacturing process, managing hazards (i.e. using safer, less toxic chemicals) is a more achievable goal than managing risk (trying to change procedures and practices so that the actual process is inherently less hazardous) (6).

Figure 1: Percentage distribution of 797 Levi's contracted factories (8)



Greenpeace

This non-governmental organization, known to be one of the most visible environmental groups in the world, was established in the late 1960's with a stated mission to ensure the Earth's ability to nurture life in all its diversity. It currently has offices in over 40 different countries and is funded strictly by individual supporters (in fact, 2.9 million individual supporters) and foundation grants (9). Greenpeace's approach for advocacy includes research, lobbying, and direct action; the latter being a point of criticism for some and a point of comfort for others. Today, their priorities range from energy policy reform and strengthening environmental protection and include the creation of "a toxin free future with safer alternatives to hazardous chemicals in today's products and manufacturing." (9)

Figure 2: Greenpeace's Detox Campaign directed at Levi's (10)

Greenpeace activists placed this banner at a wastewater treatment plant for Lavamex, a Levi's supplier in Mexico, after they discovered nonylphenol (a hormone disrupting compound), during tests from their discharge pipe. Eight days later Levi's signed onto Greenpeace's detox campaign.

Zero Discharge of Hazardous Chemicals Group (ZDHC)

This coalition is made up of sixteen brand members that represent the "who's who" within multinational textile corporations. Included in this group are footwear moguls like Nike Inc. and the Adidas Group as well as retail clothing giants like H&M and Gap Inc. With the group's global reach, they have the potential to make a large impact within the textile industry. The plan set by the ZDHC is ambitious: a roadmap that sets new environmental performance benchmarks for the global apparel and footwear industry. This living document, intentionally designed to be continuously refined and transparent, includes specific commitments and timelines to realize a shared goal – zero discharge of hazardous chemicals by 2020. This is a goal that Levi's shares but has committed to achieve by 2015 (10). The ZDHC's process roadmap is summarized in the following seven work streams (11). Note the italicized work stream in the below list indicates the focus for this project:

1. ***Chemical Hazard Assessment, Prioritization and Action***
2. Training
3. Right to Know
4. Assessment and Auditing
5. Management Systems Approach, Structure and Documentation
6. Stakeholder Partnering
7. Chemicals Management Best Practices Pilot

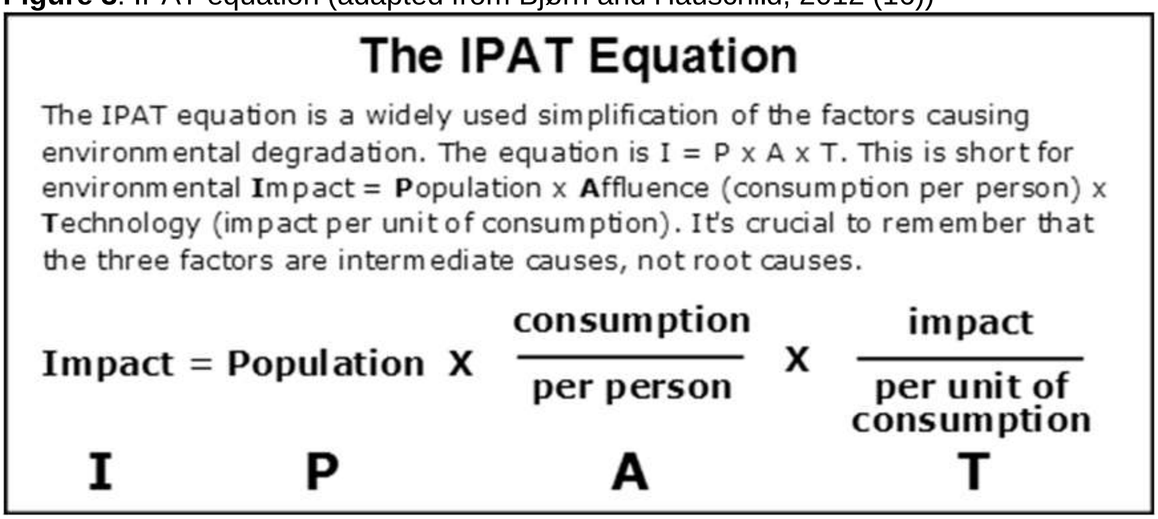
2.2 Defining a "Greener Solution"

As a group we felt it was important to address this early on in our project because terms like green, greener, and sustainability are too often used casually. Knowing such terms are socially derived, meaning that they are co-constructed within their relative communities rather than by individuals alone (12); we looked at both theoretical approaches and market conditions to define our greener solution.

Eco-Efficiency

This concept is commonly defined as "adding maximum value with minimum resource use and pollution" and has gained wide acceptance in the last couple of decades as a technological means to achieve "relative sustainability", or incremental change (13). Though its aim is to reduce the negative environmental impacts associated with human activity, its main drawback is implicit. There is no long-term vision or strategy—the concept is relative and an absolute. Eco-efficiency is a harm reduction strategy, and one of harm elimination. In 1972, Commoner contextualized the relationship between environmental impacts (I), population (P), material affluence per capita (A), and eco-efficiency (material affluence per environmental impact, 1/T) using this formula: I = PAT. Since both population (P) and material affluence (A) are globally on the rise, the debate is ongoing concerning how much eco-efficiency (T) needs to increase to keep environmental impact (I) at a steady-state. Factors as high as 50 and as low as 4 have been proposed, when translated it means products and systems will need to be improved to deliver the same standard of service at 2 - 25% of the current environmental impact (14,15).

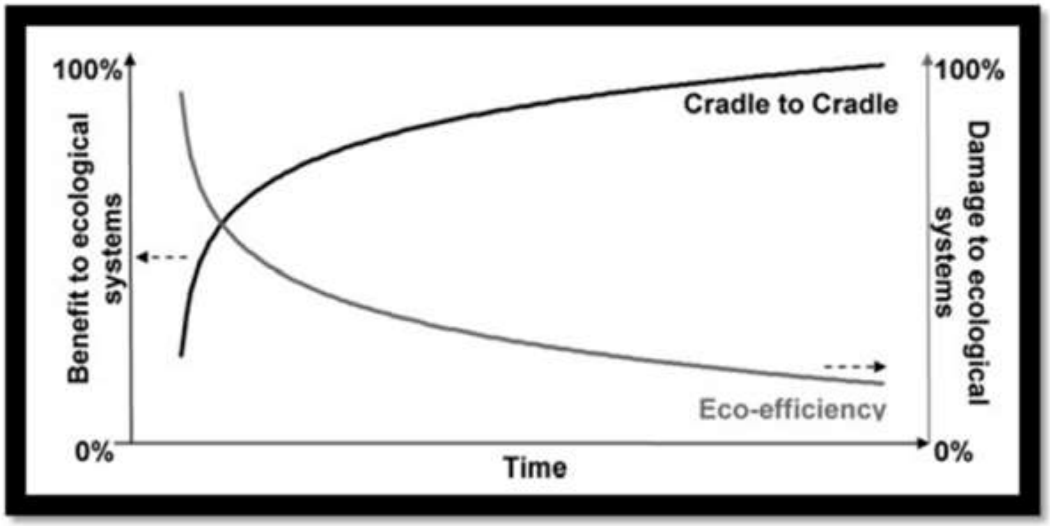
Figure 3: IPAT equation (adapted from Bjørn and Hauschild, 2012 (16))



Cradle to Cradle (C2C)

Coined by German chemist Michael Braungart and U.S. architect William McDonough, this concept is based on three principles: waste = food, use current solar income (optimize use of renewables), and celebrate diversity (17). The difference that distinguishes this concept from eco-efficiency is that Cradle to Cradle adds positive value rather than reducing loss, as illustrated in Figure 4. The aim of Cradle to Cradle is to design systems where emissions can be taken up as nutrients instead of trying to reduce the amount of waste generated; waste = food. Implicit is that it tries to "envision" sustainability as an absolute. If there is no waste but food instead, an eco-efficiency approach becomes theoretically contradictory. It stands as a visionary concept that has its place in inspiring the possibility of something beyond eco-efficiency.

Figure 4: The eco-efficiency and cradle-to-cradle (C2C) concepts (Bjørn and Hauschild, 2012) (18)



12 Principles of Green Chemistry

Also known as "sustainable" chemistry, Paul Anastas and John C. Warner developed these twelve principles to help operationalize green chemistry into practice. The principles were designed to be applied across the life cycle of the product, from design and manufacturing to use (19). They were meant to be guidelines and/or rules to be used in practice. Guidelines followed by Levi's today, perhaps because of its a la carte approach. The 12 principles of Green Chemistry are:

1. Prevention
2. Atom Economy
3. Less Hazardous Chemical Syntheses
4. Designing Safer Chemicals
5. Safer Solvents and Auxiliaries
6. Design for Energy Efficiency
7. Use of Renewable Feedstocks
8. Reduce Derivatives
9. Catalysis
10. Design for Degradation
11. Real-time Analysis for Pollution Prevention
12. Inherently Safer Chemistry for Accident Prevention

Biomimicry

This concept is meant to support rather than supplant the above two theories. It is literally the science and art of emulating nature's best biological ideas to solve human problems (20). The concept central to biomimicry is that nature has had 3.8 billion years of trial and error in refining living organisms, processes, and materials in both nano and marcroscales (21). Janine Benyus founder of the Biomimicry Institute, has described the process as "looking at nature as a model, measure, and mentor." As an approach, biomimicry can be used to support both an eco-efficiency and/or a paradigm shift toward absolute sustainability.

Our "Greener Solutions" Approach

As a group we realized a lot of good engineering and design was being wasted trying to address the wrong problem. While a disruptive approach of identifying and functionalizing that problem first within a whole system would have been ideal, stakeholder constraints beyond our control made this option untenable. Instead, we decided to use a biomimetic approach in defining our substitutive "greener solution" to resolve some of the conflicts that exist between relative and absolute sustainability. Although we are not sure if we are addressing the right problem, our "greener solution" focuses on using nature as inspiration to present, at the very least, a less hazardous substitutive solution. In other words, our "greener solution" addresses eco-efficiency but if used in the right context for future design incarnations, has the potential to contribute to benefiting ecosystems (human and organism health and the environment) rather than just reducing harm to them. Beyond the theoretical implications, this hazard management approach ensures that "downstream" chemical processes will be less toxic and safer to handle. When considering that the majority of manufacturing facilities are located in developing countries that have few enforceable occupational health and safety standards for their workers, this becomes especially important.

2.3 Currently Available "Greener" Solutions

We researched "greener" solutions that have been proposed and marketed in order to better understand where there is room for improvement, and where to focus our research efforts. Formaldehyde-containing permanent press fabric finishes have been popular since the 1950s. Beginning in the 1960s, concerns about the release of formaldehyde prompted the development of lower- and no-formaldehyde resins. Low-formaldehyde resins (e.g. a mixture of dimethylol dihydroxyethyleneurea, or DMDHEU, and diethylene glycol) have continued to dominate the market because of their superior performance and cost-benefit ratio compared to resins without formaldehyde (Schindler 2004). The most widely researched formaldehyde-free durable-press finishes and their shortcomings are listed below:

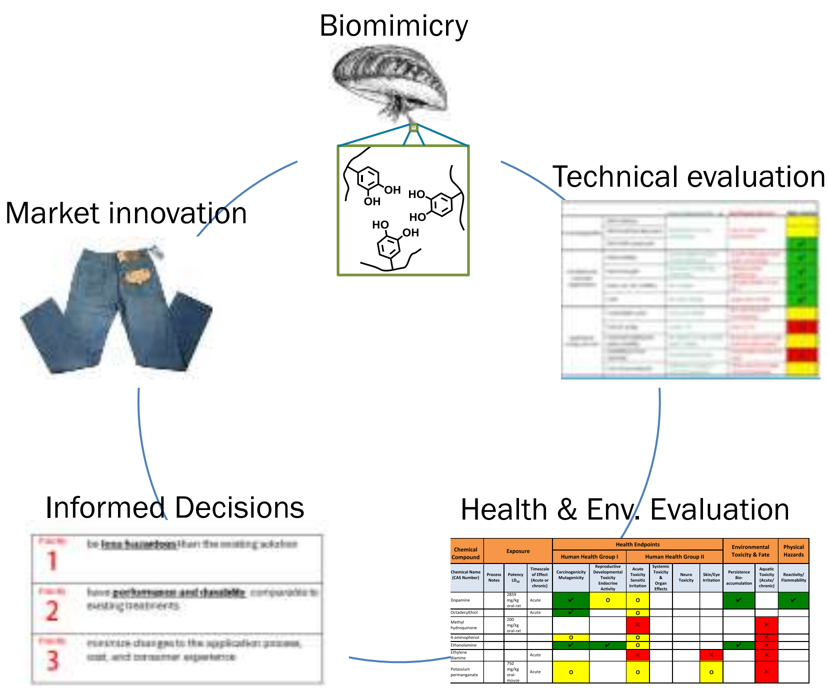
- DMeDHEU: less durable than DMDHEU, and approximately four times as expensive
- Butanetetracarboxylic acid (BTCA): less durable than DMDHEU (hydrolysis of ester bonds), approximately four times as expensive
- Citric acid: less durable than DMDHEU (hydrolysis of ester bonds), yellows fabric significantly

A multitude of other chemical approaches have been explored, though their use has been limited by high cost or insufficient technical advantages. Promising results with BTCA prompted the exploration of cheaper acids including citric acid, malic acid, maleic acid, and itacaonic acid. Unfortunately, they also have limited durability and tend to be less reactive than BTCA. Little additional information is available on the crosslinkers dimethylol ethylene or propylene urea, diglyoxal urea, triazons, urons, carbamates, diepoxides, and diisocyanates. (22,23)

3.0 APPROACH

The flow chart below summarizes our approach (Figure 5). First, we looked to nature for inspiring crosslinking mechanisms. Next, we translated our biological crosslinking inspirations into chemical solutions, and evaluated those solutions based on their technical feasibility. After determining which solutions were technically feasible, we evaluated them based on their health and environmental impacts. Finally we made informed decisions based on the information gathered through these evaluative frameworks and selected proposed solutions that showed the most promise for future market innovation and implementation.

Figure 5. Approach flow diagram



3.1 Biomimicry: Translating biological crosslinking inspirations into chemical solutions for fabric finishing

Biomimicry 3.8 provided information on 12 biological crosslinking examples to inspire new chemical crosslinking solutions. We began translating these biological examples by organizing them into categories based on the material being crosslinked. The first group of crosslinking examples contained pure protein, the second group consisted of proteins that promote mineralization, and the third group was comprised of predominantly crosslinked carbohydrates. We eliminated the proteins promoting mineralization as we did not think these strategies were applicable to crosslinking in non-regenerative, non-living systems. We focused on the eight remaining biological examples (Table 2) as well as our own research expertise to generate creative chemical solutions for alternative fabric treatments.

Table 2. Biomimetic crosslinking strategies found in eight organisms

Crosslinked Protein	Crosslinked Carbohydrates
Tree frog foam nest Snail epiphragm Human cytoskeleton Mussel cuticle Slug glue Human cartilage	Wood hemicellulose Flax stem fiber

3.2 Framework: Technical Feasibility

As possible chemical solutions began to emerge, we created and applied a framework for evaluating the technical feasibility of each solution. Using information in the literature and our chemical intuition, we assessed each proposed chemical for crosslinking ability with cellulose, itself (as a possible solution for permanent press), and with other functional groups (as a possible solution for DWR). After this initial assessment, we turned to other technical considerations such as color formation, durability, application/curing, and cost. Our evaluation table and metrics for each proposed solution is shown below (Table 3). We evaluated four existing and eight novel strategies based on crosslinking ability, durability, application and curing, cost, and consumer acceptance. Based on the available data, and our predetermined metrics, we assigned the strategies a score of good (green), medium (yellow—not shown), or bad (red) in fourteen sub-categories. In section 5.0, we show our applied framework (Table 8).

Chemical solutions with undesirable attributes were noted but not initially eliminated. We chose to keep these solutions to help ourselves and others working on alternative fabric treatments map out the possible solution space and recognize limitations and boundaries of the bio-inspired solutions.

Table 3. Evaluation Metrics for Technical Feasibility

	Crosslinking Ability			Durability			Application and Curing				Cost		Consumer Expectations	
	With Cellulose	**With Itself (DP)**	**Add Func. Groups (DWR)**	**Stable Through Multiple Washes**	**Fabric Strength**	**Withstands foods, sun, etc.**	**Controllably Cured**	**Time of Curing**	**Chemical Stability & Water Solubility**	**Existing Process Machinery**	**Per kg Raw Material**	**Per yard fabric**	**Color**	**Consumer Trends**
Green	Multitude of strong interactions	Multitude of strong interactions	Multitude of strong interactions	No negative interactions with detergents and bonds are	No acid or other known weakening treatments	No issues	Very controllable	< 1 hour	No Refrigeration or other special storage, water soluble	Existing machinery can be used	Same price or cheaper than existing tech	Same price or cheaper than existing tech	No color change	Huge marketing plus!
Red	No or unknown interactions	No or unknown interactions	No or unknown interactions	laundry detergent has the potential to undo the crosslinking	weakens fabric significantly	Not stable to something that would contact clothing during normal wear	no control at all (as soon as its on the fabric it will react)	Over 12 hours	requires special storage and not water soluble	New machinery needed	**More than double existing tech**	**More than double existing tech**	**Large color change**	They would hate it

3.3. FRAMEWORK: HEALTH AND ENVIRONMENTAL HAZARD ASSESSMENT

Evaluating health and environmental hazard endpoints for current chemicals and proposed solutions

In order to assess and classify health and environmental hazards associated with chemical solutions currently in use in the finishing process as well as our proposed solutions, we developed a chemical hazard assessment framework. We looked to GreenScreen for safer chemicals as a model; GreenScreen is a comparative hazard assessment tool used widely in industry and by NGOs. As GreenScreen is an intricate and complex tool--the process of completing an entire screening for one chemical is time and resource intensive--we adapted a simplified framework so our chemicals could be more rapidly assessed.

We first evaluated health and environmental hazards for a representative group of currently used chemicals in the fabric finishing process. After establishing baseline criteria and seeing where there is room for improvement, we applied our framework our proposed solutions.

The first step in the process of assessing and classifying a product's chemical hazards involves research and data collection on 18 Human and Environmental Health endpoints. We looked to sources including authoritative lists compiled by PHAROS, as well as using PubMed, Google Scholar, Web of Science, to search the peer-reviewed primary scientific literature. In the case where data for a particular chemical was lacking, we turned to resources such as the Hazardous Substances Data Bank (HSDB), EPA Integrated Risk Information System (IRIS), Agency for Toxic Substances Disease Registry (ATSDR) Toxic Substances Portal, and as a last resort, material safety data sheets (MSDS) or other sources of product information from manufacturers. If there was no data available on a chemical, we used models to estimate environmental hazards such as bioaccumulative potential and persistence.

Using GreenScreen, we established a key (Table 4) in order to assess and evaluate the research on each chemical and assign a score of red (high hazard), yellow (medium hazard), or green (low hazard). We also assessed the weight of evidence for each chemical we researched. Lastly, established a benchmark tool that laid out criteria for assessing whether or not a chemical would be a good option.

The following steps summarize the health and environmental hazard assessment process:

1. Evaluate health and environmental hazards for currently used chemicals, thus establishing a baseline
2. Assess and classify chemicals through research and data collection on 18 human and environmental health endpoints (as adapted from GreenScreen)
    a. ***Health Endpoints***
        i. Human health Group I: chronic, life-threatening effects, potentially induced at low doses, transferred between generations
        Carcinogenicity, Mutagenicity & Genotoxicity, Reproductive Toxicity, Developmental Toxicity (includes neurodevelopmental toxicity), Endocrine Activity
        ii. Human Health Group II: also important for understanding and classifying chemicals, these hazards may be mitigated

Acute toxicity, Systemic toxicity and organ effects, neurotoxicity, skin irritation, eye irritation

b. ***Environmental Toxicity & Fate***: An indication of where these chemicals end up in the environment and in organisms
Acute aquatic toxicity, chronic aquatic toxicity, other ecotoxicity studies when available, persistence, bioaccumulation
c. ***Physical hazards***: Reactivity, flammability
d. We additionally gathered information on ***exposure***
    . Process notes: information relating to potential exposure
    i. Potency (LD50): Lethal Dose 50 is an indicator of a substances' acute toxicity
    ii. Timescale of effect (acute or chronic):
    Acute- sudden and severe exposure, often reversible (such as carbon monoxide poisoning)
    Chronic- prolonged or repeated exposure over many days, months or years; symptoms may not be readily apparent

3. Established and applied a color-coded key (Table 4) in order to assess and classify hazard based on scores of red (high hazard), yellow (medium hazard), or green (low hazard). The color-coding system allowed us assess, at-a-glance, the relative toxicity of each chemical compound.

4. Assessed weight of evidence:
    a. Strong weight of evidence: information from authoritative lists and peer-reviewed literature indicated by a **bold** marking
    b. Limited weight of evidence: research that was not from peer-reviewed scientific literature (MSDS for example), preliminary findings in the scientific literature, or where research was inconclusive (i.e. not enough evidence of a hazard) were left unbolded.

5. Using a benchmark system also adapted from GreenScreen (Table 5), we made informed decisions about which chemicals were appropriate for further use, and which we should rule out as possibilities. If any chemicals were classified as a Benchmark 1 chemical, it was immediately ruled out. Benchmark 2 chemicals were evaluated further, while Benchmark 3 chemicals were considered for use.

Table 4. Evaluation Metrics for Human Health & Environmental Hazard Endpoints

		Evaluation Metrics		
		High	Moderate	Low
		▯	O	▯
Human Health Group I	Carcinogenicity Mutagenicity Reproductive Developmental Toxicity	Known or presumed for any route of exposure; authoritative lists, strong weight of evidence (human)	Suspected for any route of exposure; limited or marginal evidence (animal)	Adequate data, negative studies, or clear evidence of no effect
	Endocrine	Evidence of endocrine activity and related human health effect	Evidence of endocrine activity	Adequate data available; negative studies
Human Health Group II	Acute Toxicity	GHS category 1,2,3; any route of exposure;	GHS category 4; any route of exposure	GHS Category 5, adequate data, negative studies, or GHS not classified
	AT Oral LD_{50} (mg/kg)	0-300	>300 – 2000	> 2000
	Systemic Toxicity Organ Effects	GHS category 1,2 single exposure for any route of exposure	GHS category 3 for single exposure any route of exposure	Adequate data available, negative studies, GHS not classified
	Neurotoxicity	GHS category 1,2; single exposure any route	GHS category 3; single exposure any route	Adequate data, negative studies; not classified
	Sensitization	High frequency of occurrence	Low to moderate frequency of occurrence	Adequate data, negative studies; not classified
	Skin Irritant	GHS category 1,2 (Corrosive/irritating)	GHS category 3 (Mild irritant)	Adequate data, negative studies, not classified
	Eye Irritant	GHS category 1,2 (Irreversible/irritating)	GHS category 3 (Mild irritant)	Adequate data, negative studies, not classified

Source: Adapted from GreenScreen for Safer Chemicals (24)

		Evaluation Metrics		
		High	Moderate	Low
		▯	O	▯
Environmental Toxicity & Fate	**Persistence**			
	Soil ($t_{1/2}$ life in days)	60 to >180	16 to 60	<16 or rapid degradability
	Water ($t_{1/2}$ life in days)	40 to >60	16 to 40	< 16 or rapid degradability
	Air ($t_{1/2}$ life in days)	>2 to 5	–	<2
	Long-Range Environmental Transport	Evidence	Suggestive evidence	–
	Bioaccumulation			
	BAF (Bioaccumulation factor)	1000 to >5000	>500 to 1000	0 to 500
	BCF (Bioconcentration factor)	1000 to >5000	>500 to 1000	0 to 500
	Log K_{ow} (Log octanol-water partition coefficient)	4.5 to > 5.0	>4.0 to 4.5	≤4
	Monitoring Data	Evidence	Suggestive Evidence	–
	Aquatic Toxicity (chronic/acute)	GHS category 1,2	GHS category 3	Sufficient data available and not classified
Physical Hazards	**Reactivity (Rx)**	GHS unstable, category 1,2	GHS category 3; any route of exposure	Adequate data, and GHS not classified
	Flammability	GHS category 1,2	GHS category 3,4	Adequate data, and GHS not classified

Table 5. Evaluation metrics for determining health and environmental benchmarks

Benchmarks	**Criteria**				
Benchmark 1: Avoid—chemical of concern	PBT= High P + High B + High T (Group I or II Human or Ecotoxicity)	PB = High P + High B	PT = High P + High T (Group I or II Human or Ecotoxicity)	BT = High B + High T (Group I or II Human or Ecotoxicity)	High T (Group I Human)
Benchmark 2: Use—but search for safer substitutes	PBT = Moderate P + Moderate B + Moderate T (Group I or II Human or Ecotoxicity)	High or Moderate P or B + High or Moderate T (Group I or II Human or Ecotoxicity)	Moderate T (Group I or II Human)	High or Moderate T (Group II Human)	High or Moderate Flammability or Reactivity
Benchmark 3: Prefer—safer chemical	Low P + Low B + Low T (Group I or II Human or Ecotoxicity)		Low Physical Hazards (Flammability and reactivity) + Low (additional ecotoxicity endpoints when available)		

Source: Adapted from GreenScreen for Safer Chemicals (24)

3.4 Making Informed Decisions

After compiling the data and evaluating each proposed solution based on the technical feasibility framework and the health and environmental impacts framework, we needed to make informed decisions. We weighted the criteria based on their importance and likelihood for improvement. A For example, a carcinogen is not likely to become less hazardous, but a slow reaction may be improved by the discovery of a catalyst. Additionally we applied the principles and definition of green chemistry discussed in the background to develop the following definition for our greener solutions:

- Priority 1: the new solution must be known or suspected to be less hazardous than currently used chemistry (formaldehyde or diisocyanates).
- Priority 2: the crosslinking ability and durability should be comparable to existing treatments
- Priority 3: minimize changes to the application process, cost, and consumer experience

Priority 1	be <u>less hazardous</u> than the existing solution
Priority 2	have <u>performance and durability</u> *comparable* to existing treatments
Priority 3	minimize changes to the application process, cost, and consumer experience

4.0 PROPOSED STRATEGIES

Our technical feasibility evaluation framework allowed us to quickly compare the existing and proposed strategies and chose the four most promising for a more detailed analysis. Each solution is discussed in greater detail below.

4.1 Sea Mussel Inspired Solution

Biological Inspiration

Catechol, incorporated as Dopa from the post-translational modification of tyrosine residues, is found in the adhesive proteins secreted by a variety of aquatic organisms, such as mussels, sandcastle tubeworms, and caddis fly larvae. These chemical groups are an important part of a suite of adhesion molecules which allow marine organisms to form durable, resilient attachments to almost any surface (25). While specific interactions vary with each surface, attachment to organic substrates has not been well characterized. In general, catechols can mediate adhesion by irreversible polymerization in the presence of oxygen as well as by reversibly chelating ions such as Fe^{3+}, both of which are available in seawater.

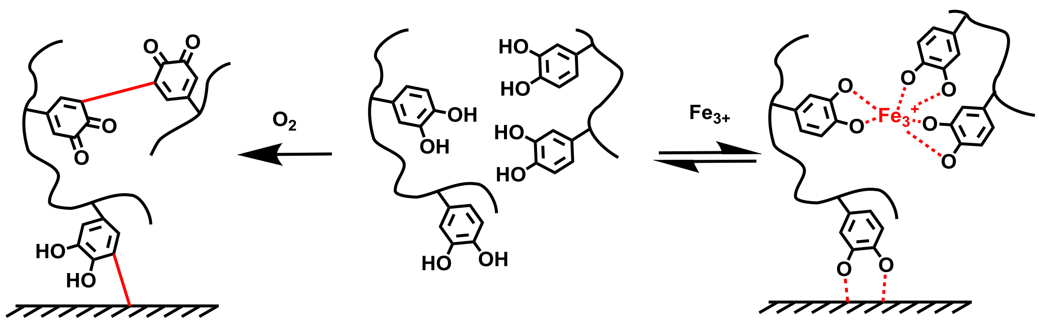


Figure 6. Formation of covalent and coordination bonds between catechol groups. Dopa side chains on adhesive proteins can form covalent networks in the presence of oxygen, or coordinate complex networks in the presence of ions such as Fe^{3+}.

Fabric Finishing Solution

Catechols are an important and versatile building block for the design of mussel-inspired synthetic adhesives and coatings. Their ability to establish a range of interactions with both organic and inorganic substrates has promoted their use as a universal anchor for surface modifications. Dopamine is a natural catechol that polymerizes in basic, aqueous solutions containing oxygen. Once polymerized, it can bind to many surfaces, including cellulose (26,27). Furthermore, a polydopamine coating on polyester has been reported to withstand at least 30 washes (28). This polymer network has the potential to provide durable press finish by preventing the rearrangement of hydrogen bonds that causes wrinkling.

Polydopamine is even more promising as an adhesive for a durable water repellent (DWR) fabric finish. After coating the cotton fabric it can form strong covalent bonds with nucleophiles such as amines and thiols. A simplified scheme for this process is shown in **Figure 7**, where dopamine is polymerized around cellulose and used to anchor a water repellent additive (red) (29). This process has been shown to create a water repellent layer on many surfaces (26). A range of potential water repellent additives such octadecylthiol can be derived from vegetable oils and are commercially available.

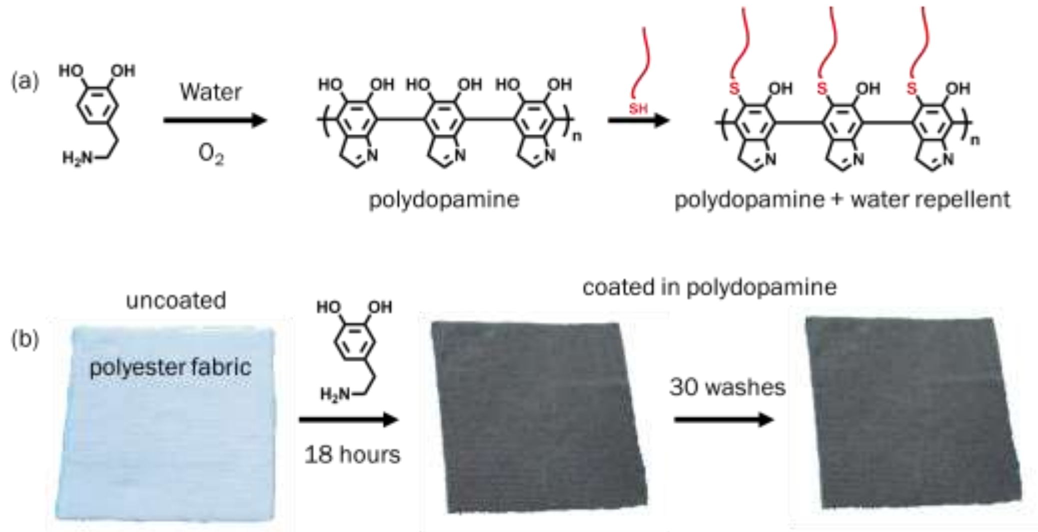


Figure 7. Polymerization of dopamine by oxygen encapsulates fabric in polydopamine. (a) A water repellent chemical (red) could be reacted to form a coating on the surface of the polydopamine. (b) Polyester fabric has been coated with polydopamine and shown to withstand at least 30 washes (28).

This fabric finishing solution would be best applied in the fabric form to minimize worker exposure. While there are no known long-term health or environmental effects of dopamine or octadecylthiol, the former is a biologically active drug (used to treat heart attacks among other conditions) while the latter is an irritant. After curing, the resulting hydrophobic fabric finish is expected to be biologically inert.

Challenges

1. <u>Possible color formation:</u> When catechols such as dopamine polymerize they turn dark brown. The opacity of a polydopamine coating depends on its thickness. It may be possible to apply a thin layer that does not alter the fabric color significantly. If not, this would drastically limit the range of colors for DWR-treated garments.
2. <u>Slow process:</u> The published protocol for coating surfaces with polydopamine takes 12-18 hours. It may be possible to develop a catalyst to shorten this reaction time.
3. <u>Moderately hazardous chemicals:</u> Octadecylthiol is an irritant. Care would need to be taken when disposing/reusing water used for wet processing.

Next Steps

Consider funding a research project to screen

1. The color change upon formation of polydopamine coatings on denim (possible test method in ISO105-C10:2006)
2. The water repellency of polydopamine coatings + water repellent additive on denim (e.g. AATCC Test Method 22-2010)

3. The durability of polydopamine coatings + water repellent additive on denim (e.g. AATCC Test Method 22-2010)

Table 6. Proposed experiments to measure the potential DWR properties of polydopamine + octadecylthiol.

Thickness of polydopamine coating (vary reaction time)	**Color change of fabric**	**Degree of water repellency after reaction with octadecylthiol 0 washes**	**10 washes**	**20 washes**	**30 washes**
1 hour reaction					
3 hour reaction					
9 hour reaction					
15 hour reaction					

Using the proposed experiments tabulated above, 20 measurements would be taken. These experiments require a colorometer, washing machine, and water-repellency testing apparatus.

If the results of the research project are promising, LS&Co may want to consider partnering with a textile chemistry company such as Scholler to develop and optimize this fabric finish.

4.2 Plant Crosslinker (Lignin) Inspired Solution

Biological Inspiration

Lignin is a complex, three-dimensional polymer of phenylpropane units found in the secondary cell walls of plants. It strengthens and protects the cell by filling in the space between cellulose, pectin, and hemicellulose. It is covalently crosslinked with hemicellulose and binds non-covalently to cellulose. Along with providing mechanical strength, lignin enables water transport in plants by reducing the cells permeability to water. Lignin also plays an important function in a plant's natural defense against degradation by impeding penetration of destructive enzymes through the cell wall. Lignin's three functions (mechanical strength, reduced water permeability, and resistance to biological degradation) make it a very attractive crosslinker to investigate for fabric finishing alternatives.

In the plant cell wall, lignin polymerization is initiated by oxidation of the phenylpropane phenolic hydroxyl groups by laccase or peroxidase enzymes (Figure 8). A monolignol free radical can then undergo radical coupling reactions, producing a variety of linkages with other monolignols and with hemicellulose. The nature of lignin polymerization results in the formation of a three-dimensional, highly branched, interlocking network throughout the cell wall.

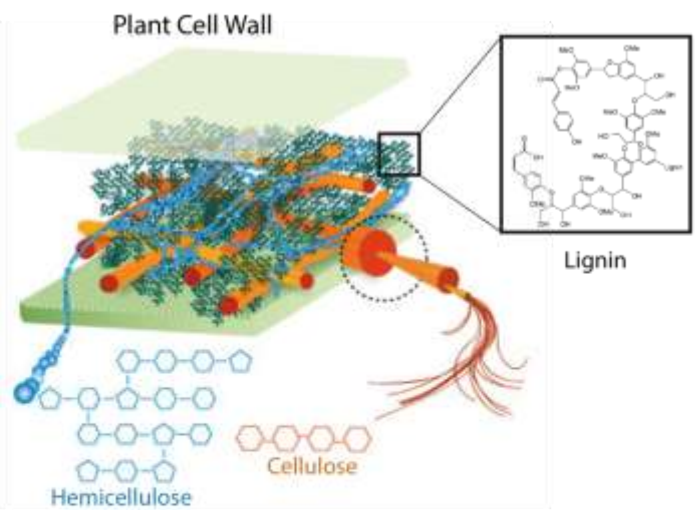


Figure 8. Lignin polymerization in the plant cell wall

Fabric Finishing Solution

The chemistry of lignin crosslinking has many features that are desirable in new fabric treatments from both a technical and health standpoint. The crosslinking is initiated by a class of enzymes that are already used industrially in applications such as textile dyeing and teeth whitening. Along with lignin monomers, the enzymes are also active on a variety of other substrates including ortho and paradiphenols, aminophenols, polyphenols, polyamines, and aryl diamines. This promiscuity in substrate selectivity allows a lot of flexibility to choose chemicals that are less hazardous than current treatments but provide the same technical performance. We evaluated the health effects of laccase, peroxidase, and a small fraction of potential substrates (Table 4) (p-coumaric acid, methyl hydroquinone, 2,5-Dihydroxybenzoic acid, and 4-aminophenol). A third promising feature is that once the enzyme initiates crosslinking, radical transfer can occur. This should enable polymerization to occur throughout the fabric even if the enzyme is not distributed everywhere.

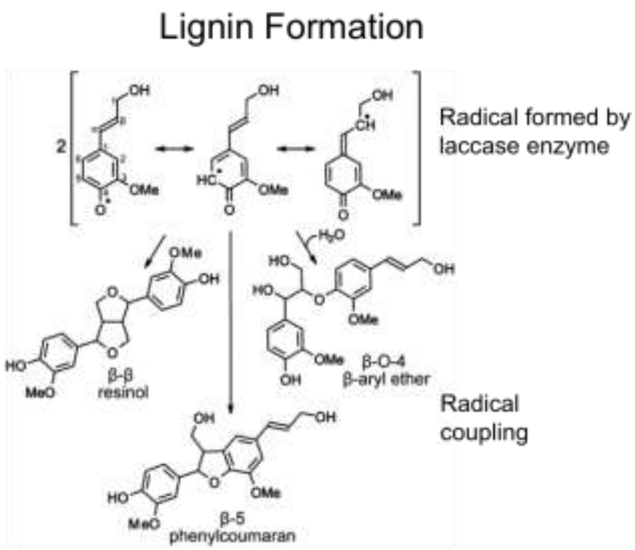


Figure 9. Lignin formation

Challenges

1. <u>Possible dye bleaching</u>: Laccases have been used in the textile industry to bleach dyes in wastewater and in fabric. Investigating different types of laccases or similar enzymes such as peroxidases may yield an efficient crosslinker that does not bleach dyes. It is also unknown how the enzyme will perform with an excess of crosslinking chemical substrates (non-dyes). If the enzyme is more selective for the crosslinking substrate, the conditions and time of treatment could be set such that bleaching is minimized.

2. <u>Possible color formation:</u> Many of the possible substrates form colored compounds when polymerized. This will depend on the substrate and will need to be evaluated along with other technical and health considerations for each potential substrate.

3. <u>Uncertain durability:</u> It is not clear if this strategy will covalently attach the chemicals to cellulose. Lignin, the inspiration for this solution, is bound strongly to cellulose and covalently attached to hemicellulose, a branched polysaccharide. It is therefore likely that finishes developed with this strategy would be durable.

Summary and next steps

This is a very promising solution that relies on enzymes to initiate radical coupling. There is a lot of work required to make this solution commercially viable, however. To begin pursuing this solution, laccases should be tested under varying conditions for their ability to bleach dyes used on textiles. We are confident that with the right enzyme and conditions, this challenge can be overcome. The next step is to choose substrates. Laccases are active on a plethora of compounds, which should allow only chemicals with low hazard to be chosen for testing. We evaluated the health impacts of only a small fraction of the possible substrates and identified a few chemicals to avoid. Once multiple substrates with low hazard have been identified, they should be tested with laccases. The products generated from reactions of pure and mixed substrates should be thoroughly evaluated for degree of polymerization, color, and stability. Promising mixtures should be polymerized on fabric and the resulting properties tested.

4.3 Enzymatic Cellulose Degradation Inspired Solution

Biological Inspiration

Polysaccharide monooxygenases (PMOs) are copper containing enzymes that oxidatively cleave cellulose. They are found in many fungi and bacteria that degrade plant matter (Figure 10). They create single strand breaks in accessible, crystalline cellulose chains to generate a lactone and ketone (30). Although unable to degrade cellulose into soluble sugars themselves, they generate chain breaks on the surface of cellulose that facilitate the action of other enzymes.

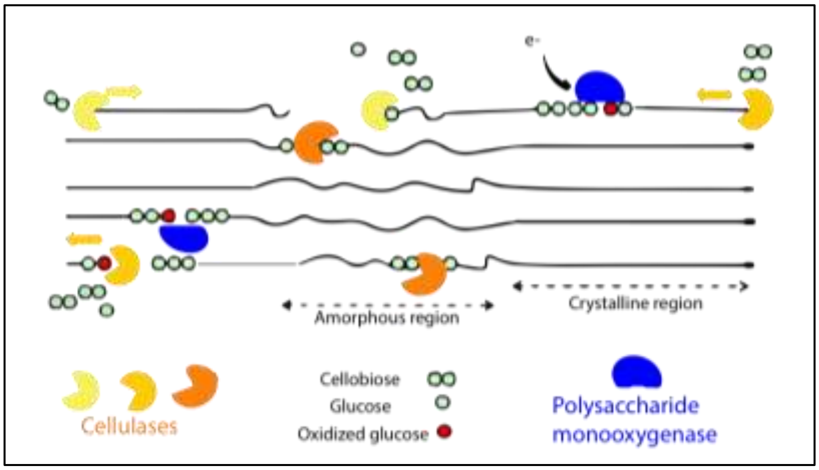
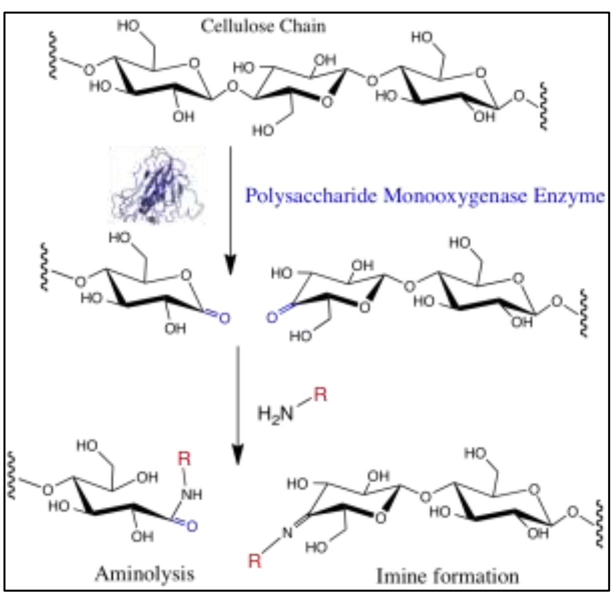


Figure 10. The cellulolytic system of the fungus Trichoderma reesei

Fabric Finishing Solution

The ketone generated by PMOs makes the cellulose more reactive for future chemical treatment, enabling the use of less reactive chemicals. The enzyme's ability to selectively modify cellulose without degrading it is a key feature. The newly created ketone groups on the cellulose surface can be reacted with chemicals containing an amine to generate an imine bond between the cellulose and another functional group such as a DWR chemical.



A benefit of this solution is that the enzyme works under mild conditions and is very selective. This solution is also very versatile. Any chemical containing an amine can be covalently attached to fabric. We evaluated the health effects of a few sample amines in Table 4 (ethanolamine, p-Phenylenediamine, o-phenylenediamine, ethylene diamine, 1,3-Propanediamine, 1,2-Cyclohexanediamine).

Challenges

1. <u>Slow and expensive enzyme:</u> Polysaccharide monooxygenases are both slow and expensive. They are currently produced with a cocktail of cellulase enzymes and are unavailable industrially in a purified form. The price and availability may

improve if/when PMO enzymes are produced industrially for the biofuels industry. If the enzyme could be applied and work during transport of the fabric, their slow speed may be acceptable.
2. Uncertain extent of crosslinking: Another potential issue is that the enzyme may never be able to modify enough of the cellulose surface to enable a thorough finishing treatment. This is due to the enzymes requirement for a crystalline, accessible surface of cellulose. Cotton contains both crystalline and amorphous regions, so some areas may not be modified at all.
3. Two step process: Finally, this strategy requires a second step after enzyme treatment to generate an imine bond between the cellulose and chemical crosslinker.

Summary and next steps

Although innovative and potentially low hazard, this strategy is not technically feasible at this time. PMO enzymes are not well characterized and not produced industrially in a pure form. The cost of the enzyme, the uncertain level of fabric modification, and the time of treatment make this strategy very unlikely to be successful.

4.4 Slug Inspired Solution

Biological Inspiration

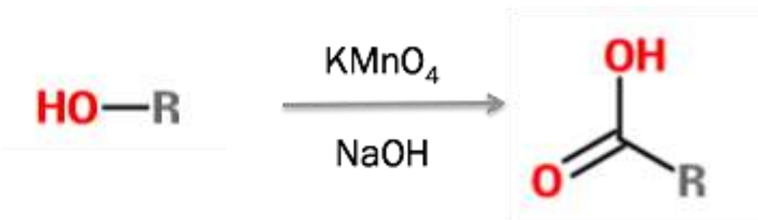
When the terrestrial slug (*Arion subfuscus)* feels threatened, it secretes a defensive, quick-setting mucous adhesive to protect it from predators. The adhesive, though composed nearly entirely of water (95% water), contains protein polymers that are able to crosslink in alkaline environments. The crosslinking mechanism occurs when carboxylic acid functional groups on the protein polymers coordinate around divalent metal cations found in the secreted glue, namely, calcium, magnesium, zinc, manganese, iron and copper (31).

Fabric Finishing Solution

It is possible to functionalize the primary alcohol groups on cellulose chains to carboxylic acids to promote crosslinking between the cellulose chains similar to the slug's defensive mucous.

In order to functionalize the primary alcohols on cellulose to carboxylic acids, the cellulose must be exposed to a strong base to provide the alkaline environment necessary for the oxidation reaction, the most effective bases for this reaction being aqueous NaOH or KOH (32). Of these two, we choose to study NaOH. In addition, the cellulose must be exposed to the permanganate ion (MnO_4^-), the ion responsible for the oxidation of alcohol to carboxylic acid. The accompanying figure represents the oxidation process. The R group represents the cellulose chain.

Acetone, pyridine, tBu-OH, and dioxane are possible mixing agents for this reaction. This means they have the ability to increase the speed of the reaction, as well as the ability to increase the yield of desired product as opposed to undesirable side products.



Challenges

1. A drawback to this technology is that laundry detergents are designed to remove metal cations from clothing, specifically those that are commonly found in hard water (33). So, this technology may be limited to the use of Fe^{2+}, which may affect the color of the material in an undesirable way.
2. In addition to the Fe^{2+} ion's color issue, potassium permanganate ($KMnO_4$) also poses its own unique color challenge. Currently potassium permanganate is the chemical used in the bleaching step of garment manufacturing, which may be problematic if the goal is to keep color in the garment.
3. Durability may also be a challenge. The slug's protective mucous layer is temporary, therefore it is unclear how long the crosslinking will last in a garment finish.

Summary and next steps

Technically, this solution shows a lot of promise for the permanent press, wrinkle free finish. Although technically feasible, the health and environmental effects of potassium permanganate and sodium hydroxide, the two required chemicals for the oxidation of alcohol groups to carboxylic acid groups, are undesirable. So, this may not be a promising direction for Levi's in their current hazard based approach.

4.5 Summary of Proposed Solutions

Below is a summary of the four solutions chosen for further investigation. A list of proposed chemicals were provided and assessed in the evaluation frameworks established in the approach.

Table 7. Summary of solutions

Solution	Summary of chemistry	Proposed chemicals
Polysaccharide Monooxygenase (PMO) Enzyme inspired by cellulase enzymes	Functionalize cellulose and crosslink with substrate	**Enzyme**: Polysaccharide Monooxygenase **Possible primary amine crosslinkers**: ethanolamine, p-phenylenediamine (PPD), o-phenylenediamine (OPD), ethylene diamine, lysine
Laccase Enzyme inspired by Lignin	Crosslink network around cellulose	**Enzyme**: Laccasse enzyme, peroxidase enzyme **Possible substrates**: p-coumaric acid, methyl hydroquinone, 2,5-dihydroxybenzoic acid, 4-aminophenol, vanillin
Dopamine inspired by the Sea Mussel	Crosslink network around cellulose	**Crosslinker**: Dopamine **Buffer salt**: Tris HCL **Water repellent chemical**: octodocylomine
Potassium Permanganate inspired by the Slug	Functionalize cellulose and crosslink with substrate	**Required Chemicals**: potassium permanganate, sodium hydroxide **Substrates**: Iron(II) **Recommended Chemicals for Mixing**: acetone, pyridine, dioxane, t-butyl alcohol

5.0 EVALUATING TECHNICAL FEASIBILITY

After we selected the four most promising solutions, we applied the technical feasibility framework to each set of chemicals comprising each solution. For details of this approach, see Section 3.

5.1 Technical feasibility baseline

We evaluated the technical feasibility of our ‘proposed solutions’ relative to the baseline of the ‘existing solutions,’ formaldehyde and di-isocyanate based resins. The results are tabulated below in ‘Technical Evaluation of Greener Crosslinking Solutions Compared to Current Chemistry’ (Table 8). The legend for technical feasibility table is above in our approach section, Section 3.0.

Table 8. Technical Evaluation of Greener Crosslinking Solutions Compared to Current Chemistry

			Evaluation Metrics													
	Chemical Compound	Durable Press or DWR	Crosslinking Ability			Durability			Application and Curing				Cost		Consumer Expectations	
			With Cellulose	With Itself (DP)	Add Func. Groups (DWR)	Stable Through Multiple Washes	Fabric Strength	Withstands foods, sun, etc.	Controllably Cured	Time of Curing	Chemical Stability & Water Solubility	Existing Process Machinery	Per kg Raw Material	Per yard fabric	Color	Consumer Trends
Existing Solutions	DMDHEU	DP	▯	▯	▯	▯	O	▯	▯	▯	O	▯	▯	▯	▯	O
	DMeDHEU	DP	▯	▯	▯	O	O	▯	▯	▯			▯	▯		
	Citric Acid	DP	▯ O			O			▯				▯		O	▯
	BTCA	DP	▯	▯		O			▯						O	▯
	Other															
	Other															
Proposed Solutions	Polydopamine	DWR	O	▯	▯	▯	▯	▯	▯	▯			▯	▯	▯	
	Silane modification of cotton & reaction with aldehydes	Either	O	O	▯	O	▯	O	▯	▯			O			
	Lacasse oxidation & radical crosslinking	DP	O	▯	▯	▯	▯	▯	O	O	O		▯		▯	
	PMO enzyme oxidation of cellulose and reaction with amine	DWR	▯	O	▯	▯	▯	▯	O	▯	O		▯		O	
	Permanganate															
Rejected Solutions	4-Arm PEG catechol solution		▯	O	▯	O	?	▯	▯	?	▯		▯			
	Cellulose binding modules		O	▯	O	▯		▯	▯	▯	O		▯	▯	▯	▯
	Polyacrylic acid on cellulose															
	Permanganate functionalized cellulose															

5.2 Results from applying technical feasibility evaluation framework to proposed solutions

After applying the technical feasibility evaluation framework to each of the proposed solutions, we summarized the benefits and challenges of each solution below. Additionally, we list here which challenge the solution is most applicable to- either the wrinkle-free permanent press or durable water repellent challenges.

Table 9. Results from technical feasibility evaluation framework

Solution	Challenge	Technical Benefits	Technical Challenges
PMO Enzyme inspired by cellulose enzymes	Water repellent	• Covalent bond to fabric • Variety of chemicals possible	• Enzyme is not available commercially • Uncertain level of fabric modification • Slower than current finishes
Laccase Enzyme inspired by Lignin	Wrinkle resistant or Water repellent	• Enzyme initiated coupling • Wide range of substrates can be oxidized and coupled • Radical transfer can occur	• Laccases have been used to bleach dyes in the textile industry • May discolor fabric
Dopamine inspired by the Sea Mussel	Water repellent	• Likely more durable than current water repellent finish • Starting materials largely benign and readily biodegradable	• Likely slower than current finish • May discolor fabric • Likely more expensive than current finish
Potassium Permanganate inspired by the Slug	Wrinkle resistant	• Potassium Permanganate and sodium hydroxide already used in Levi's production line	• May discolor fabric • Optional mixing agents are toxic • May be less durable than existing finish

5.3 Recommendations Based on Technical Feasibility

After comparing all the four proposed solutions, the most technically unfeasible solution at the time of writing of this report is the PMO enzyme solution because the key enzyme needed is not available in its pure form. If the PMO enzyme were readily available, it would be more technically feasible. The laccasse enzyme, dopamine and potassium permanganate solution all have their respective problems but are somewhat technically feasible. We have not yet fully taken health and environmental impacts into account yet so this is not a final recommendation

6.0 ASSESSING HEALTH AND ENVIRONMENTAL HAZARDS

6.1 Health and Environmental Impacts Baseline & Results

We applied our health and evaluation hazard framework (Section 3.3) to each set of chemicals for each proposed solution. The results are below (Tables 11-13).

Similar to the technical feasibility section, we first evaluated the health and environmental hazard endpoints of currently used chemistry (Table 10). We then had a baseline to compare our proposed solutions to and understand which areas are in need of improvement. Some of the key points we discovered were that as a class of chemicals, isocyanates are both sensitizers and irritants. Additionally, toluene di-isocyanate is a probable human carcinogen (34). Formaldehyde is a Benchmark 1 chemical, and is listed as a Class 1 carcinogen by the International Agency for Research on Cancer (IARC) (4).

Table 10. Summary Health Assessment of Currently Used Textile Chemistry[2]

Chemical Compound		Exposure			Health Endpoints					Ecological Effects		
Chemical Name	**(CAS Number)**	**Dose**	**Potency (LD_{50})**	**Timescale of Effect (Acute or chronic)**	**Carcinogenicity Mutagenicity Reproductive Toxicity**	**Developmental Toxicity Endocrine Activity**	**Acute Toxicity Sensitization/ Irritation**	**Other Health Effects**	**Physical Hazard**	**Persistence Bioaccumulation**	**Aquatic Toxicity**	**Other Ecotoxicity**
Di-isocyanates												
Diphenylmethane di-isocyanate	9016-87-9						▯				▯	
Hexamethylene di-isocyanate	822-06-0						O					
Isophorone di-isocyanate	4098-71-9						O					
Tetramethylxylene di-isocyanate (TMXDI)	2778-42-9						▯					
Toluene Di-isocyanate TDI (both 2,4,TDI and 2,6 TDI)	584-84-9 91-08-7				O		O					
Durable Press Resins												
Formaldehyde	50-00-0				▯		▯		▯	▯		
Dimethylol dihydroxyethyleneurea (DMDHEU)	97123-53-0											
DMeDHEU	3923-79-3											
Citric Acid												
Other Chemicals												
Potassium Permanganate	7722-64-7		750 mg/kg (mouse)		O		O		O			
1,3-diamineopropane	109-76-2						O		▯			

[2] This list is not intended to represent a complete list of chemicals used in Levi's fabric finishing processes

Table 11: Health and Environmental Hazard Evaluation for Mussel and Plant Crosslinker Inspired Solutions

Chemical Compound	Exposure			Health Endpoints						Environmental Toxicity & Fate		Physical Hazards
				Human Health Group I		Human Health Group II						
Chemical Name CAS Number	Process Notes	Potency LD_{50}	Timescale of Effect (Acute or chronic)	Carcinogenicity Mutagenicity	Reproductive Developmental Toxicity Endocrine Activity	Acute Toxicity Sensitiz Irritation	Systemic Toxicity & Organ Effects	Neuro Toxicity	Skin/Eye Irritation	Persistence Bio-accumulation	Aquatic Toxicity (Acute/ chronic)	Reactivity/ Flammability
Mussel Inspired Solution												
Dopamine 51-61-6		2859 mg/kg oral-rat	Acute	▯	O	O				▯		▯
Tris-HCl 1185-53-1	Buffer salt to raise pH										▯	
~~Octadecylamine~~ 124-30-1		2000 mg/kg oral - rat	Acute			▯						
Octadecylthiol 2885-00-9			Acute	▯		O						
Plant Crosslinker (Lignin) Inspired Solution												
Laccasse enzyme	Crosslinks substrates					▯						
Peroxidase enzyme												
p-coumaric acid 501-98-4	Potential substrate for crosslinking					▯						
Methyl hydroquinone 95-71-6		200 mg/kg oral-rat				▯					▯	
2,5-Dihydroxybenzoic acid 490-79-9						▯						
4-aminophenol 123-30-8	Would need to be substituted			O		O					▯	
Vanillin											▯	

Table 12: Health and Environmental Hazard Evaluation for Enzyme Inspired Solution

Chemical Compound	**Exposure**			**Health Endpoints**						**Environmental Toxicity & Fate**		**Physical Hazards**
				Human Health Group I		**Human Health Group II**						
Chemical Name CAS Number	**Process Notes**	**Potency LD_{50}**	**Timescale of Effect (Acute or chronic)**	**Carcinogenicity Mutagenicity**	**Reproductive Developmental Toxicity Endocrine Activity**	**Acute Toxicity Sensitiz Irritation**	**Systemic Toxicity & Organ Effects**	**Neuro Toxicity**	**Skin/Eye Irritation**	**Persistence Bio-accumulation**	**Aquatic Toxicity (Acute/ chronic)**	**Reactivity/ Flammability**
Enzyme Inspired Solution												
Polysaccharide Monooxygenase												
Ethanolamine 141-43-5				▯	▯	▯				▯	▯	
***p*-Phenylenediamine (PPD)** 106-50-3	Can use any primary amine					O		**O**			▯	
o-phenylenediamine (OPD) 95-54-5				O					▯	O?	O?	
Ethylene diamine 107-15-3			Acute			▯			▯		▯	
1,3-Propanediamine, n,n-dimethyl- 109-55-7						O					▯	O
Lysine 923-27-3	biologically derived molecules– be wary of ingestion or stereoisomers			▯	▯	▯	▯				▯	▯

Table 13: Health and Environmental Hazard Evaluation for Slug Inspired Solution

Chemical Compound	Exposure			Health Endpoints						Environmental Toxicity & Fate		Physical Hazards
				Human Health Group I		Human Health Group II						
Chemical Name CAS Number	Process Notes	Potency LD_{50}	Timescale of Effect (Acute or chronic)	Carcinogenicity Mutagenicity	Reproductive Developmental Toxicity Endocrine Activity	Acute Toxicity Sensitiz Irritation	Systemic Toxicity & Organ Effects	Neuro Toxicity	Skin/Eye Irritation	Persistence Bio-accumulation	Aquatic Toxicity (Acute/ chronic)	Reactivity/ Flammability
Slug Inspired Solution												
Potassium permanganate 7722-64-7	Already used in Levi's process	750 mg/kg oral-mouse	Acute	O		O			O		▯	
Sodium hydroxide 1310-73-2	Conditions require high pH, Levi's processes	40mg/kg intraperi-toenal mouse	Acute						▯		O	
Dioxane 123-91-1	cosolvent would need to be replaced/removed	2000mg/kg oral rat		▯				O				O
Acetone 67-64-1	(cosolvent) non-essential, would need to be replaced/removed	oral mouse 3000mg/kg			O			O	O		▯	▯
Pyridine 110-86-1	(cosolvent) non-essential, would need to be replaced/removed			▯	O				▯		▯	O
tBu-OH 75-65-0	(cosolvent)				O							O

6.2 Recommendations based on health and environmental impacts

Based on the health and environmental impact analysis, the sea mussel inspired solution (Section 4.1), PMO enzyme and the laccasse enzyme inspired solution (Section 4.2) are the solutions that have the least detrimental health and environmental impacts.[3]

The major concern in the lignin inspired solution is 4-aminophenol. This chemical is a suspected mutagen, suspected to be acutely toxic and confirmed to be acutely toxic to aquatic life. Additionally, methyl hydroquinone and 2,5- dihydroxybenzoic acid demonstrate high acute toxicity and p-coumaric acid and laccasse demonstrate moderate acute toxicity. The major concern in the slug inspired is pyridine, a reproductive toxicant. Additionally, potassium permanganate demonstrates moderate acute toxicity and mutagenicity. This solution also incorporates several corrosive substances such as potassium permanganate and sodium hydroxide.

The toxicity of 4-aminophenol and pyridine make their associated solutions poor candidates as greener crosslinking solutions. If 4-aminophenol and pyridine are replaced with comparably effective substitutes with the same chemical functionality, they may still be worthwhile candidates for further investigation. However, given that no comparably effective substitutes are readily available or well researched in the literature, the sea mussel inspired solution and the enzyme inspired solution still stand as the most favorable candidates as greener solutions for Levi's challenge. In comparison to the eliminated solutions, the sea mussel inspired solution and the enzyme inspired solution call for the use of relatively safer chemicals.

The sea mussel inspired solution's primary crosslinker is dopamine, a substance well documented in the literature as not carcinogenic, physically safe and is not known to be persistent/bioaccumulative. Dopamine will still need to be handled with care due to potential acute endocrine effects. The potential water repellent additive octadecylthiol poses some concern because it is an irritant. However, this additive is not an integral part of this proposed solution and further research can be conducted to find a safer alternative. Moreover, the resulting polymerized hydrophobic fabric finish is expected to be biologically inert and thus safe for consumer use. Little hazard data is available on the last chemical listed in this solution, Tris-HCl, except that is has low hazard to aquatic life. Overall, the hazard endpoints are less harmful than the hazard endpoints of both the eliminated solutions and the original formaldehyde or di-isocyanate containing resins.

The enzyme inspired solution functionalizes cellulose with polysaccharide monooxygenase, making it reactive to amines. This proposed solution is very versatile and can work with many different amines. A range of potential amines was examined to preliminarily gauge the toxicity range of these amines. As a general note, low molecular weight amines are generally skin irritants. One study showed that the environmental concentrations that exceed the following threshold concentrations could potentially cause environmental harm (i.e. 500 ng/L amines; 1200 ng/L amides). This report consolidated data from tests on invertebrates and fish. The best amine candidate in the investigation is lysine, which is not carcinogenic, not developmentally toxic, and readily biodegradable. If it

[3] Please note that we have not accounted for technical feasibility in making these recommendations in this section as they are only based on health data. We will present a summary comparison of all of these solutions at the end of the report.

functions as well as predicted, this solution is very viable and reasonably safe compared to the eliminated solutions and the original formaldehyde or di-isocyanate containing resins.

7.0 RECOMMENDATIONS FOR PROPOSED SOLUTIONS

7.1 Making Informed Decisions based on definition of "greener solutions"

The purpose behind evaluating our proposed solutions with a technical feasibility framework and a health and environmental safety framework is so that we can compare the proposed solutions and make an informed decisions and recommendations based on our definition of a greener solution. The priorities for our greener solutions determined in the Approach Section are revisited here.

Priority 1	be less hazardous than the existing solution
Priority 2	have performance and durability *comparable* to existing treatments
Priority 3	minimize changes to the application process, cost, and consumer experience

There are many nuances in the proposed solutions that make it difficult to concretely determine which solution is the best of four. The following recommendations should be viewed as guidelines and should in no way completely eliminate further investigation into any of the four proposed solutions.

Based on our research of the available data for each proposed solution's technical feasibility and health and environmental impact, we conclude that the lacasse enzyme and the dopamine solutions hold the highest promise for further development and industrialization as fabric finishes.

Laccasse Enzyme Solution

The laccasse enzyme solution demonstrates substantial technical feasibility and less detrimental health and environmental impacts relative to currently used technologies. The versatile selection of substrates that can be used in this solution is one of its biggest advantages but much caution still needs to be exercised in selecting a safe substrate. Lacasses have also been used in the textile industry before and though it was used as a bleaching agent; its familiarity to the industry may prove to be an advantage. Moreover, this solution is adaptable for both the wrinkle resistant permanent press and water repellent challenges proposed by Levi's.

Dopamine Solution

The dopamine solution also demonstrates substantial technical feasibility and less detrimental health and environmental impacts relative to currently used technologies. Several studies of dopamine-based fabric finishes have been conducted and makes this solution one of, if not the most, well technically researched proposed solution. Results from these reports demonstrate the dopamine's solution's superior durability to existing water repellent finishes. The water-repellent substrates in use are currently irritants but substitutes may be further investigated if desired. However, cost, discoloration and speed of curing are standing concerns for this solution. Additionally, dopamine is commonly used in the pharmaceutical industry, which may lead to some health and environmental concerns.

PMO Enzyme Solution

The PMO Enzyme solution demonstrates health and environmental safety comparable to that of the laccasse Enzyme but unfortunately pales in comparison in terms of technical feasibility. This solution is very similar to the laccasse enzyme solution because it employs a relatively safe enzyme and also requires caution in substrate selection to ensure health and environmental safety. However, its greatest downfall is that the enzyme is not commercially available in an isolated form. If it were available in such a form, further research on this solution would certainly be encouraged but is not technically feasible at the time this report was written.

Potassium Permanganate Solution

The Potassium permanganate solution demonstrates great technical feasibility but had more severe health and environmental impacts than the other proposed solutions. One of the required chemicals of this solution, potassium permanganate, was recognized by Levi's as a hazardous chemical that will be phased out of their current manufacturing process. Although the potassium permanganate solution has safer health and environmental impacts compared to the baseline of the formaldehyde and di-isocyanate based resins, it will not be applicable to the Levi's challenge.

7.2 Summary of tradeoffs: technical feasibility and health and environmental impact evaluations

Below is a combined summary of the technical feasibility and health and environmental impacts evaluations.

Table 14: Summary of technical feasibility and health and environmental hazards for proposed solutions

Solution	Water Repellency or Permanent Press?	Technical Benefits	Technical Challenges	Health effects summary
PMO Enzyme inspired by cellulose enzymes	Water repellent	Covalent bond to fabric Variety of chemicals possible	Uncertain level of fabric modification Slow Enzyme is not available commercially	Enzyme- likely safe Amines- generally toxic, lysine is safest because biologically derived
Laccase Enzyme inspired by Lignin	Wrinkle resistant permanent press Water repellent	Enzyme initiated coupling Wide range of substrates can be oxidized and coupled Radical transfer can	Laccases have been used to bleach dyes in the textile industry! Possible color formation	Enzyme- likely safe Possible substrates- generally toxic, vanillin is safest

		occur		
Dopamine inspired by the Sea Mussel	Water repellent	Likely more durable than current water repellent finish Starting materials largely benign and readily biodegradable	Likely slower than current chemicals May discolor fabric Likely more expensive than current finish	Dopamine may be neurotoxin Water repellent substrates mildly toxic
Potassium Permanganate inspired by the Slug	Wrinkle resistant permanent press	Potassium Permanganate and sodium hydroxide already used in Levi's production line	Color problems (Fe2+ and KMnO4) Safety of mixing agents Durability	Required chemicals are corrosive and toxic Substrates are ok Mixing chemicals range from slightly to very toxic

7.3 Directions for Future Research and Development

Several future research directions exist in improving the technical feasibility and health and environmental impacts of the proposed solutions. The evaluative frameworks developed and established in this report should prove to be a helpful tool for future research and can be further improved to maximize its utility.

Technical feasibility

We did not conduct any tests of experiments during the course of this report. Therefore, many aspects of the proposed solutions need to be further investigated in order to bring a product to fruition. Future steps for each specific solution are outlined in the Proposed Solutions (Section 4.0). This section addresses future research direction common to many, if not all, the proposed solutions.

In order to move the proposed solutions forward, researchers need to further investigate where in the textile manufacturing process each solution can be implemented. Additionally, researchers will have to select the best substrates and solvents with consideration to the trade-off between technical feasibility and health and environmental safety.

Several proposed solutions had common technical challenges including discoloration, slowness in curing and cost. Discoloration may be addressed if fabric finishes or their pre-cursors can be applied before the fabric is dye. Additionally, researchers can seek ways to minimize or limit color changes when chemicals in the proposed solutions are applied. From a different angle, discoloration can be seen as an opportunity for design innovation if chemists and designers can work together to create designs that incorporate the discoloration effects of the proposed solutions. Lastly, more cost-effective methods of producing the required chemicals may be found with further research and development.

Health and environmental impacts

The health and environmental impacts of chemicals listed in the proposed solutions within this report serve as a guideline for future health and environmental impact investigations. The list of chemicals for each proposed solutions, in particular, the substrates and solvents, are only a representative list of what may be used in final fabric finishes. It is highly possible that other substrates and solvents with superior technical feasibility may be found in further steps of research. Those chemicals would also need to be evaluated for health and environmental safety. Furthermore, the results in this report are summarized from data gathered from authoritative lists and primary literature but an even more thorough search in primary literature and the use of models should be exercised for the final fabric finishing. Furthermore, data relating to exposure (number of works, method of exposure, etc.) should be gathered to better evaluate health and environmental impacts. Lastly, it is important for Levi's and other researchers to maintain the integrity of a hazard-based approach and not use a risk-based approach because a hazard-based approach does not leave worker safety in the hands of chance and promotes the development of safer and greener chemistry. Additionally, it is highly recommended that any chemical hazard data be made transparent and publicly available so as to bridge the chemical data gap.

8.0 CONCLUSIONS

In this report, we have established the groundwork for finding greener solutions to the two chemical groups on Levi's restricted substances list, formaldehyde resins and di-isocyanates. We defined our greener solution by prioritizing health and environmental safety first, technical feasibility second and other factors last. We established a general approach for finding a greener solution beginning with translating biological crosslinking into chemicals. This was followed by evaluative frameworks for technical feasibility and health and environmental impacts. The proposed solution that proved to be most promising were the lacasse enzyme and dopamine solutions but given the trade-offs and nuances of each solution, each proposed solution should be further investigated, especially if new literature is available. Additionally, these proposed solutions may prove to be applicable to other fields that use formaldehyde or di-isocyanate based chemicals for similar functions. While our proposed solutions may be applicable to varying degrees, our approach and evaluative frameworks should prove to be valuable tools for future research and development of greener solutions not just in the textile industry but also in other industrial sectors.

There were several challenges and obstacles that limited our report including translating biological crosslinking into chemicals and the availability of health and environmental safety data. There were significant challenges in translating biological crosslinking strategies into chemicals. Several biological crosslinking used mineralization and self-repairing strategies that could not be translated in a useful way because there is a fundamental difference between living organisms and textiles. Nonetheless, the biomimicry translation process was made easier by focusing on the functionality of the chemicals in the organisms. Another large obstacle we faced was finding adequate and accurate chemical hazard data to assess the health and environmental impacts of our proposed solutions. This data is currently very widespread with many authoritative lists and very few central sources that agglomerate the data in an accessible and reliable fashion. Although PHAROS was a useful tool for preliminary chemical hazard research, it was still challenging to find data for several chemicals that are less well-studied. It is our hope that these challenges may be overcome as the field of green chemistry progresses and as further research is conducted.

Given the challenges of a project of this nature, we applaud Levi's for its efforts and pioneering spirit to seek out a greener solution for formaldehyde and di-isocyanate based resins. We also strongly encourage Levi's to continue to pursue greener solutions to the hazardous chemicals they currently used and to continue to influence other players in the textile industry to cooperate with them towards this cause.

There are clearly many tradeoffs and factors to consider in finding a greener solution and unfortunately, the chemical industry in the United States largely values performance over safety. Thus, there are significant financial, technical, organizational and cultural barriers that need to be overcome in order to implement these greener solutions and make them successful in the broader market context (35).

We limited our report to research on finding greener solutions to just two classes of chemicals within a larger list of hazardous chemicals in the textile industry. We also prioritized technical and health factors above market factors largely due to our lack of expertise and information in this area. Nonetheless, it is important to realize that the marketplace plays an enormous role in ensuring the success of implementing greener solutions. Both supply-side and demand-side policies need to work together. On the supply-side, technology gaps need to be acknowledged such that greener solutions are made available for industrial use. On the demand-side, a market need for new technology and greener solutions needs to be established. According to a report on drives for industrial innovation, surveyed businesses indicated public policy and market demand as the two most important factors that are needed for motivating environmental innovation in companies (36).

Our proposed solutions are examples of supply-side solutions in the textile industry and our report outlines useful tools for the further pursuit of greener solutions. The frameworks and proposed solutions will require support and further investigation from experts from many different fields. There are certainly many more hazardous chemicals and informational gaps that need to be addressed under the bigger umbrella of managing the health and environmental safety of chemicals. It is clear to us that it will take a cooperative effort between businesses, scientists, government, and the public and other stakeholders in order to make concrete progress towards greener chemistries.

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