Greener Solutions for Thermoplastic Polyolefin Polymer Membrane Roofing Additives

UV Absorbers, Antioxidants, and Thermal Stabilizers

Partnered with The Oakland EcoBlock Project

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Executive Summary

Oakland EcoBlock is an innovative urban pilot project aimed at retrofitting an existing mixed development community at the neighborhood scale. These retrofits include the installation of solar panels, energy storage units, and integrated waste water systems that will reduce the net energy consumption and potable water demand. For buildings with low-slope or flat roofs, EcoBlock proposes using thermoplastic polyolefin (TPO) membrane roofing, which is currently considered the greenest roofing option due to its recyclability, innocuous chemical hazards of the base polymer, and the light color which tends to reduce the heat island effect and keep home cooling energy demands to a minimum.

However, light and thermal stabilizer additives in TPO that protect the polymer, enhance the performance, and extend the lifetimes of TPO roofs have been found to pose potential hazards to human health and the environment. In this project, we investigated greener strategies that reduce or eliminate these hazards while maintaining technical performance. Herein, we present six strategies ranging from short- to long-term solutions depending on estimated time for implementation. The short-term strategies consist of market-available physical blockers. Medium-term strategies are aimed to partially or fully substitute currently used additives through innovation in materials. Finally, our long-term strategy is a novel system that we hope inspires further research and development in green roofing technology for sustainable building design.

Short term

    i.   Living roof
   ii.   Metal roof

Medium term

    i.   Vitamin E-poly(tannin) regenerative antioxidation
   ii.   Lignin-TPO biopolymer blend
  iii. TiO_2 coated-bacterially derived $CaCO_3$ composite nanoparticles

Long term

    i.   Rooftop solar powered microbial fuel cells

Introduction

Oakland EcoBlock – Retrofitting at the Neighborhood Scale

The Oakland EcoBlock, a pilot urban project based in Oakland, California, aims to retrofit communities with renewable technologies at the neighborhood scale (30-40 buildings) to reduce energy consumption and water demand.[1,2] Aggregating resources and technology to retrofit neighborhood blocks is proposed to reduce overall waste and offer greater benefits, which would otherwise be impossible at the individual building scale.

EcoBlock estimates *50% reduction in annual electricity consumption and near zero carbon emissions* by installing rooftop solar panels to generate electricity and an innovative flywheel energy storage device (Figure 1A). An electric car sharing program and smart street lighting will further reduce carbon emissions.

EcoBlock estimates a *70% reduction in potable water demand* by collecting and using rainwater for toilets and irrigation, treating and recycle greywater from drains and washing machines, using recycled fluid for gardening and irrigation, installing efficient fixtures and taps, and treating solid waste for compost (Figure 1B).
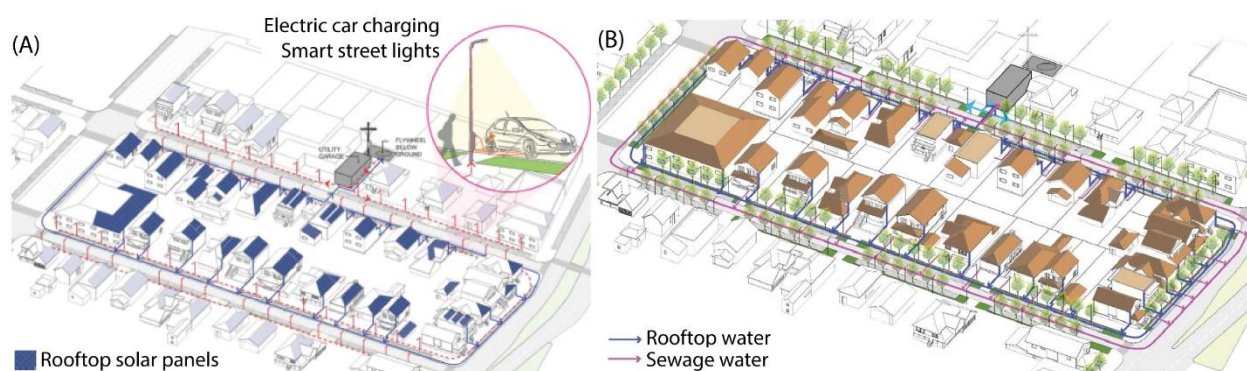
Figure 1. EcoBlock design for (A) communal roof-top solar panels (blue) and flywheel energy storage (grey) and (B) integrated water and wastewater systems. Images adapted from "Oakland EcoBlock: Implementing Urban Climate Change Adaptation By Means of an Integrated Design Solution".

This proof-of-concept pilot project is currently in its planning stages as of December 2018. The first construction site is proposed in a residential neighborhood in Oakland, California (Figure 2, red). If successful, there is interest to replicate this project in communities across the U.S. and globally.

Challenge and Motivations

Our project focused on *synthetic polymer membrane roofing* for retrofitting buildings with low-sloped or flat roofs (Figure 2, blue). EcoBlock has proposed using **thermoplastic polyolefin (TPO) membrane roofing** due to its favorable properties. Compared to other market-available synthetic polymers, TPO is considered the *greenest* option. Table 1 highlights the advantages and disadvantages of three major commonly used synthetic polymer membrane roofing materials.

Figure 2. Aerial photograph of proposed EcoBlock neighborhood in Oakland, CA (red). Buildings suitable for synthetic membrane roofing application are indicated in blue. Image adapted from Google Earth.

Table 1. Overview of commonly used market-available synthetic polymer membrane roofing materials.

Material	Notes
Polyvinyl chloride (PVC)	Strong, flexible, and durable (20+ years, properly installed)
	Available in different colors and thicknesses
	Resistant to moisture, wind, fire, and chemicals
	Contains chlorine and plasticizers
	Releases bioaccumulative toxicant (dioxin) during manufacture and disposal
Ethylene propylene diene monomer (EPDM)	Low cost, shorter lifetime (~15 years)
	Incompatible with asphalt products
	Seams prone to leaking; requires regular maintenance
	Most widely available in black (poor energy efficiency)
Thermoplastic polyolefin (TPO)	Flexible, versatile, easy to install
	No chlorine and plasticizers
	Additives increase life expectancy to at least 20-30 years
	Recyclable
	Installation requires aggressive cleaning solvent before heat welding seams
	Additives pose health and environmental concerns

Although TPO roofing is currently considered the greenest membrane roof available by building designers and homeowners, the *additives pose human health and environment hazards*. In this project, we investigated stabilizer additives (UV absorbers, antioxidants, and thermal stabilizers) that protect the TPO membrane from degradation.

Light and heat are the primary causes of degradation in polymers and plastics. Solar irradiation at the Earth's surface ranges from ultraviolet (UV) to infrared wavelengths (Figure 3).[3] UV photons (wavelengths shorter than 400 nm) carry sufficient
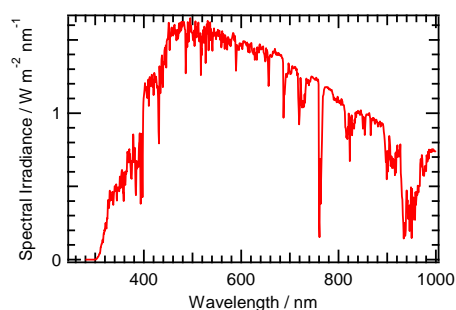

Figure 3. Terrestrial solar irradiance spectrum generated by the SMARTS atmospheric model.

energy to break chemical bonds and create highly reactive free radicals; carbon-carbon single bonds have bond dissociation enthalpies of 3.6-3.9 eV per bond corresponding to 315-345 nm. At high temperatures, under prolonged direct sun exposure on rooftops or during manufacturing and installation, chemical bonds can also break and generate free radicals.
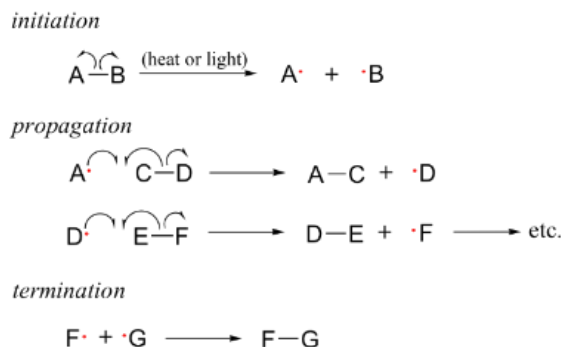
Free radicals initiate *chain-reaction processes* leading to breaks in the polymer backbone structure (Scheme 1). Once a radical reaction is initiated, further reactions propagate throughout the material in a chain-reaction manner until termination. At the macroscopic scale, exposure to UV radiation and heat can lead to cracks, brittleness, polymer loss, and discoloration, resulting in overall roof performance degradation.

UV absorbers, antioxidants, and thermal stabilizers protect polymers and plastics by absorbing UV photons or efficiently terminating radical chain-reactions (i.e., radical scavenging). Over the last

Scheme 1. General radical chemical reactions showing initiation (radical formation), propagation (chain reactions), and termination steps. Red dot indicates a radical (i.e., unpaired) electron.

several decades, research and development of stabilizer additives and formulations has extended the lifespans of TPO membrane roofs to over 25 years, with some manufacturers offering warranties up to 30 years.

However, stabilizer additives in TPO membranes raise concerns for *short- and long-term human health and environmental hazards*. Herein, we present an overview of hazards associated with stabilizer additives in current TPO formulations and propose greener alternative strategies that align with the sustainability goals of EcoBlock while maintaining technical performance. We classify each strategy into one of three categories described below, depending on estimated time and cost for research, development, and performance testing before implementation.

1. **Short Term Strategy**: a greener solution readily available on the market today that could be implemented *within two years*. Minimal performance testing would likely be required.
2. **Medium Term Strategy**: partial or full chemical substitution of commercially available TPO additive(s) with greener chemical alternative(s) that could be implemented in *2-10 years* with significant investment and collaborative partnerships in academia and industry. Extensive performance testing would likely be required.
3. **Long Term Strategy**: innovative idea aimed to venture outside of traditional roofing materials and push the boundaries of science and technology that could be implemented in *10+ years* with significant basic research and system characterization still required.

In our investigations, we focused on light and heat stabilizer additives in TPO membrane roofing. TPO membranes contain additional chemicals (e.g., lubricants, fire retardants) that we did not investigate. Furthermore, TPO roofing requires cleaning solvents and adhesive bonding agents during installation that contain chemicals that raise additional human health and environmental concerns that were not included in the scope of our investigation.

Current State of Industry: TPO Membrane Roofing

TPO membrane roofing consists of a reinforcing polyester scrim between two polymer layers with standard thicknesses of 45-mil (1.1 mm), 60-mil (1.5 mm), and 0.80-mil (2.0 mm). Manufacturers use different formulations that lead to measurable performance differences in their products. In 2015, Structural Research, Inc. conducted a large-scale independent study on the performance of TPO membrane from several major manufacturers and found (1) all brands exceeded ASTM D6878 minimum standards,[4] (2) significant differences exist between manufacturers for failure time (e.g., cracking) and weight loss in ASTM D573 @275 °F accelerated weathering tests,[5] and (3) variation in consistency of membranes produced by each brand.[6,7] GAF EverGuard Extreme® 60-mil, the top performing TPO membrane in the study, showed no cracking at 275 °F for 96 days (all other competitors showed cracking) and more than double the performance of typical membranes on UV weathering tests. Table 2 Table 2lists the chemical composition of GAF EverGuard Extreme®.[8,9] Although stabilizer additives account for less than 3% by weight, potential bioaccumulation and long persistence pose concerns for human health and environment.

Table 2. GAF EverGuard Extreme® TPO polymer membrane composition and primary function of each compound. Trace compounds (<0.01%) are not included.[8]

Compound Name	CAS	%w/v	Function
Ethylene-propylene copolymer	9010-79-1	76.04%	Base polymer
Magnesium hydroxide	1309-42-8	21.77%	Fire retardant
Titanium dioxide	13463-67-7	1.20%	UV absorber, pigment
Calcium stearate	1592-23-0	0.10%	Lubricant
Chimassorb® 944	71878-19-8	0.08%	Hindered amine light stabilizer
Irgafos® 168	31570-04-04	0.08%	Antioxidant

TPO Polymer Membrane Lifecycle – Human Health and Environmental Hazards

Below, we briefly describe the life cycle of TPO membrane and describe the salient hazard information during each stage.

Manufacturing

Roofing membrane manufacturers purchase additives from large chemicals companies, such as DuPont and BASF. The additives and TPO pellets are then combined and the mixture is blended together, heated to approximately 200 °C (400 °F), and extruded onto the top and bottom of a polyester reinforcing scrim to form laminated layers with precisely controlled thickness. The polymer membrane is then cooled by passing through a series of temperature-controlled rollers and cut into desired sizes and packaged.[10]

During manufacturing, the primary human health concerns are the physical mixing and heating processes. When physically mixed, powders and nanoparticles can be released in the immediate working area as dust. At high temperatures, volatile chemicals with lower boiling points may be released into the surroundings as vapor. On-site engineering controls (e.g., ventilation) and personal protective equipment (e.g., safety goggles, respirator masks) should be in place to minimize human exposure. Wastewater and exhaust fumes released into the environment should also be considered in the engineering controls to limit release of toxic chemicals.

Roof Installation

TPO membrane roofing can be installed on an underlying substrate material (e.g., cover board, insulation layer) with adhesives, mechanical plates and fasteners, or ballast.

1. *Adhesion:* chemical bonding adhesive mixture attaches the TPO membrane to the underlying substrate and the membrane seams are heat-welded together.
2. *Mechanical:* metal screw-type fasteners and plates secure the membrane on the substrate. Membrane sections are then overlapped to cover the fasteners and heat-welded at the seams.
3. *Ballasted:* membrane is laid on top of the substrate, heat-welded and sealed on the perimeter, and heavy material is placed on top of the polymer membrane to secure the membrane in place. Common ballast material includes gravel, sand, and rocks.

For all installation methods above, a strong chemical cleaning solution is required before heat-welding. Human exposure and environmental release of cleaning solvents and adhesive bonding agents pose additional concerns during installation. Johns Manville TPO Membrane Cleaner contains *m*-xylene (35-50%), *p*-xylene (10-20%), ethylbenzene (10-20%), *o*-xylene (5-15%), and toluene (0-1%).[11] Johns Manville Bonding Adhesive for TPO and EPDM Membrane contains toluene (30-50%), *n*-hexane (20-30%), and acetone (10-20%).[12] Cleaners and adhesives were outside the scope of our investigation, but greener alternatives should be investigated. During heat-welding of the seams, high temperatures may release volatile chemicals, such as those in cleaning solvents and adhesive bonding mixtures, to the surrounding. Care should be taken to avoid unsafe human exposure and excessive environmental release of these chemicals.

In-Use

Once installed, the primary human health and environmental hazard concern is the *leaching* of additives. Leaching is expected to be a slow process; thus, acute exposure is highly unlikely to occur. However, for chemicals that bioaccumulate and/or have high persistence, *long-term low-level exposures* raise a concern. Since EcoBlock aims to reclaim rooftop water as part of their integrated water system design, reducing or eliminating leaching should be a high priority.

Recycling and Disposal

TPO is 100% recyclable due to its polymeric nature. Scraps produced during manufacturing and construction can be collected and re-incorporated into the manufacturing process. Recycled TPO can be incorporated in small fractions (5-15%) of new TPO membrane, thereby diverting waste from landfills and reducing pollution into the surrounding environment. Hazards during the melting and re-extrusion process are similar to hazards associated with manufacturing (i.e., dust, nanoparticles, fumes, and vapors).

If not recycled, other endpoints include incineration and landfills. Incineration of TPO will produce carbon dioxide, water, and heat. Inorganic additives (e.g., titanium dioxide) will not combust, forming solid oxides that are typically dumped into landfills. No stable toxic compounds are produced following incineration.[13] In landfills, TPO will eventually decompose and additives will be released, albeit slowly, into the environment. Depending on the reactivity and stability of the compound, some will quickly decompose to harmless compounds in nature while others will persist for much longer. *The human health and ecological effects of low-dose, long-term release of stabilizer additives from plastics and polymers are not well-understood.*

Approach

Quantitative and Qualitative Performance Measures

Market-available TPO membrane roofs meet minimum requirements established by ASTM D6878, which sets standards for physical properties (e.g., thickness, breaking strength, water absorption).[4] Simulated UV solar radiation and heat weathering tests give quantitative and qualitative performance measures of stability (e.g., polymer weight loss, discoloration, cracking).[5,14–17]

Polymer membrane roofing for EcoBlock must meet performance specifications, some of which are presented in Table 3. Given the limited time and scope of this investigation, we focused on physical and chemical properties of additives that serve as indirect measures in extrapolating their performances as additives in TPO membranes.

Table 3. Roof performance characteristics and their associated physical and chemical properties.

Performance	Physical & Chemical Properties
Durability UV & heat weathering resistance	UV-Vis absorbance Radical scavenging Thermal stability Kinetics
Reduce heat island effect High solar reflectivity index	Refractive index
Rain water collection compatible Low leaching of additives	Water solubility Octanol-water partition coefficient Molecular weight Functional groups

Human Health and Environmental Hazards

When assessing the safety of a chemical compound, human health and environmental hazard endpoints can be categorized into four broad groups (Table 4): (1) Human Health Group I, (2) Human Health Group II, (3) Environmental Health, and (4) Environmental Fate.

Human Health Group I endpoints, which include carcinogenicity and reproductive toxicity, are considered chronic or life-threatening and potentially induced at low doses or transferred between generations. Human Health Group II endpoints, such as acute mammalian toxicity and skin irritation, can typically be mitigated.

Environmental Health endpoints focus on short- and long-term effects on aquatic systems. Environmental Fate measures persistence and bioaccumulation in the ecosystem.

Table 4. Human health and environmental hazard endpoints investigated in hazard assessments.

Human Health Group I	Human Health Group II
Carcinogenicity Mutagenicity & Genotoxicity Reproductive Toxicity Developmental Toxicity Endocrine Activity	Acute Mammalian Toxicity Systemic Toxicity & Organ Effects Neurotoxicity Skin Sensitization Respiratory Sensitization Skin and Eye Irritation
Environmental Health	**Environmental Fate**
Acute Aquatic Toxicity Chronic Aquatic Toxicity	Persistence Bioaccumulation

We investigated human health and environmental hazards of currently used additives and our proposed alternative compounds by searching in authoritative lists, databases, and scientific literature. When no hazard information was found for an endpoint, we used VEGA-QSAR software to predict hazards based on data of similar chemical compounds.[18]

For each endpoint with sufficient information, we assigned a hazard score: High Hazard (H), Moderate Hazard (M), or Low Hazard (L). Endpoints with no available data were Unknown Hazard (U). Our hazard scores were based loosely on the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).[19] Several endpoints have very broad categorization criteria. For example, carcinogenicity is assessed based on the overall strength of the available scientific data and types of studies (e.g., human, animal). In these cases, we relied more heavily on classifications from authoritative lists to guide our hazard scores. For other endpoints, the hazard categories are quantitatively defined. Two measures that are frequently reported are LD_{50} (lethal dose required to kill 50% of the test population) and LC_{50} (lethat concentration required to kill 50% of the test population). The GHS hazard categories for acute mammalian toxicity, for example, are defined by LD_{50} or LC_{50} values and route of exposure. For acute aquatic toxicity, GHS hazard categories are defined by the LC_{50}, the test organism, and the duration of exposure.

Implications and Limitations of Hazard Information
The purpose of our hazard assessments was to understand the hazards of currently used chemicals and guide our alternative chemical strategies in order to mitigate some of those hazards. For endpoints assigned "Unknown Hazard" scores, the absence of hazard data does not imply safety.

It should also be noted that chemical hazard assessments are generally based on pure, isolated forms of the compound. This is especially important for assessing hazards of additives because some endpoint hazards will change if the compound is incorporated in the plastic or polymer matrix. Thus, our hazard assessments provide a starting point for guiding safer chemical choices, but additional research and testing on relevant chemical interactions and how those affect endpoint hazards in the context of polymers are necessary.

Greener Solution Strategies

Strategy I: Vitamin E & Polymerized Tannins

Background

Hindered amine light stabilizers (HALS) act as *antioxidants* in polymers and plastics, protecting the material from photodegradation. In TPO membrane roofing, HALS concentrations range from 0.1-1% by weight. All HALS contain the 2,2,6,6-tetramethyl-piperidine structure (Figure 4). The lone pairs on the nitrogen and the fully substituted tertiary carbons are critical in their functions. The 2,2,6,6-tetramethyl-piperidine structure does not absorb in UV wavelengths, but UV-absorbing functional groups (e.g., conjugated pi-system) can be attached to the ring structure so that the molecule has both antioxidation and UV absorbing properties. Additionally, HALS can be easily polymerized to control the molecular weight and related chemical properties.
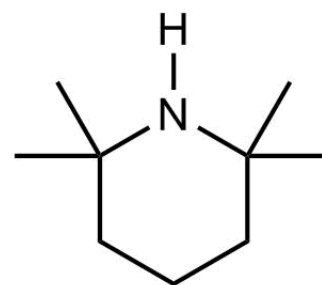

Figure 4. 2,2,6,6-tetramethyl-piperidine structure.

Two examples of currently used HALS in TPO membranes are shown below in Table 5. Tinuvin® 770 is a low molecular weight HALS that contains a nonpolar UV-absorbing (260-290 nm) chain.[20] Chimassorb® 944 is a polymerized high molecular weight HALS that shows excellent compatibility in polymers.[21] The versatility of HALS structures allows for optimization of various chemical and physical properties for application in many different plastics and polymers, depending on the needs of the consumer. For HALS in TPO membrane roofing applications, (1) *stability* during manufacturing and use and (2) *low migration and leaching* are most desired performance characteristics.

Table 5. Examples of HALS used in TPO membranes.[20,21]

HALS	Performance	Hazards
Tinuvin® 770 BASF (CAS 52829-07-9)	Absorbs 260-290 nm Good light stability Broad compatibility Easily dispersed	Low molecular weight Aquatic toxicity Interacts with membrane receptors in vitro cells
Chimassorb® 944 (CAS 70624-18-9)	High Molecular Weight (MW) Excellent compatibility Excellent light stability Low volatility High extraction resistance	Aquatic toxicity Long-term effects Persistence

HALS protects plastics and polymers from photo-oxidation via the proposed Denisov Cycle (Scheme 2).[22] Here, a generic HALS molecule reacts with a polymer peroxy or alkyl radical to stabilize the polymer and convert the HALS to its aminoxyl form. Additional radical reactions take place to regenerate the HALS, allowing for highly efficient radical scavenging, making it suitable in their applications as stabilizers in plastics and polymers.
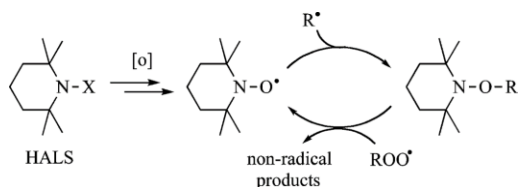
Scheme 2. Denisov Cycle illustrating the regeneration of HALS. Figure reproduced from Hodgson et al.[22]

Motivation

HALS compounds pose human health and environmental concerns. Tinuvin® 770 is acutely toxic to aquatic life and has shown in vitro Ca^{2+} channel blocking behavior,[23] inhibition of nicotinic acetylcholine receptors,[24] and dose-dependent cytotoxicity of isolated cardiomyocytes.[25] Chimassorb® 944 poses acute respiratory hazards and long-term effects on aquatic systems.[26]

Since EcoBlock aims to reclaim rooftop water, HALS additives leaching into the runoff water is a human health and environmental concern. Leaching of additives would also reduce the performance of the TPO membrane roof. Additionally, TPO membrane disposed in landfills will leach additives into the environment over time that will then degrade and decompose (thermally, chemically, bacterially, or by other pathways), releasing other degradation products.

Approach

In pursuing a greener solution, we sought to find an efficient regenerative antioxidative system that maintains technical performance while reducing and/or eliminating some of the hazards and risks presented above. Addition of non-polar groups to the HALS structure reduces mobility and leaching. Increasing the molecular weight (e.g., polymerization) also reduces migration within the polymer matrix. However, one drawback of polymerized or high molecular weight HALS is that it becomes difficult to obtain a homogeneous distribution within the polymer matrix. Non-uniform distribution of HALS within the polymer could lead to areas more prone to photodamage. Additionally, stability (melting and boiling points) in the polymer matrix at the high processing temperatures was considered.

Inspiration

In the body, Vitamin E and Vitamin C react with free radicals in a synergistic manner. Although Vitamin C concentration (2 mM) in the body is generally much higher than Vitamin E concentration (0.02 mM), Vitamin E is considered a more potent antioxidant, especially towards hydrophobic substrates (e.g., lipids).[27] To maintain Vitamin E levels in the body, Vitamin C, a secondary antioxidant, readily reacts with and regenerates Vitamin E after it has undergone oxidation ($k=1.55\pm0.2\times10^6$ $M^{-1}s^{-1}$).[27,28] This regeneration prevents degradation and depletion of Vitamin E in the body.[29] The primary degradation pathway for the Vitamin E radical is an initial isomerization to the benzyl radical, which can then form spiro-dimers, dihydroxy-dimers, trimer-aldehydes, and quinoidal products.[30] In the body, cofactor NADH (nicotinamide adenine dinucleotide) reacts with oxidized Vitamin C and regenerates Vitamin C to complete the synergistic antioxidation cycle (Scheme 3).
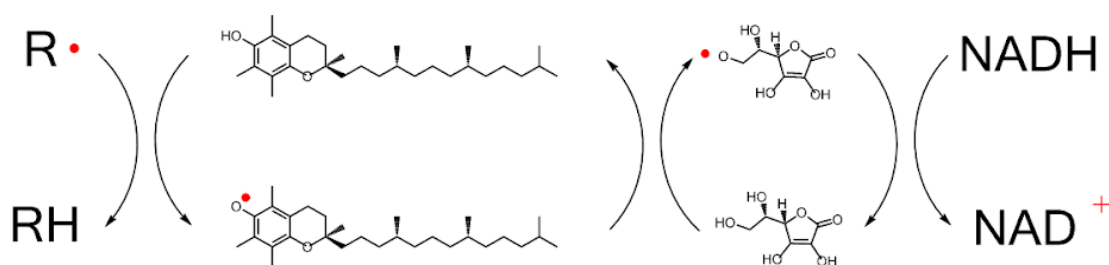
Scheme 3. In the body, Vitamin E acts as a primary oxidant for lipophilic substrates that have undergone oxidative damage. The resulting radical Vitamin E is then regenerated by a secondary antioxidant, Vitamin C. Vitamin C is then regenerated through reaction with cofactor NADH.

Technical Performance

Vitamin E has been utilized as an antioxidant in high-density polyethylene (HDPE) and low-density polyethylene (LDPE).[31] Vitamin E benefits from having a relatively high molecular weight (430.72 g mol^{-1}), high octanol-water partition coefficient (log P_{ow}=9.98), low melting point (3 °C), potential for cost effective mass production, favorable consumer image, and good melt flow stabilization properties. These factors contribute to its superior performance, comparable to commonly used synthetic antioxidants butylated hydroxytoluene (BHT) and Irganox® 1010.[31,32]

However, Vitamin E by itself turns an off-yellow color over time due to degradation and formation of aggregates (spiro-dimers, dihydroxy-dimers, trimer-aldehydes, and quinoidal products) as mentioned above. To reduce and prevent Vitamin E degradation, we propose a secondary antioxidant that readily reacts with and regenerates Vitamin E with excellent TPO compatibility. We propose two possible strategies below.

Reduced concentration of HALS

By incorporating Vitamin E as a primary antioxidant, less HALS would be required to maintain technical performance. Reducing the amount of HALS in TPO formulation would lower overall human health and environmental hazards, though it would not eliminate associated hazards.

Polymerized tannins as a secondary antioxidant

Catechin has shown promise as an efficient secondary antioxidant to react with oxidized Vitamin E and regenerate Vitamin E.

Studies have shown catechin at low polymerization (*n*=40) maintains the antioxidant efficiency of catechin monomers (Figure 5).[33,34] The catechin monomer has a flavone backbone structure and can be naturally derived from green tea and many other plant-based sources.[35] Polymerized catechin resembles the structure of condensed tannins that are commonly found in tropical woods and are also known for their antioxidant properties.[36]
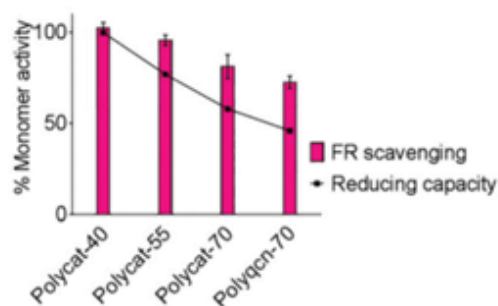
Figure 5. Free radical scavenging and reducing capacity of poly(catechin) relative to catechin monomer. Figure reproduced from Oliver et al.[33]

Furthermore, poly(catechin) has absorbance bands in the UV wavelengths that could be effective in reducing TPO photodamage (Figure 6).

Scheme 4 below shows the proposed regenerative antioxidation pathway for TPO membrane containing Vitamin E and poly(catechin). Vitamin E acts as the primary antioxidant, scavenging a TPO radical, and reacts with secondary antioxidant poly(catechin) to regenerate Vitamin E. Further radical reactions then regenerate the poly(catechin).
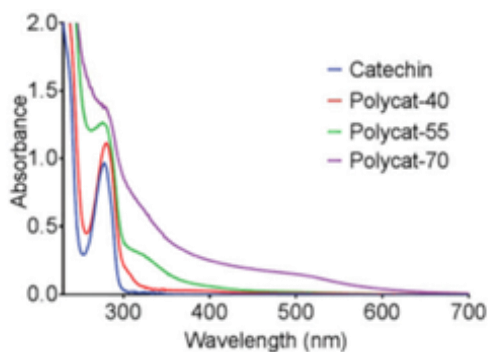
Figure 6. UV-Vis absorbance spectrum of catechin monomer and poly(catechin). Figure reproduced from Oliver et al.[33]
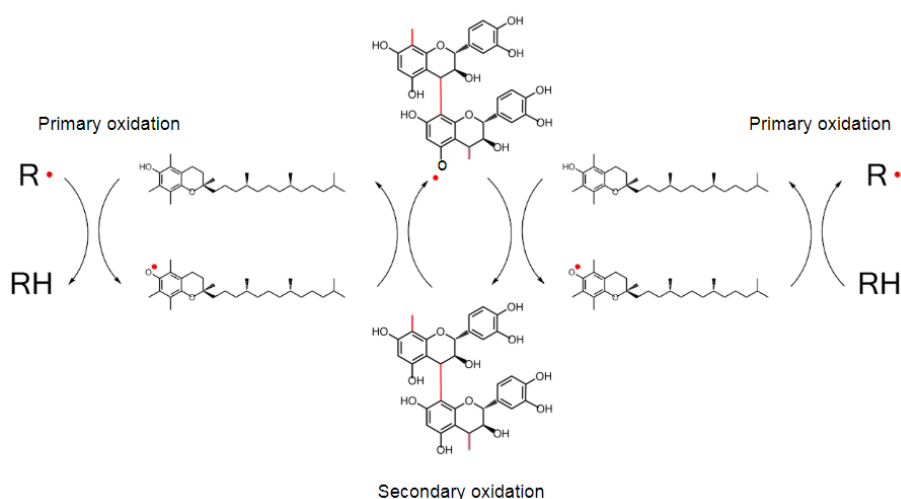
Scheme 4. Proposed Vitamin E-poly(catechin) regenerative antioxidation pathway.

The physical properties of the catechin monomer compared to poly(catechin) are presented in Table 6. Polymerization of catechin increases the molecular weight, solubility, and octanol-water partition coefficient, all favorable properties for a TPO additive.

Table 6. Comparisons of physical properties of catechin monomer and polymerized catechin.

	Catechin	Poly(catechin)
MW (g mol^{-1})	290.26	>10000
Melting Point (°C)	175	>175
Solubility, 20 °C (g/L)	7.6	insoluble
log (P_{ow})	1.5	>1.5
pK_a	16.1	16.1
λ_{max} (nm)	276	276

Health and Environmental Performance

There is strong evidence that HALS pose human health and environmental hazards. Data suggests there are moderate hazards for acute and chronic aquatic toxicity. There is empirical data that PEDA, a prototypical HALS compound (Figure 7), is acutely toxic to aquatic species**Error! Reference source not found.** (LC_{50}=7.9 mg/L f

Figure 7. Chemical structure of PEDA, a prototypical HALS molecule.

or rainbow trout, LC_{50}=0.97-1.0 for bluegill).[37] Modeled data for PEDA predicts chronic toxicity at relatively low concentrations (0.76 mg/L for fish, 2.91 mg/L for algae). This aquatic toxicity is even more concerning, given that additional empirical and modeled data suggest that PEDA is also persistent in aquatic systems. If released into the environment, HALS pose a *long-term environmental hazard* to aquatic systems.[38]
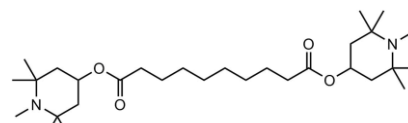
There is not much available data on the effects of HALS on most human health endpoints. However, there is indication of high acute mammalian toxicity. Chimassorb® 994 has an LC_{50} of 0.112 mg/L and bis-TMPS has an LC_{50} of 0.5 mg/L, as measured in rats with inhalation as the route of exposure.[39,40] These values place these HALS in the second worst hazard category (out of 5) for acute toxicity hazard under the GHS classification. Since inhalation would be the main route of exposure in occupational settings, these chemicals pose a human health hazard during manufacturing of TPO membranes.

Vitamin E and tannins (e.g., catechin, apigenin) have environmental and human health hazard profiles that are promising compared to HALS. No effect or positive effects were observed on fish health (tilapia) when exposed to Vitamin E via their diet (500 mg/kg).[41] VEGA software predictions indicate that catechin is likely not persistent in soil nor water. The Canadian Domestic Substances List flags Vitamin E as very persistent in the environment, but evidence of lower aquatic toxicity suggests persistence is less of a concern. While there is no aquatic toxicity data available for catechin, apigenin has shown low aquatic toxicity (LC_{50}=757.78 mg/L, brine shrimp larvae).[42] The alternative chemicals show lower hazard for acute mammalian toxicity; a derivative of Vitamin E showed no toxic effect in mice (orally administered 7 g/kg)[43] and catechin showed some adverse effect on the liver in mice (orally administered 750 mg/kg).[44] Primary literature suggests low hazards for most Human Health Group I endpoints for Vitamin E and catechin. This is certainly preferred over the sparse data available for HALS. However, one potential concern is that much of the human health hazards for Vitamin E and catechin are reported by dietary studies, which may not directly translate to inhalation exposures likely to occur in occupational settings. Low dietary hazards, however, alleviate some concerns about oral exposure from additives leaching out of the polymer into the water system in EcoBlock roofing applications.

Table 7. Summary of hazard assessment of hindered amine light stabilizers (HALS) and proposed alternative antioxidants.

	Human Health Group I					Human Health Group II							Environmental Health		Environmental Fate	
	Carcinogenicity	Mutagenicity & Genotoxicity	Reproductive Toxicity	Developmental Toxicity	Endocrine Activity	Acute Mammalian Toxicity	Systemic Toxicity & Organ Effects	Neurotoxicity	Skin Sensitization	Respiratory Sensitization	Skin Irritation	Eye Irritation	Acute Aquatic Toxicity	Chronic Aquatic Toxicity	Persistence	Bioaccumulation
HALS																
Tinuvin 770	U	U	U	U	U	H	H	M	U	U	U	H	H	H	H	H
Chimassorb 994	U	U	U	U	L	H	H	M	U	U	U	U	M	M	H	U
Alternative Antioxidants																
Vitamin E	L	L	U	L	M	L	U	U	U	U	U	U	L	U	H	M
Catechin	L	L	U	L	M	M	M	U	U	U	M	M	U	U	L	L
Apigenin	L	L	U	U	M	M	U	L	U	U	U	U	L	U	L	L

Remaining Questions: Exploring alternative secondary oxidants

The presence of the catechol moiety in poly(catechin) could reduce stability and lifetime as it could undergo oxidative transformation into highly reactive quinone species. Although not experimentally demonstrated, apigenin may be a better alternative. Apigenin is also a flavonoid compound that has been shown to be a strong antioxidant, but lacks the catechol functional group on its aromatic B ring as shown below (Figure 8).[45] Another possible alternative would be to use ortho-methoxy-catechin (OMe-Catechin), which would be less susceptible to undesired polymerization reactions.

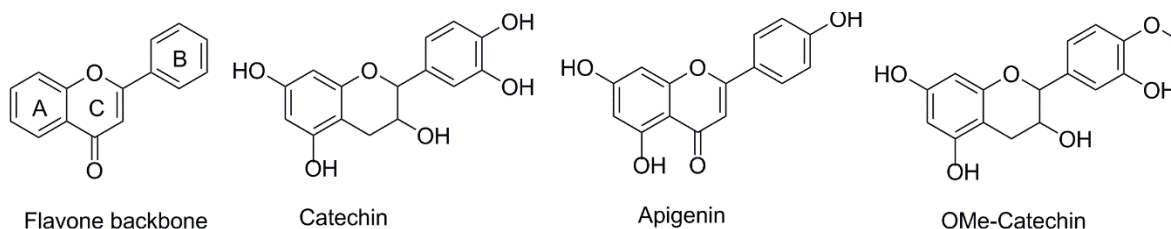Flavone backbone   Catechin   Apigenin   OMe-Catechin

Figure 8. Chemical structures of Flavone derived antioxidants Catechin and Apigenin. Presence of a phenol as opposed to a catechol functional group on the B ring may help to prevent unwanted oxidation and further polymerization of flavonoid based secondary antioxidant.
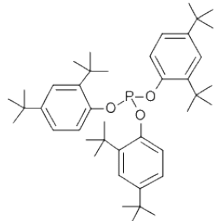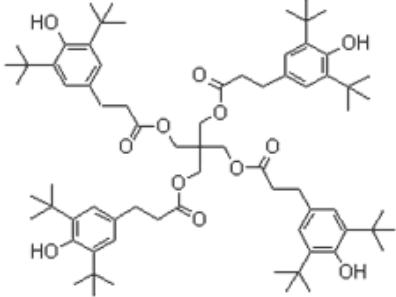
Strategy II: Lignin-TPO Biopolymer Blend Roofing

Motivation

Process stabilizer additives in TPO membrane reduce and/or prevent thermal degradation at high temperatures (~200 °C) during manufacturing and installation (i.e., heat-welding). High temperatures can break chemical bonds in polymers and additives, generating free radicals that propagate via chain-reactions and cause polymer degradation. Additionally, these process stabilizers increase the lifetimes of other antioxidant additives in TPO, such as HALS.

Two main categories of process stabilizers are phosphite and phenolic based compounds. Table 8 shows two examples of process stabilizers used in TPO membranes. Although these process stabilizers are commonly used in other industries (e.g., food packaging, cosmetic products, medical applications), the *long-term human health and ecological impacts are not well-understood*.

Table 8. Examples of process stabilizers in TPO membrane.

Process Stabilizer	Performance	Hazards
Irgafos® 168 (CAS 31570-04-4)	Phosphite processing stabilizer Used in food packaging	Acute dermal toxicity Harmful to aquatic life May cause lasting harmful effects to aquatic systems
Irganox® 1010 (CAS 6683-19-8)	Low volatility Long-term stability Used in cosmetic products	Harmful to aquatic life May cause lasting harmful effects to aquatic systems

Approach

Since these thermal stabilizers function primarily as process stabilizers to scavenge radicals and prevent oxidation at high temperatures during manufacturing, exceptional thermal stability and efficient antioxidation are key properties in seeking a substitute. High thermal stability is correlated with high molecular weight and strong intermolecular forces that increase the boiling point of the compound, thereby preventing the loss of additives due to vaporization during processing.

Lignin provides structural support in vascular tissues of plants through its branched and polymeric structure and serves as a potent antioxidant, providing protection against UV radiation induced photodamage (Figure 9).[46]   The branched phenolic structure that highly resembles synthetic phenolic process stabilizers, such as Irganox® 1010, allows for efficient radical scavenging. Lignin is a major byproduct of the cellulose harvesting process in the paper and pulp industry. More than 50 million tons of lignin are produced as byproduct and is valued at approximately $0.05/pound. Recently, interest has grown in repurposing lignin as a component in bioplastics and biopolymers.[47]   Lignin has already been shown to be compatible with several plastic resins (25-85% lignin composition), such as acrylonitrile-butadiene, polyurethanes, epoxies, and polylactic acid.
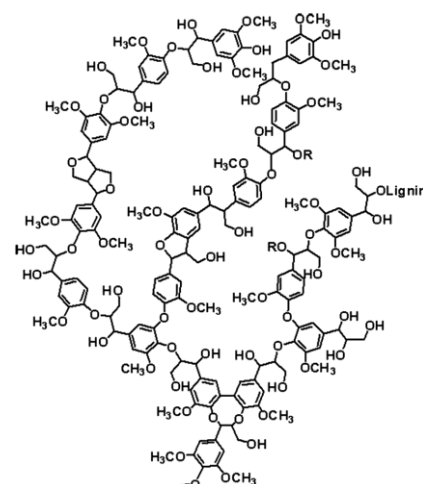

Figure 9. Example chemical structure of lignin.   Figure reproduced from Harlan et al.[46]

Here, we propose the incorporation of lignin in the TPO membrane as a *lignin-TPO biopolymer blend*. Lignin will act as a naturally derived biodegradable free radical scavenger and structural support in the polymer matrix, while also reducing the amount of TPO in the formulation and provide a green use for an industrial waste product.

Technical Performance

The major source of industrial lignin production comes as a byproduct of the Kraft process for extracting cellulose and hemicellulose from wood. During this process, lignin becomes sulfonated, which increases its hydrophilicity and makes it poorly compatible with a hydrophobic polymer such as TPO. To create a lignin-TPO biopolymer blend, we must first desulfonate the Kraft process lignin product.

De-sulfonation of lignin: Lignin can easily be desulfonated on a large scale through base hydrolysis of the sulfonate group (Scheme 5).[48]   Briefly, lignin is dissolved in a 0.2 M solution of sodium hydroxide (NaOH), then heated to 180 °C for 3 h. The reaction can be quenched through the addition of 5% solution of sulfuric acid (H_2SO_4).   The final desulfonated product is insoluble in water and will precipitate out of solution. Desulfonated lignin can then be filtered and dried prior to incorporation into the TPO membrane manufacturing process.
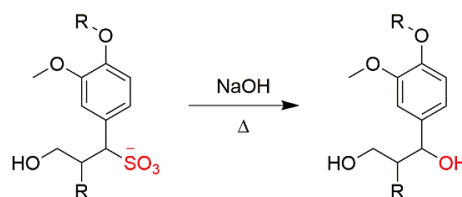
Scheme 5. Desulfonation reaction of Kraft lignin.

Synthesis of lignin-TPO biopolymer blend: To incorporate lignin into the TPO, desulfonated lignin and TPO beads can be dissolved into an organic solvent (e.g., dichloromethane) at various weight percentages during initial performance testing. To ensure adequate distribution of the lignin in the TPO polymer blend, the mixture must be heated to >180 °C and subjected to high speed stirring and sonication. The mixture can then be extruded into membranes and cooled. Different weight percentages of lignin in the biopolymer blend should be tested for thermal and UV degradation, glass transition temperature (T_g), surface morphology, tensile strength, UV-VIS absorbance, water permeability, and other key performance metrics.

Based on a study that incorporated desulfonated lignin into a polylactic acid (PLA) matrix, we believe that lignin will not adversely affect the performance of the polymer and will contribute to an increased UV absorbance and possibly enhanced thermal properties.[48]

Once the lignin-TPO blend ratio is optimized, further performance tests should be performed to determine use of additional additives, such as HALS and pigments, that will help improve aesthetics and durability.

Health and Environmental Performance

There is limited hazard data for phenolic antioxidants currently used in TPO membranes as well as for our proposed alternative compound, lignin. The available information suggests that lignin should be a safer option for environmental endpoints and that it may be comparable or possibly somewhat safer for human health endpoints. However, more research is necessary, especially for lignin, before we can confidently recommend it as a less hazardous alternative.

Table 9. Summary of hazard assessment of currently used phenolic antioxidants and lignin.

Key	Carcinogenicity	Mutagenicity & Genotoxicity	Reproductive Toxicity	Developmental Toxicity	Endocrine Activity	Acute Mammalian Toxicity	Systemic Toxicity & Organ Effects	Neurotoxicity	Skin Sensitization	Respiratory Sensitization	Skin Irritation	Eye Irritation	Acute Aquatic Toxicity	Chronic Aquatic Toxicity	Persistence	Bioaccumulation
	Human Health Group I					**Human Health Group II**							**Environmental Health**		**Environmental Fate**	
Irganox 1010	M	L	U	U	L	M	U	U	U	U	H	U	M	U	H	L
Butylated hydroxytoluene	M	L	M	M	H	M	M	U	H	U	U	M	M	U	M	M
Lignin	L	L	U	U	L	L	U	U	H	U	U	U	L	U	L	L

Key: H = High Hazard, M = Moderate Hazard, L = Low Hazard, U = Unknown Hazard

Irganox® 1010 and butylated hydroxytoluene (BHT) are two common phenolic antioxidants. The European Chemicals Agency identifies Irganox® 1010 as a compound that may cause cancer and skin irritation, and pose acute oral toxicity.[49] Studies indicate that BHT may increase the incidence of liver cancer in rats fed doses up to 250 mg/kg and that BHT may have toxic effects on the liver, kidneys, and lungs in rats exposed orally or dermally.[50] The International Chemical Secretariat also includes BHT on its Substitute It Now List due to its endocrine activity.[51]

Available data shows lignin has comparable or lower hazards than currently used phenolic antioxidants. Lignin has very low hazard for acute mammalian toxicity (LD_{50}=12 g/kg).[52] *In vitro* experiments using human and hamster cells suggest that lignin has an antimutagenic effect.[53] Similarly, in a human case-control study, lignin in diet was shown to be associated with reduced risk of nasopharyngeal carcinoma.[54] However, this apparent anti-cancer effect may not be entirely applicable to other routes of exposure, like dermal exposure and inhalation, as we expect in an occupational setting.

A study of acute aquatic toxicity of BHT reported LC_{50} of 3 mg/L in rainbow trout, which is low enough to raise some environmental health concerns.[55] BHT also has a moderately high octanol-water partition coefficient (5.10), which exceeds the GHS cutoff (4.00) to be considered potentially bioaccumulative. We rated BHT as a moderate hazard for environmental persistence because a Japanese study found that 48.4-57.3% of BHT degraded after 24 days in different sludge mixtures, which does not meet the threshold of >70% degradation in 28 days set by GHS to be considered rapidly degradable.[56] Irganox® 1010 also poses an environmental concern; the European Chemicals Agency identifies it as harmful to aquatic life and predictive models generated by VEGA software indicate that it may not be readily biodegradable.[49]

Scientific literature was not readily available regarding the persistence or bioaccumulation of lignin, but model predictions from VEGA software suggest that the monomers of lignin are readily biodegradable and predict a bioconcentration factor (BCF) of 0.84 which is far below the GHS cutoff for bioaccumulation (BCF=500). More importantly, there is research showing that lignin is a relatively low hazard for acute aquatic toxicity. Relatively low aquatic toxicity (LC_{50}=220 mg/L, Pacific white shrimp) indicates there is less of a concern about the persistence and bioaccumulation of lignin, though more research should still be done to confirm the low hazard predictions for environmental fate.[57]

Remaining Questions

Because lignin is a naturally occurring polymer, microbial degradation of the embedded lignin in the lignin-TPO polymer blend is a concern. The benzene rings that dominate the lignin structure are resistant to decomposition by micro-organisms.[58] The carbon-carbon and ether bonds that join lignin monomers together must be cleaved by an oxidative process and enzymes, such as peroxidases or laccases, are required. Thus, only certain fungi (e.g., white-rot fungi) and bacterial species can decompose lignin, which is promising for enhanced biodegradation after disposal.[59] Field tests and laboratory studies are required to measure the extent of possible biodegradation during TPO membrane lifetime.

The dark color of industrial lignin has prevented its widespread use in sunscreens, plastics, and other UV applications. It presents a concern for the lignin-TPO polymer blend and desired high solar reflectivity for roofing membrane material. Physical and chemical processes, including UV irradiation in tetrahydrofuran solvent and acetylation of lignin[60], have been shown to reduce the color, but the effects on the properties of lignin are not well-characterized. Further studies on the effects of reducing lignin color and lignin-TPO blend ratios are necessary.

Strategy III: TiO_2 Coated-Bacterially Derived $CaCO_3$ Nanoparticles

Background

Rutile titanium dioxide (TiO_2) nanoparticles (NPs) that range in size from 200-300 nm is the primary pigment used in TPO membrane roofing. TiO_2 exhibits strong absorbance in the UV wavelengths and efficiently scatters visible and near IR wavelengths, which contribute to the high solar reflectivity index of TPO roofs and reduces the heat island effect. The strong UV absorption of TiO_2 protects TPO and the additives from UV photodegradation. TiO_2 NPs are also commonly used in cosmetics and sunscreen products as well as paints and coatings. Because it is an inorganic compound, TiO_2 has excellent stability at high processing temperatures and a long lifetime.

Motivation

TiO_2 NPs pose a human health and environmental hazard due to their nanoscale. Human exposure risk is significantly higher during manufacturing where TiO_2 NPs have yet to be incorporated within the polymer matrix. After disposal, nanoparticles have long persistence and can have long-term negative aquatic impacts.

Inspiration

Calcium carbonate ($CaCO_3$) in coral exoskeletons is thought to be an integral component in protecting coral reef organisms from solar UV radiation. The white $CaCO_3$ skeleton is highly reflective and efficiently scatters longer wavelength visible-light, which is then used for photosynthesis by surrounding organisms. Upon irradiation by UV photons, fluorescence and phosphorescence are observed, attributed to organic humic acids and inorganic metal ions such as calcium and trace elements such as magnesium, manganese, and zinc that are incorporated into the carbonate skeleton.[61]

Approach

$CaCO_3$ has been widely used as a filler and extender pigment in polymer materials. It is generally obtained through the mining of natural limestone deposits. Thus, we have developed a method to produce on-site, non-destructive, and CO_2 negative $CaCO_3$ that could then be used in conjugation with a reduced amount of TiO_2 in TPO formulation.

To lower energy costs and minimize environmental destruction, we propose using bacterially derived $CaCO_3$ as an alternative source of the commonly used pigment extender. The biomineralization of calcium by bacteria to produce calcite or aragonite, two mineral forms of $CaCO_3$, occurs through a process known as microbially induced calcium carbonate precipitation (MICP).[62] MICP occurs in nature, for example, in soil, limestone caves, and seas. Genetic engineering has improved the precipitation process, allowing for large scale production of $CaCO_3$ in a short time period in various conditions.

To produce $CaCO_3$, bacteria sequester calcium from waste-water and carbon dioxide from the atmosphere, leading to a net negative carbon dioxide consumption in the process. Furthermore, since only a small starter culture, nutrient media, waste-water, and carbon dioxide is necessary to produce $CaCO_3$, on-site $CaCO_3$ production is possible, reducing environmental impacts of shipping and other energy costs. We propose using bacterial strains *Sporosarcina pasteurii* or *Methylocystis parvus*.

S. pasteurii sequesters carbon dioxide as its main carbon source and is known to produce $CaCO_3$ in higher yields (2-3x greater) in comparison to *M. parvus.*[63] The major drawback of using *S. pasteurii* is that it utilizes a urease enzymatic pathway that produces ammonium (NH_4^+) as a byproduct. It is unclear whether the amount of ammonium produced would be problematic or not, so we suggest further experimental studies to study the effects of ammonium. Other bacteria employing the urease pathway have been used to precipitate calcium from industrial wastewater, as excessively high levels of calcium can lead to clogging of pipes and other manufacturing equipment.[64]

M. parvus precipitates $CaCO_3$ via a formate oxidation-driven method that uses methane as a feed source.[65] This could be problematic for on-site

Figure 10. Bacterially precipitated $CaCO_3$. Over the course of 2 days, a solution containing the bacterium S. pasteurii and growth media supplemented with Ca^{2+} can precipitate $CaCO_3$ in the form of calcite. Figure reproduced from Bhaduri et al.[63]

production if a nearby natural source of methane is not available. *M. parvus* is the same bacteria used to make polyhydroxybutyrate (PHB) biopolymer, commonly used in bioplastics, indicating that it is viable for large scale production of $CaCO_3$.

To produce bacterially derived $CaCO_3$, frozen bacterial aliquots of *S. pasteurii* or *M. parvus* can be used to inoculate a small starter culture in a sterile buffer solution containing yeast extract.[65] This starter culture is grown for 1-2 days at approximately 30 °C to produce a high density of the desired bacterial strain. This starter culture is then poured into a larger solution of either waste-water, tap water, or reclaimed water (heat treated and filtered to remove naturally occurring bacterial organisms) and supplemented with 2 g/L urea (*S. pasteurii*) or 5 g/L formate salt (*M. parvus*) and a final concentration of 1 g/L NH_4Cl, 212 mg/L Na_2CO_3, and 280 mg/L $CaCl_2$, where the amount is adjusted based on the natural abundance of these ions. The final solution is then allowed to sit at approximately 30 °C for 2 days, allowing $CaCO_3$ precipitation to occur. The precipitated $CaCO_3$ settles to the bottom of the solution and can be removed via filtration. The $CaCO_3$ crystals can be dried and then crushed into a uniform particle size and be added to the TPO membrane along with other additives such as TiO_2, allowing for lower material cost due to the reduction in TiO_2 and an overall greener production.

Other potential sources of calcium carbonate include waste shells of marine organisms. However, proteins, metals, and other ions may be incorporated into the calcium carbonate matrix in shells produced by organisms. Thus, the chemical composition, optical properties, and compatibility should be carefully examined before incorporation into materials.
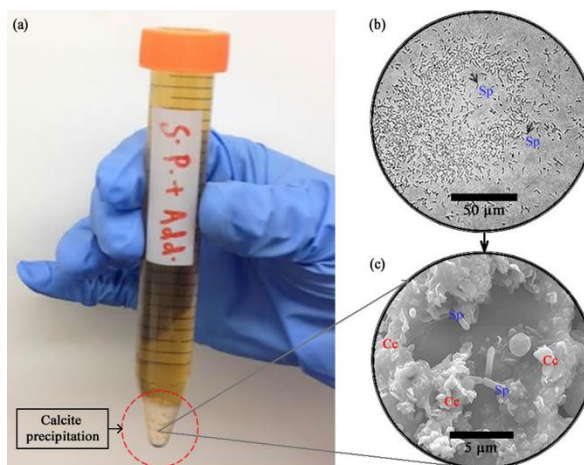
Technical Performance

An ideal substitute for TiO_2 nanoparticles must have high refractive index in the visible and near IR wavelengths and strongly absorb UV light. $CaCO_3$ has slightly lower refractive indices in the visible and near IR wavelengths compared to TiO_2.[66] In the UV wavelengths, however, $CaCO_3$ has significantly lower absorbance relative to TiO_2 (Figure 11). Thus, elimination of TiO_2 as a pigment is not feasible at this point. However, $CaCO_3$ nanoparticles coated with TiO_2 shows strong absorption in UV wavelengths, comparable to pure TiO_2 nanoparticles.[67,68]

Refractive Index	
TiO_2 (rutile)	2.874 (633 nm)
$CaCO_3$ (aragonite)	1.53-1.69 (589 nm)
$CaCO_3$ (calcite)	1.49-1.66 (589 nm)
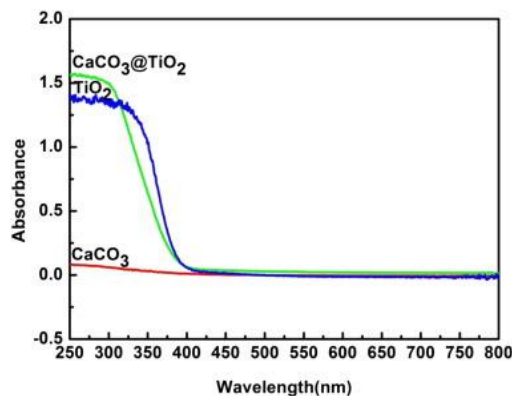
Figure 11. UV-VIS absorbance of calcium carbonate, titanium dioxide, and calcium carbonate-titanium dioxide blend. Figure reproduced from Wang et al.[67]

Health and Environmental Performance

There is compelling evidence that TiO_2 NPs in TPO membranes pose a meaningful hazard to environmental and human health. Conversely, there is also a sizable collection of data that indicate $CaCO_3$ presents minimal hazards on most environmental and human health endpoints (Table 10). Hazards for both compounds are well-established and based largely on classifications from authoritative bodies and scientific literature.

Table 10. Summary of hazard assessment of titanium dioxide and calcium carbonate.

Key: H = High Hazard, M = Moderate Hazard, L = Low Hazard, U = Unknown Hazard

	Human Health Group I					Human Health Group II								Environmental Health		Environmental Fate	
	Carcinogenicity	Mutagenicity & Genotoxicity	Reproductive Toxicity	Developmental Toxicity	Endocrine Activity	Acute Mammalian Toxicity	Systemic Toxicity & Organ Effects		Neurotoxicity	Skin Sensitization	Respiratory Sensitization	Skin Irritation	Eye Irritation	Acute Aquatic Toxicity	Chronic Aquatic Toxicity	Persistence	Bioaccumulation
Titanium Dioxide	M	M	H	M	M	L	M	H	M	L	M	L	M	M	M	H	H
Calcium Carbonate	L	L	L	L	U	L	M	L	L	L	U	L	L	L	L	H	L

A notable concern about TiO_2 is that it presents a moderate or high hazard on all Human Health Group I endpoints. The International Agency for Research on Cancer (IARC) categorizes TiO_2 as possibly carcinogenic to humans. An *in vitro* study of several types of human cells have identified TiO_2 as potentially genotoxic.[69] Reproductive toxicity in mice (impaired testicular function) was reported at very low doses of TiO_2 (0.1 mg/kg).[70] Adverse effects on development of the central nervous system in offspring of female mice exposed orally (1-3 mg/kg) during pregnancy and lactation have been reported.[71] The Endocrine Disruption Exchange (TEDX) lists TiO_2 as a potential endocrine disruptor, citing effects of TiO_2 on zebrafish exposed to low concentrations (0.1 mg/L).[72]

TiO_2 is also an environmental health concern. Moderate aquatic toxicity has been reported in crustacean species *Daphnia magna* (LC_{50} = 5.5 mg/L).[73] TiO_2 is included on the Canadian Environmental Protection Act Domestic Substances List as a very persistent compound in the environment and high bioaccumulation has been reported in fish, plants,[74] and crustaceans.[75] The long persistence and bioaccumulation of TiO_2 further raise concerns for its aquatic toxicity than the moderate rating would suggest because the compound is likely to remain in the ecosystem for a long period of time, resulting in long-term negative effects.

The associated hazards for $CaCO_3$ are substantially lower compared to TiO_2. A certified GreenScreen® for Safer Chemicals Assessment based on available authoritative lists and scientific literature did not indicate any hazard to Human Health Group I endpoints.[76] Studies support its low hazard rating for carcinogenicity,[77] mutagenicity, reproductive toxicity, and developmental toxicity.[78] There was no available data regarding the effects of $CaCO_3$ on endocrine activity. The lack of data on the effects of $CaCO_3$ on respiratory sensitization is also an unfortunate gap because respiratory exposure of TiO_2 is one of the hazards that we are attempting to mitigate by partially substituting TiO_2 with $CaCO_3$ in TPO formulations.

The European Chemicals Agency (ECHA) reports that the LC_{50} for $CaCO_3$ is greater than the saturation limit.[78] The Hazardous Substances Data Bank (HSDB) from the U.S. National Library of Medicine listed the LC_{50} value as greater than 56,000 mg/L.[79] These results suggest that there is a very low aquatic toxicity hazard for $CaCO_3$.[79] Since $CaCO_3$ is an inorganic salt, the European Commission indicates that it would not be easily biodegraded (i.e., high persistence) and that it would not be bioaccumulative.[79] Although $CaCO_3$ has a high hazard rating for persistence, very low aquatic toxicity hazard rating means that there would be very little concern for environmental health from $CaCO_3$.

Remaining Questions
Optimization of bacteria derived $CaCO_3$ production is the most uncertain aspect of this strategy. Maintaining bacteria cultures and processing $CaCO_3$ may be cost prohibitive until large-scale production is well-established. As mentioned above, ammonium formation as a byproduct of the urease enzymatic pathway could be an issue, but ammonium could be incorporated into other industrial products, such as fertilizers and cleaning products.

Strategy IV: Physical Blockers

Motivation

Physical blockers prevent UV light from reaching the TPO membrane. The lifespans of current market-available TPO membranes are approximately 30 years. By placing a layer of material(s) that are more resistant to UV radiation on top of the TPO membrane, UV photodegradation of TPO can be eliminated, and thus increase the lifetime of TPO membranes with lower amounts of photo-stabilizer additives and pigments. The following are short-term strategies that can be implemented immediately using market-available roofing material.

Approach, Technical Performance, Human Health & Environmental Hazards

Living Roof

Living roofs or green roofs have become increasingly common in recent years in urban areas and green buildings with flat or low-slope rooftops. On these roofs, mat-forming plants such as sedum, ferns, and moss are grown in the outermost layer. The underlying layer consists of a waterproofing layer (e.g., TPO), root barrier to prevent bacterial and mold growth on the underlying layer, a drainage system, and growing medium for the plants (Figure 12).

Green roofs provide many benefits including reducing storm water runoff, improving water quality by acting as a primary filter, reducing the heat island effect, increasing lifetimes of underlying membranes, sequestering carbon dioxide, and increasing local biodiversity by providing a habitat for wildlife.

Figure 12. Moss roofing. Image from http://www.mossacres.com.

Completely covering the base waterproofing TPO layer from solar radiation eliminates photodegradation of the TPO membrane, which can extend the lifespan of the TPO polymer an additional 30 years. Furthermore, concentrations of photo-stabilizer additives can be decreased or even eliminated from the TPO formulation. Additionally, pigment TiO_2 nanoparticles can be removed from the formulation as TPO would not be the outermost roofing layer, thereby eliminating the high health and environmental hazards presented above. Furthermore, the layers above the TPO membrane could effectively act as a ballast, thus reducing or eliminating the need for adhesive bonding solvents during TPO installation. Process stabilizer additives, however, would still be required to prevent thermal degradation at high temperatures during TPO manufacturing and installation.

We were unable to find significant human health concerns for moss, but inhalation of spores poses a potential concern for residents, especially for vulnerable groups. Water absorption and retention by the roof and associated increase in weight presents a structural concern. Additionally, depending on the climate and location, available plant species may be limited.

Metal Roofing

Common metal roofing materials include zinc, copper, and aluminum (Figure 13). Although expensive, metal roofing has the longest lifetime (50+ years) because metal is not prone to UV photodegradation. Metal roofing also possesses many favorable performance characteristics including recyclability, durability, low maintenance, and high reflectivity. Metal roofing materials can be sourced from pre-consumer or post-consumer recycled content, reducing environmental impacts and energy costs. Furthermore, metal has unmatched strength and durability, resilient in the most extreme climates.

Figure 13. Examples of metal roofing. Image from http://www.interlockroofing.com.

The high reflectivity of metal contributes to its high solar reflectivity index and can reduce building cooling costs by 10-25%.

One concern, however, is chemical-based coatings and paints on the surface of the metal for aesthetics and UV protection that contain additives such as HALs and TiO_2 nanoparticles. The outermost coatings and paints are highly susceptible to UV photodegradation, leading to fading, chalking, and cracking over time. Like TPO, leaching of the additives from the paints and coatings off the roof is a concern. It should be noted that metal roofs are not easily compatible with flat roofs. Additionally, metal roofs are expensive (around $10/sq ft. installed) compared to other traditional roofing materials such as asphalt shingles.

Solar Panels

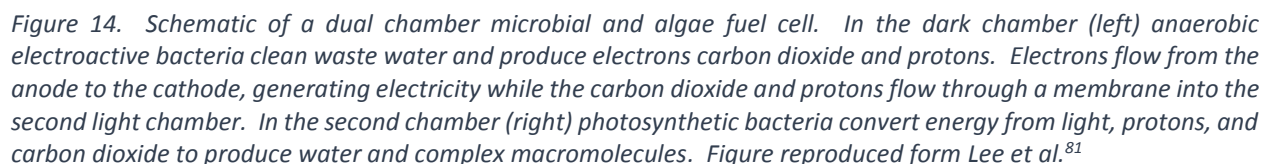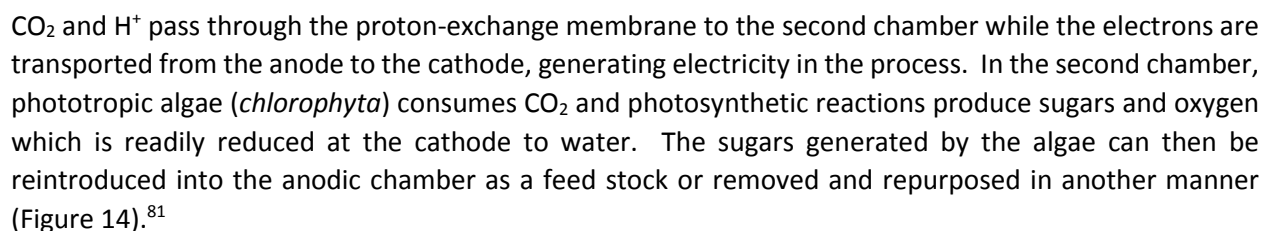EcoBlock plans to install solar panels on rooftops as part of the energy system; these solar panels could effectively act as physical blockers for the underlying TPO membrane. Because solar panels will not completely cover the exposed TPO membrane surface, metal or green roofing (plants) can be installed to physically block UV radiation in areas where solar panels do not completely cover the TPO membrane.

Strategy V: Microbial Fuel Cells

The primary goals of Oakland EcoBlock are to reduce carbon emissions and potable water demand. Microbial fuel cells (MFCs), an emerging technology, have the potential to do both, and rooftops provide an ideal location for these fuel cells.

A continuous flow, two-compartment microbial fuel cell for electricity generation and water remediation shows promise as an ideal rooftop energy generation-water reclamation system.[80] The anode consists of a graphite plate or mesh; the cathode is a platinum doped metal catalyst that increases the rate of oxygen reduction and serves as the electron acceptor. A proton-exchange membrane separates the anode and cathode. The electrical current generated from the microbial fuel cell is directly proportional to the energy content of the waste water used as fuel.

Most microbial fuels cells are electrochemically inactive. Electron transfer from microbial cells to the electrode is facilitated by mediators such as thionine and humic acid. Mediator-free MFCs on the other hand, use electrochemically active bacteria, such as *Shewanella putrefaciens* and *Aeromonas hydrophila*, to transfer electrons to the electrode. However, mediator-free MFCs are not well characterized and further research is necessary. Under anaerobic conditions, *Shewanella oneidensis* converts waste substance (e.g., sugars) and produce carbon dioxide (CO_2), protons (H^+), and electrons (e^-):

$$C_{12}H_{22}O_{11} + 13\,H_2O \rightarrow 12\,CO_2 + 48\,e^- + 48\,H^+$$

CO_2 and H^+ pass through the proton-exchange membrane to the second chamber while the electrons are transported from the anode to the cathode, generating electricity in the process. In the second chamber, phototropic algae (*chlorophyta*) consumes CO_2 and photosynthetic reactions produce sugars and oxygen which is readily reduced at the cathode to water. The sugars generated by the algae can then be reintroduced into the anodic chamber as a feed stock or removed and repurposed in another manner (Figure 14).[81]

Figure 14. Schematic of a dual chamber microbial and algae fuel cell. In the dark chamber (left) anaerobic electroactive bacteria clean waste water and produce electrons carbon dioxide and protons. Electrons flow from the anode to the cathode, generating electricity while the carbon dioxide and protons flow through a membrane into the second light chamber. In the second chamber (right) photosynthetic bacteria convert energy from light, protons, and carbon dioxide to produce water and complex macromolecules. Figure reproduced form Lee et al.[81]

Although MFCs are recently being used in pollution treatment, significant further research and field testing are required before this technology would be feasible for rooftop implementation. Effectively controlling the metabolism of microbes and scaling up are the main challenges in the field today. Figure 15 shows a representative schematic of a proposed microbial fuel cell that can generate electricity and clean waste water.
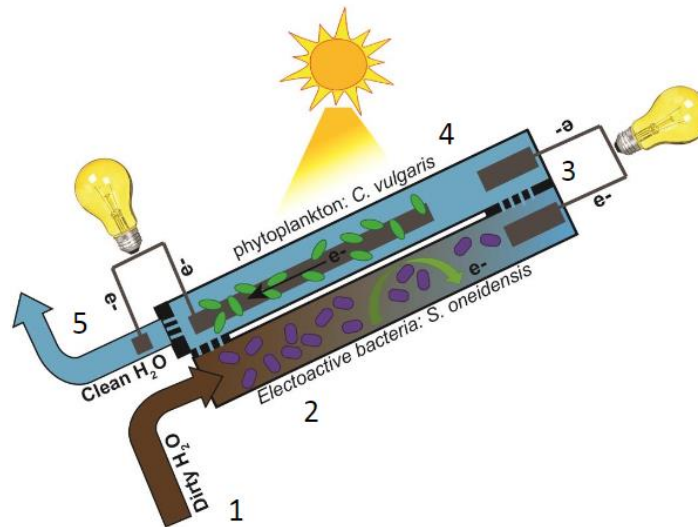

Figure 15. Schematic of two chamber microbial-algae fuel cell. (1) Dirty water reclaimed from roof tops or household waste is pumped into a chamber (2) containing the electroactive bacteria S. oneidensis. The bacteria convert organic waste product to electrons, protons, and carbon dioxide. (3) Electrons move from the anode in the first chamber to the cathode in the second chamber, generating electricity. (4) Protons and carbon dioxide pass through a membrane into the second chamber containing the phytoplankton C. vulgaris which, when exposed to sun light, will generate another round of electrons as well as produce complex macromolecules. (5) Electrons produced in the algal chamber will flow from the anode to a cathode, generating a second round of electricity. Clean water will be allowed to pass through the membrane and re-enter the community water system.

Recommendations for Oakland EcoBlock

Human health and environmental hazards of current light and thermal stabilizer additives in TPO membrane roofing were investigated. We proposed several greener strategies that range from market-available solutions for immediate implementation, medium-term strategies that would require further research and field testing, and innovative technologies that require significant investment in research before implementation. In presenting these greener solutions, we aimed to maintain or enhance performance while minimizing human health and environmental hazards associated with currently used chemicals. The strategies are summarized below:

1. Short-term: physical blockers to block sunlight from reaching TPO membrane surface
   a. Living roof
   b. Metal roof
2. Medium-term: partial/full chemical substitution
   a. Vitamin E-poly(tannin) regenerative antioxidation to partially or fully substitute HALS antioxidants
   b. Lignin-TPO blend biopolymer to partially or fully substitute phenolic antioxidants
   c. TiO_2-coated bacterially-derived $CaCO_3$ nanoparticles to reduce TiO_2
3. Long-term: innovative technology
   a. Solar powered microbial fuel cell for rooftop energy generation and water remediation

Future Directions

Partnerships with research and academic institutions, chemicals companies, and roofing membrane manufacturing companies will be critical in pursuing greener alternatives for stabilizer additives in TPO membrane roofing. As the fastest growing synthetic polymer membrane in commercial roofing, TPO and greener additives should be a high priority for materials and engineering research, especially in industry. As a pilot project at the forefront of sustainable building designs, Oakland EcoBlock has a unique opportunity to further motivate the building and materials industry towards greener, safer materials.

Additives that were investigated are not limited to TPO; stabilizer additives are ubiquitous in plastic and polymer products. Our greener strategies can potentially be extended for implementation in other plastic and polymer applications where stability and leaching are a concern. For example, automobile and building exteriors, food and beverage packaging, and medical applications.

We hope that our investigations of stabilizer additives and their associated hazards in TPO membrane roofing and proposed greener solutions stimulate further discussion and research, both in academia and industry, to continue moving forward towards a safer, healthier, and environmentally friendly world.

Appendices

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Complete Hazards Table

Summary of hazard assessment of additives currently used in TPO and our proposed alternatives.

Key		Human Health Group I					Human Health Group II							Environmental Health		Environmental Fate	
		Carcinogenicity	Mutagenicity & Genotoxicity	Reproductive Toxicity	Developmental Toxicity	Endocrine Activity	Acute Mammalian Toxicity	Systemic Toxicity & Organ Effects	Neurotoxicity	Skin Sensitization	Respiratory Sensitization	Skin Irritation	Eye Irritation	Acute Aquatic Toxicity	Chronic Aquatic Toxicity	Persistence	Bioaccumulation
H High Hazard																	
M Moderate Hazard																	
L Low Hazard																	
U Unknown Hazard																	
Current Additives																	
Tinuvin 770		U	U	U	U	U	H	H	M	U	U	U	H	H	H	H	H
Chimassorb 994		U	U	U	U	L	H	H	M	U	U	U	U	M	M	H	U
Irganox 1010		M	L	U	U	L	M	U	U	U	U	H	U	M	U	H	L
Butylated hydroxytoluene		M	L	M	M	H	M	M	U	H	U	U	M	M	U	M	M
Titanium Dioxide		M	M	H	M	M	L	M H	M	L	M	L	M	M	M	H	H
Proposed Alternatives																	
Vitamin E		L	L	U	L	M	L	U	U	U	U	U	U	L	U	H	M
Catechin		L	L	U	L	M	M	M	U	U	U	M	M	U	U	L	L
Apigenin		L	L	U	U	M	M	U	L	U	U	U	U	L	U	L	L
Lignin		L	L	U	U	L	L	U	U	H	U	U	U	L	U	L	L
Calcium Carbonate		L	L	L	L	U	L	M L	L	L	L	U	L	L	L	H	L

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